

Highly Toxic Non-Ortho-Chlorine substituted Coplanar PCBS in White-Tailed Sea Eagles *Haliaeetus albicilla* from Poland

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INTRODUCTION

The Baltic Sea continues to be highly contaminated by polychlorinated biphenyls (PCBs) and other persistent organochlorine compounds, prompting concern for the welfare of marine predators at the higher trophic levels, including mammals and eagles (Melvasalo *et al.* 1981, Baltic Marine Environment Protection Commission 1990). Particularly high levels of total PCBs and *p,p'*-DDE have been reported in the tissues of White-Tailed Sea Eagles, *Haliaeetus albicilla*, found dead in locations around the Baltic Sea, *i.e.* in the Archipelago of Stockholm in Sweden (Jensen *et al.* 1972) and in the Finnish Archipelago (Paasivirta *et al.* 1983).

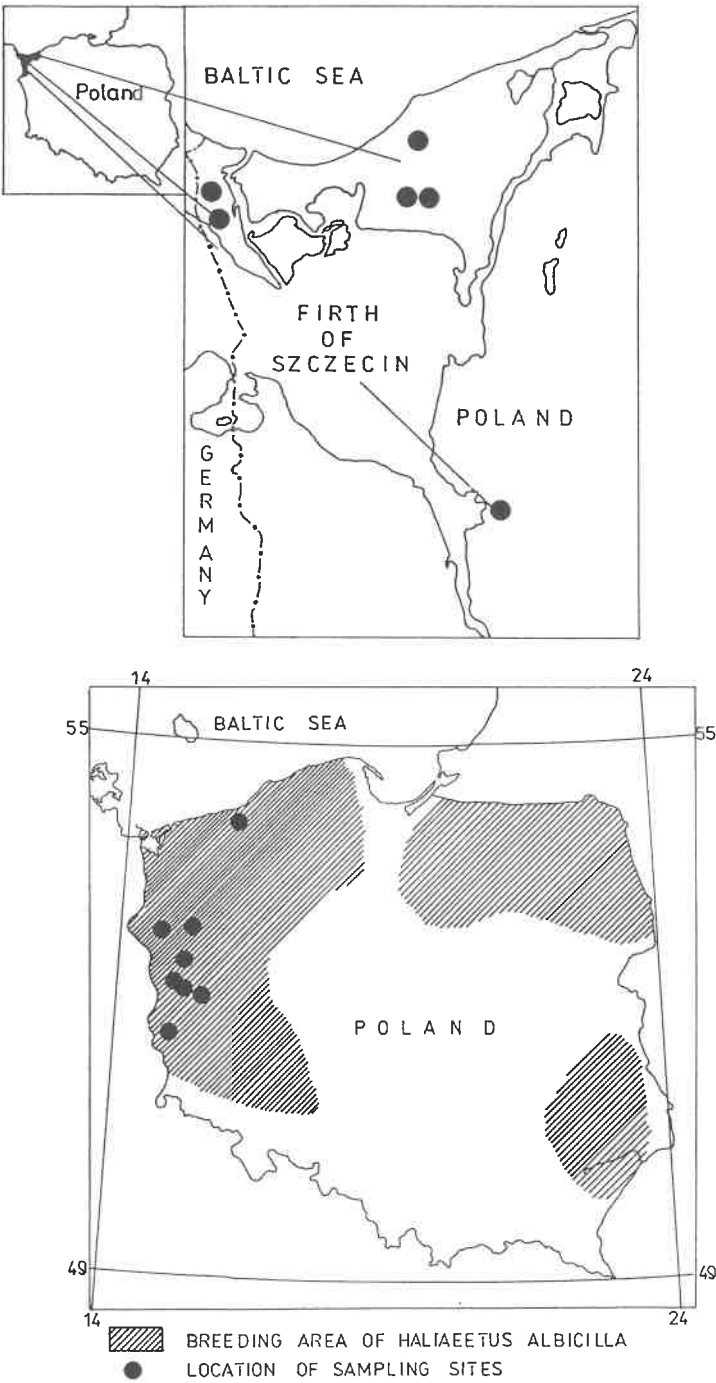
Our recent findings have indicated a steady-state of contamination by PCBs in the southern part of the Baltic proper over the last two decades (Kannan *et al.* 1992). Among the PCB congeners, No. 77 (3,3',4,4'-tetrachlorobiphenyl), No. 126 (3,3',4,4',5-pentachlorobiphenyl) and No. 169 (3,3',4,4',5,5'-hexachlorobiphenyl) are the most active inducers of microsomal aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin *o*-diethylase (EROD) enzymes and therefore pose the greatest threat of dioxin-type effects. Due to the absence of chlorines in the *ortho* positions of the biphenyl rings, these PCB congeners attain coplanarity, making them structurally similar to the dioxins (Tanabe *et al.* 1987, Voogt *et al.* 1990). In this paper we report the concentrations of these non-*ortho*-chlorine coplanar PCB isomers in White-Tailed Sea Eagles found dead in the breeding areas of coastal and inland Poland between 1982 and 1990, and evaluate the toxicology of these residues.

MATERIALS AND METHODS

Sample Preparation

Autopsy material consisted of specimens of White-Tailed Sea Eagles collected since 1982 from two breeding areas of Poland (Figure 1). Six of the birds examined originated from the southwestern coast of the Baltic Sea (an area of the Wolinski National Park and its surroundings), and three were from a woodland area of the western part of Poland (Province of Gorzów). A single

Figure 1: Breeding areas of the White-tailed Sea Eagle from which sample specimens collected for autopsy since 1982 a) in NE Poland, b) N Poland



immature male was a bird that was electrocuted in the northern part of the country (Table 1). Breast muscle was selected for determination of the PCBs. The samples were stored frozen (-20°C), with the exception of the carcass collected in 1982; a lipid extract was prepared (with light petroleum in a Soxhlet apparatus) and kept in a sealed vial until analysis.

Chemical analysis

About 10 g of breast muscle were digested with alkaline-alcohol, re-extracted with hexane, and cleaned-up using silica gel (Wako gel S-1) column chromatography and 5% fuming sulfuric acid treatment. Non-*ortho* coplanar PCBs (IUPAC Nos. 77, 126 and 169) were separated from other isomers and congeners using carbon column chromatography (Tanabe *et al.* 1989).

A gas chromatograph/mass spectrometer (Hewlett-Packard 5890 GC with 5970 mass selective detector) in electron impact (EI) mode at 70 eV was equipped with a fused silica capillary column (30 m x 0.25 mm i.d., film thickness 0.25 μm , DB-1701 for the coplanar congeners and an analogous DB-1 column for the other PCB congeners). The operating conditions were as follows: injection port 260°C ; transfer line 280°C ; initial temperature for analysis of coplanar PCBs 180°C , rate $2^{\circ}\text{C}/\text{min}$, final temperature 250°C ; initial column temperature for other PCBs 140°C , rate $2.5^{\circ}\text{C}/\text{min}$, final temperature 250°C , hold time 10 min.

For the confirmation/quantification of the coplanar PCBs, M+ and (M+2)+ cluster ions were monitored at m/z 290 and 292 for No. 77, m/z 324 and 326 for No. 126, and m/z 358 and 360 for No. 169. The other PCB isomers and congeners were quantified by selective ion monitoring (SIM) at m/z 222, 256, 292, 326, 360, 394, 428 and 464 for di-, tri-, tetra-, penta-, hexa-, hepta-, octa- and nonachlorobiphenyls, respectively. Authentic standards of PCBs 77, 126, and 169 were of 98-100% purity. A mixture of Kanechlors 300, 400, 500 and 600, equal amounts of each, with known PCB composition was used as a standard for the quantification of total PCBs by GC-MS.

RESULTS AND DISCUSSION

With the exception of the specimen taken from the outskirts of the Firth of Szczecin, eagles from the coastal region of the Baltic Sea contained strikingly high concentrations of total and non-*ortho* coplanar PCBs in their breast muscle, ranging from 66,000 to 480,000 ng/g and from 16 to 340 ng/g, respectively, on a wet weight basis. Birds from the interior were relatively much less contaminated (Table 1).

Comparably high concentrations of total PCBs have been reported in tissues of White-tailed Sea Eagles found dead elsewhere in the Baltic Sea, *i.e.* in the Archipelago of Stockholm in Sweden (Jensen *et al.* 1972) and in the Finnish Archipelago (Paasivirta *et al.* 1983).

Data on total PCBs (Table 1) are in very good agreement with those reported earlier that were obtained with conventional packed glass columns (Falandysz 1984, 1986; Falandysz *et al.* 1988).

The concentrations of non-*ortho* coplanar PCBs in eagles collected in 1982 and 1987 in the Woli ski National Park appear to be the highest so far reported in wildlife tissue; on a lipid basis concentrations are 34 and 47 times higher, respectively.

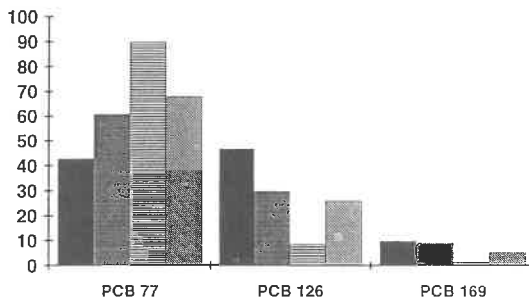
Concentrations of non-*ortho* coplanar PCBs have been reported recently in tissues and eggs of White-tailed Sea Eagles from different regions of Finland (Paasivirta *et al.* 1989; Tarhanen *et al.* 1989; Paasivirta & Rantio 1991). Two of the five Sea Eagles examined by Tarhanen *et al.* (1989) were adult females and originated from the Finnish coastal area of the Baltic Sea. Total concentrations of the 3 coplanar PCBs and of total PCBs in their muscles were 18 and 140 ng/g, and 17,000 and 250,000 ng/g on a wet-weight basis, respectively. The reports by Paasivirta *et al.* (1989) and Paasivirta & Rantio (1991) present data on the 3 coplanar PCBs in muscles of three White-tailed Sea Eagles on a lipid-weight basis (240, 260 and 620 ng/g).

The eagles from the interior contained not only considerably lower concentrations of PCBs but also differed in their isomer and congener composition - with a higher content of lower-chlorinated PCB 77 and lower contents of the penta- and hexachloro coplanars (Figure 2). This difference in congener composition between coastal and interior regions may result from a combination of different principal sources and differences in the environmental half-lives among the congeners.

An immature male collected after electrocution in Northern Poland in 1984 contained a very different pattern of coplanar contamination, with PCB 77 accounting for 90% and PCB 169 only

1.5% (Figure 2). A similar composition, 90% of PCB 77, 8.7% of PCB 126, and 1.3% of PCB 169, was reported in breast muscle of a four-months old juvenile White-tailed Sea Eagle from the Quarken Area of the Gulf of Bothnia, Baltic Sea (Tarhanen *et al.* 1989).

Figure 2. Composition (%) of non-ortho coplanar PCBs in breast muscles of White-tailed Sea Eagles from different breeding sites in Poland. ■ Coastal area (Wolinski National Park) (n=5), ▨ Coastal area (Firth of Szczecin) (n=1), ▩ Northern Poland (Immature Male) (n=1), ▧ Inland Poland (Province of Gorzów) (n=3)



Since immature White-tailed Sea Eagles frequently undertake long-range movements, their contamination patterns may not reflect that of the areas of collection.

Toxicities of the planar chlorinated aromatic compound are currently expressed in units of equivalent toxicities of the most toxic compound, 2,3,7,8-TCDD (TEQs); on the basis of their ability to induce the microsomal aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin *o*-diethylase (EROD) enzymes, the toxicities of the coplanars in the Baltic coast female eagles are estimated to range from 3,000 to 64,000 pg/g of dioxin equivalents in the AHH test and from 2,400 to 51,000 pg/g in the EROD test (Table 1). For comparison with data in other papers of this symposium, the estimated toxicities based on the factors derived by Safe (1990) are also presented.

PCB 126 clearly accounts for most of the dioxin-type toxicity in these samples (Table 1); it, and the other coplanar congeners are currently the most hazardous among the dioxin-type compounds in the Baltic (Paasivirta & Rantio 1991).

At present it seems rather difficult to relate accurately the concentrations of coplanar and total PCBs in breast muscles of female White-tailed Sea Eagles to suspected critical concentrations in eggs of 800,000-900,000 ng/g of total PCBs on a lipid weight basis (Helander *et al.* 1982) that are associated with depressed reproduction. The White-tailed Sea Eagle is a long-lived species; pairs breeding on the Baltic coast are exposed over their life-times to high contaminant levels in the food web (Jensen *et al.* 1969; Borg *et al.* 1969; Koivusaari 1976; Oehme 1980; Falandysz 1980; Falandysz *et al.* 1988; Kannan *et al.* 1992). Productivity has been depressed (Helander *et al.* 1982; Helander 1985) and higher contaminant burdens (Falandysz & Szefer 1983; Falandysz *et al.* 1988; Tarhanen *et al.* 1989) may affect the survival of adult birds.

The relatively large number of pairs breeding in interior Poland since 1981 have produced a surplus of young that have colonized the coastal areas, replacing birds that may have succumbed to contaminants. Recently, young and probably relatively uncontaminated eagles from interior Poland have been breeding in the Firth of Szczecin area (Figure 1). The number of pairs in the coastal area of the southwestern Baltic has increased from six in 1977-78 to twelve in 1982, and to seventeen in 1988; productivity has increased from 0.17 to 0.42, and to 0.88, respectively (Mizera and Szymkiewicz 1991).

No ecotoxicological studies have so far been undertaken of diverse toxic effects on White-tailed Sea Eagles in the Woli ski National Park and adjacent areas. This region of the Baltic coast is a nesting area for only about 10-15 % of the Polish population of Sea Eagles, but Pomeranian Bay and the Lower Odra and Lower Wisla Rivers are the most important wintering quarters for Sea Eagles from interior Poland and probably also from Scandinavia. During the season 1990-91 about 100 White-tailed Sea Eagles wintered in Pomeranian Bay (Czeraszewicz - personal communication). Studies of contamination sources, particularly of continuing sources of PCBs, and their effects on eagles clearly deserve continued attention.

Table 1. Non-ortho coplanar PCBs and their calculated 2,3,7,8-TCDD toxic equivalents, and total PCBs in fresh breast muscle of White-tailed Sea Eagles.

Sampling site, year, sex and cause of death	Concentration, ng/g				Total toxic equivalents pg/g, (% from PCB No. 126)		
	PCB 77	PCB 126	PCB 169	Total PCBs	AHH ^a	EROD ^b	Safe (90) ^c
Wolinski National Park							
1982; adult female, unknown	140	160	38	480,000	64,000 (99)	51,000 (99)	19,000 (83)
1984; adult female, unknown	6.3	7.5	1.9	66,000	3,000 (99)	2,400 (99)	910 (83)
1986; adult female, unknown	29	20	3.5	140,000	8,100 (99)	5,400 (99)	2,500 (81)
1987; adult female, unknown	45	53	11	340,000	21,000 (99)	17,000 (100)	6,300 (84)
1989; adult female, unknown	13	16	2.7	68,000	6,400 (99)	5,100 (100)	1,900 (86)
Firth of Szczecin							
1990; adult male, unknown	4.9	2.4	0.66	17,000	970 (99)	780 (99)	320 (75)
Northern Poland							
1984; immature male, electrocuted	18	1.7	0.35	7,000	730 (93)	560 (96)	370 (46)
Inland Poland							
1987; adult female, lead poisoning	9.5	3.0	0.55	32,000	1,200 (98)	970 (99)	420 (71)
1987; adult female, lead poisoning	2.9	1.2	0.15	12,000	490 (98)	380 (100)	160 (77)
1988; adult male, unknown	4.9	2.4	0.66	4,600	970 (99)	770 (100)	320 (75)

Conversion factors for 2,3,7,8-TCDD equivalents:

^a AAH: Smith *et al.* 1990

^b EROD: Smith *et al.* 1990

^c Safe (1990)

PCB IUPAC No. 77

PCB IUPAC No. 126

PCB IUPAC No. 169

1.60E-03

3.30E-03

5.00E-02

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