# ISOMER SPECIFIC ANALYSIS OF PCB AND PCB METHYL SULPHONES IN EGGS FROM WHITE TAILED SEA EAGLE

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Depressed reproduction in marine mammals has been linked with high concentrations of polychlorinated biphenyls (PCB)[1]. In birds, notably raptors in the Baltic, depressed reproduction has been correlated mainly to the presence of high concentrations of DDE, a metabolite of DDT[2,3,4]. In Sweden, as in many other countries, decreases in breeding success and in populations of certain birds of prey, e.g. the sea eagle, were observed[5]. Programs for monitoring the levels of DDT, including DDE and DDD, and PCB in biota were initiated. In Sweden DDT was banned in 1975 and this was the startingpoint for a change to lower DDT levels in the birds and in their eggs. The lower concentrations of DDT has in general resulted in improved hatching capacity. However, in certain areas and/or nests the hatching rate is still low. It has so far not been possible to trace any reason for this effect.

In the present study isomer specific analysis of PCB is reported in eggs from white tailed sea eagle (*Haliaetus albicilla*). The potentially most important PCB congeners for the observed insufficiency are coplanar PCB (CB-77, CB-126 and CB-169) and 1-*ortho*-PCB congeners (CB-105, CB-118, CB-156) according to data reported[6]. The concentrations of these as well as of total PCB and sDDT are reported. Furthermore, the egg homogenates were analyzed for methylsulphonyl-PCB ($MeSO_2$-PCB) and $MeSO_2$-DDE. A procedure for analysis of other xenobiotics (including hydroxylated PCBs, PCN and polybrominated diphenyl ethers) of potential interest in the egg homogenates has been developed. The general outline of the

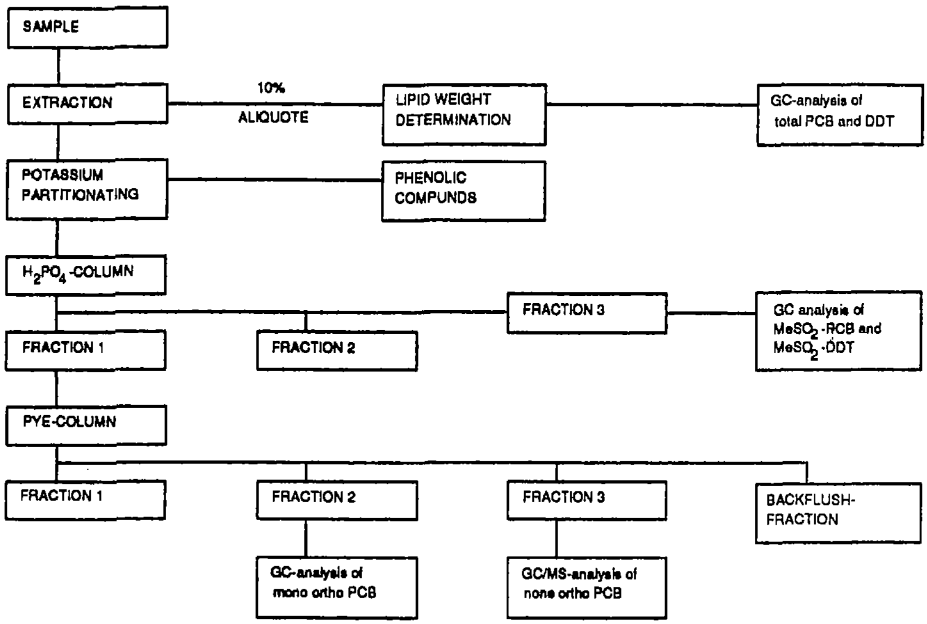


Figure 1, General presentation of cleanup procedure for egg samples from hen and white tailed sea eagle.

cleanup procedure is shown in Figure 1.

The initiation of the study has been performed with hens' eggs spiked with appropiate standard compounds to determine recovery of the selected substances. Twentyone white tailed sea eagle egg samples were obtained from the Swedish Museum of Natural History, the eggs have all been previously analysed for total PCB and sDDT on packed column GC[4]. The eggs were selected to represent eagle pairs with poor reproduction success from the early 70'ties (#1) and eagle couples showing a comparably better hatching success (#2) from the same period. The corresponding two groups of egg samples were selected from eagles hatching in the latter half of the 80'ties, #3 and #4, respectively. The eggs were homogenized in acetone:hexane (25:10) and extracted with hexane:methyl-*tert*-butyl ether (9:1). An aliquot was taken off for determination of the lipid weight. On this aliquot, total PCB and sDDT analyses were performed after the removal of lipids by conc. sulphuric acid. From the remaining extract, phenolic compounds were isolated by partitioning with potassium hydroxide (0.5 M in ethanol:water 2:5) and after acidification of the alkaline phase, reextracted into hexane. The neutral compounds were transferred to

Table 1, Mean concentrations and range based on lipid weight of coplanar-CBs (ng/g) and 1-*ortho*-CBs (µg/g) in eggs from white tailed sea eagle with different reproduction success and time. Total PCB and sDDT concentrations (µg/g) are also given.

| | EGG #1 [1] | EGG #2 [2] | EGG #3 [3] | EGG #4 [4] |
|---|---|---|---|---|
| CB-77 | 87 (19-170) | 120 (17-370) | 47 (13-19) | 16 (7.5-23) |
| CB-126 | 320 (160-560) | 200 (99-410) | 190 (120-380) | 98 (79-130) |
| CB-169 | 42 (13-72) | 24 (7.4-58) | 40 (18-81) | 17 (10-25) |
| | | | | |
| CB-105 | 14 (8-22) | 8.4 (3.8-15) | 6.9 (4.4-14) | 3.9 (3.2-4.8) |
| CB-118 | 41 (20-73) | 24 (11-46) | 22 (14-43) | 11 (9.3-13) |
| CB-156 | 13 (6.5-22) | 7.6 (4.4-14) | 7.4 (5.2-14) | 3.9 (3.2-5.3) |
| | | | | |
| Total PCB | 860 (480-1400) | 490 (300-960) | 520 (270-940) | 270 (240-300) |
| Total DDT | 730 (480-1000) | 510 (160-800) | 250 (120-510) | 120 (100-140) |

[1] Low reproduction, 1971-76, [2] Better reproduction, 1971-76, [3] Low reproduction, 1987-91, [4] Better reproduction, 1987-91.

a column of phosphoric acid impregnated silica gel ($SiO_2$:$H_3PO_4$, 2:1, 20 g). Three fractions were collected from this column; 1: unpolar xenobiotics, such as PCB, were eluted with hexane:toluene (1:1, 20 ml); 2: an intermediate fraction eluted with hexane:toluene (1:1, 30 ml) and 3: a fraction containing compounds eluted with 10% methyl-*tert*-butyl ether in hexane:toluene (1:1, 50 ml). In this latter fraction $MeSO_2$-PCB and $MeSO_2$-DDE are eluted. The non-*ortho*-PCB congeners were isolated after removal of the bulk PCB by separation on a pyrenylethyl silica column[9].

The recovery of the coplanar-CBs, CB-77, CB-126 and CB-169, were 67% ± 5, 75% ± 5 and 93% ± 10, respectively. The mean relative recovery of 1-*ortho*-CBs were 82% ± 9.

The concentrations and range of 3 coplanar-CBs, 3 1-*ortho*-CBs and total PCB and sDDT in eagle egg samples from couples showing different degrees of hatcing success are given in Table 1.

CB-126 is the dominating coplanar-CB in all groups analyzed, while CB-118 is present at the highest concentrations among the 1-*ortho*-CBs, (cf. Table 1). The results for all individual CBs, total PCB and DDT indicate relativly higher concentrations in the egg groups from eagles with less hatching success. It is also obvious that the decline in the concentrations of DDT is more rapid than that for total PCB and individual CBs. It is thus difficult to explain the observed variation in hatching success with the levels of coplanar-CBs, 1-*ortho*-CBs, total PCB or sDDT. However, the observed reproduction impairment may instead relate to some other so far unknown environmental contaminant.

$MeSO_2$-PCB and $MeSO_2$DDE, persistent metabolites of PCB and DDE were also analyzed in the present study. 3-$MeSO_2$-DDE is present in the eagle eggs as well as the 3- and 4-$MeSO_2$-CBs formed from CB-49, CB-70, CB-101, CB-87 and CB-149. The concentrations of the $MeSO_2$-PCB and the $MeSO_2$-DDE are much lower, ca. three orders of magnitude or more, than total PCB. This is a major difference compared to the observations made in mammals where $MeSO_2$-PCB is 1/10 - 1/100 of the PCB concentration[1]. This indicate a different mechanism for the formation of aryl methyl sulphones in eagles, poor transfer to the eggs or rapid excretion of the sulphones in the adult bird. The aryl methyl sulphone fraction from the cleanup procedure of the eagle eggs was also found to contain *tris*-(4-chlorophenyl)methanol as a major constituent. TCPM has been found in various seal species from the Baltic[8] and recently reported as a universal contaminant[9].

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