LEVELS OF POLYCHLORINATED DIPHENYL ETHERS, PCBs, PCDDs AND PCDFs IN THE BALTIC WHITE-TAILED SEA EAGLE

Koistinen, J.[A], Koivusaari, J.[B], Nuuja, I.[C], Paasivirta, J.[A]

[A] University of Jyväskylä, Department of Chemistry, P.O. Box 35, FIN-40351 Jyväskylä, Finland

[B] Water and Environment District of Vaasa, P.O. Box 262, FIN-65101 Vaasa, Finland

[C] Milieu-Data Cc, Vähäkuja 2, FIN-40520 Jyväskylä, Finland

INTRODUCTION

White-tailed sea eagles as top predators are good indicators of environmental contamination. Toxic organochlorine contaminants such as DDT compounds have been presented to have affected the survival of white-tailed sea eagles[1]. Eagles from the Baltic Sea environment have been indicated to have elevated levels of organochlorine compounds[2,3]: high levels of PCBs and DDE have earlier been measured both in old and juvenile white-tailed sea eagles[3].

Another group of possibly hazardous organochlorine compounds consists of polychlorinated diphenyl ethers (PCDEs). PCDEs can be formed as byproducts in the manufacture of chlorophenol formulations[4]. Combustion has also been found to yield PCDEs[5]. PCDEs which can elicit toxic properties similar to coplanar PCBs have been reported as ubiquitous contaminants in the environment[6]. Up to nanogram per gram levels of PCDEs have been measured in the Baltic Sea salmon[5,7], and lower levels in the Arctic salmon from Tana River[7]. PCDEs in pikes from Kymi River in southern Finland were at same level as in Baltic salmon at fresh weigh basis, but significantly higher at lipid weight basis[8]. White-tailed sea eagles have also been reported to contain PCDEs[3].

The purpose of the present study was to determine the levels of PCDEs in the white-tailed sea eagles nesting at the Baltic Sea area and to compare these with the levels of PCBs, PCDDs and PCDFs.

MATERIALS AND METHODS

The breast muscle of three female white-tailed sea eagles (*Haliaeetus albicilla L.*) were investigated. These individuals had been found dead from the Åland Islands in 1988 (MK-1) and from the Quarken Area in 1991 (MK-2) and 1990 (MK-3). MK-1 was three, MK-2 over five and MK-3 five years old. An aliquot (6 g) of breast muscles stored frozen were taken in analyses.

Extraction and cleanup. The extraction and clean-up procedure were based on methods developed earlier[3,8]. Briefly, the sample was ground with sodium sulfate, air-dried and extracted in a Soxhlet with a solvent mixture for 6 hours. Samples were spiked with one deuterium labeled penta-CDE, PCB 30, three ^{13}C-labeled PCBs, and ^{13}C-labeled PCDD/PCDFs before extraction.

The extracted fat dissolved in hexane was shaken with concentrated sulfuric acid. After analyses of main PCBs, one half of the extract was fractionated on a florisil column (Florisil PR deactivated with 1.25% water) to collect PCDEs and PCDD/PCDFs into separate fractions. PCDE fraction was then further cleaned on a carbon column (SK-4 carbon)[8] and PCDD/PCDF fraction on a alumina column (ICN basic alumina)[3]. Other part of the fat extract was cleaned on a carbon column (SK-4 carbon) followed on alumina columns (ICN basic alumina) for coplanar PCB analyses[3]. This fraction was also analyzed for PCDDs and PCDFs.

Analysis. Analyses were mainly performed by high-resolution gas chromatography/ mass spectrometry (HRGC/MS) and by HRGC using electron capture detection. Main PCB congeners were analyzed on a Micromat HRGC 412 gas chromatograph (Nordion) equipped with two columns and two EC detectors. Other PCBs and PCDEs were analyzed on a Hewlett-Packard 5970 mass selective detector and PCDD/PCDFs on a VG AutoSpec mass spectrometer (resolution of 10,000) in the selected ion monitoring (SIM) mode using EI ionization.

PCB, PCDD and PCDF model substances including the ^{13}C-labeled ones were commercial preparations. PCDE model substances were synthesized in our department.

RESULTS AND DISCUSSION

The results of some PCDE, PCB, PCDD and PCDF congeners are presented in Table 1. Name abbreviations for the individual PCDEs are derived by the similar way (Ballschmiter-Zell congener numbers) as PCBs[9]. PCDEs were found in all three samples. The major congeners were PCDE 47, 99, 182, 196, 197 and 203.

Table 1. Levels of PCDEs, PCBs, PCDDs and PCDFs in the breast muscle of white-tailed sea eagle as nanograms per gram in fresh weight and lipid weight. Fat per cent were 4.3, 10.2 and 1.5 for the eagles MK-1, MK-2 and MK-3, respectively.

	ng/g fresh weight			ng/g lipid weight		
PCDE	**MK-1**	**MK-2**	**MK-3**	**MK-1**	**MK-2**	**MK-3**
47	6.2	6.5	20	140	64	1300
77	0.5	0.7	2.3	12	6.9	150
118	1.2	1.5	4.1	28	15	270
126	<0.5	0.5	1.4	<12	4.9	93
147+153	15	19	71	350	190	4700
196	8.4	11	190	200	110	13000
PCB						
77	2.2	1.8	1.6	51	18	110
126	15	7.8	44	350	48	2900
169	2.6	1.4	9.2	60	14	610
105	670	510	2100	16000	5000	140000
118	2300	1500	5700	53000	15000	380000
PCDD/PCDF						
2378-TeCDD	0.018	0.010	0.040	0.42	0.10	2.7
12378-PeCDD	0.018	0.006	0.065	0.42	0.06	4.3
23478-PeCDF	0.040	0.007	0.31	0.93	0.07	21

Other PCDEs observed in the eagles were following congeners: 85, 100, 137, 138, 140, 154, 156, 163, 170, 172, 177, 180/181 (coeluting), 184, 187, 190, 194, 201, 204, 206 and 209. Same PCDE congeners as in eagles are also found in fish[7,8]. The concentrations of individual PCDE congeners ranged from < 0.5 to 190 ng/g fresh weight, whereas PCB congeners occurred even at μg/g fresh weight levels. The highest concentration was measured for PCB 138 (930000 ng/g lipid weight in the eagle MK-3).

The ratios of coplanar non-ortho-substituted PCBs were different from those measured earlier for eagle[3]. The highest concentration of non-ortho-substituted PCBs was measured for PCB 126 (44 ng/g fresh weight). Further analyses are needed to verify these results. The eagle MK-3, however, was most contaminated with PCBs as well as with PCDEs, PCDDs and PCDFs.

The concentrations of individual 2,3,7,8-substituted congeners of PCDD/PCDFs ranged between 2 and 310 pg/g fresh weight. Tetra- to hexachlorinated PCDD/PCDFs dominated and the main congener of PCDD/PCDFs found was 12378-PeCDF. 2378-TeCDF and higher chlorinated PCDD/PCDFs were at low level (<2 pg/g fresh weight).

The main toxic load in these eagles seems to be due to PCBs. Calculated TCDD equivalents (TEQs) of PCBs ranged from 3 to 16 ng/g fresh weight (sum of the concentrations of PCB congeners 77, 126, 169, 105, 118, 138, 153, 156 and 180 multipled by toxic equivalency factors (TEF) from Safe[10]).

The present results verify earlier observations that PCDD/PCDF concentrations in white-tailed sea eagles are much lower than those of toxic PCBs[3]. Considering the toxicity, for example, by using the approach of Safe[10], one can conclude that PCBs constitute the main TCDD-related toxic load in eagles, and load from PCDEs, PCDDs and PCDFs is significantly lower. The toxicity of most PCDE congeners is yet unknown, however. In addition to fish, PCDEs accumulate in human[11], as well. Therefore, more investigation is needed to estimate the environmental hazard of PCDEs.

ACKNOWLEDGEMENTS

Financial support from the Natural Science Council of the Academy of Finland is gratefully acknowledged. Model substances of PCDEs were synthesized by Tapio Nevalainen, Marja-Liisa Säämänen, Esa Vilen and Hu Jivei.

REFERENCES

1 Koivusaari J, Nuuja I, Palokangas R, Vihko, V. Degrease in eggshell thickness of the white-tailed eagle in Finland during 1884-1971. *Ornis fenn.* 1972;49:11-13.
2 Jensen S, Johnels AG, Olsson M, Otterlind G. DDT and PCB in marine animals from Swedish waters. *Nature* 1969;224:247-250.
3 Tarhanen J, Koistinen J, Paasivirta J, Vuorinen PJ, Koivusaari J, Nuuja I, Kannan N, Tatsukawa R. Toxic significance of planar aromatic compounds in Baltic ecosystem - new studies on extremely toxic coplanar PCBs. *Chemosphere* 1989;18:1067-1077.
4 Firestone D, Ress J, Brown NL, Barron RP, Damico JN. Determination of polychlorodibenzo-p-dioxins and related compounds in commercial chlorophenols. *J. Ass. Offic. Anal. Chem.* 1972;55:85-92.
5 Paasivirta J, Tarhanen J, Soikkeli J. Occurrence and fate of polychlorinated aromatic ethers (PCDE, PCA, PCV, PCPA and PCBA) in the environment. *Chemosphere* 1986;15:1429-1433.
6 Becker M, Phillips T, Safe S. Polychlorinated diphenyl ethers - a review. *Toxicol. Environ. Chem.* 1991;33:189-200.
7 Koistinen J, Vuorinen PJ, Paasivirta J. PCDEs in salmon from the Baltic Sea, River Teno and Lake Saimaa. Manuscript in preparation.
8 Koistinen J, Paasivirta J, Lahtiperä M. Bioaccumulation of dioxins, coplanar PCBs, PCDEs, HxCNs, R-PCNs, R-PCPHs and R-PCBBs in fish from a pulp mill recipient watercourse. *Dioxin'92 Proceedings, Special Issue of Chemosphere*, in press.
9 Paasivirta J, Koistinen J. Chlorinated Ethers. Chapter 4 of the Part 4 (Chlorinated Hydrocarbons and Ethers) in: Kiceniuk JW, Ray S, eds. *Analysis of Contaminants in Edible Aquatic Resources*. VCH Publishers, Inc. Manuscript.
10 Safe S. Development, validation and limitations of toxic equivalncy factors. *Chemosphere* 1992;25:61-64.
11 Stanley JS, Cramer PH, Ayling RE, Thornburg KR, Remmers JC, Breen PH, Schwemberger J. Determination of the prevalence of polychlorinated diphenyl ethers (PCDPEs) in human adipose tissue. *Chemosphere* 1990;20:981-985.