Methyl sulfonyl PCBs in cormorant chicks from The Netherlands

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1. Introduction

Methylsulfonyl-polychlorinated biphenyls ($MeSO_2$-PCBs) are highly persistent metabolites of PCBs, which have been found in many wildlife species. In mammals, $MeSO_2$-PCB concentrations up to 20% of the levels of their parent compounds have been reported. Information on the abundance of $MeSO_2$-PCBs in birds is scarcer. From the available literature it appears that the relative amounts of $MeSO_2$-PCBs levels in bird liver, muscle or eggs are much lower than those found in mammals.

The present study is part of a larger survey organised in the Netherlands by the National Institute of Inland Water Management and Waste Water (RIZA, Ministry of Transport and Waterworks, Dordrecht), Bureau Waardenburg (Culemborg) and the Institute of Environmental Studies (Free University, Amsterdam). The survey aims to determine levels of a large series of environmental contaminants (including heavy metals, pesticides, industrial organics like PCBs, brominated diphenylethers, PCDDs and PCDFs), biochemical parameters (e.g. EROD, Vitamin A) and collect biological data in two series of five cormorant chicks each. The chicks were collected from two colonies in the Netherlands, known for their significant differences in PCB contents of cormorant eggs[1]). The present study focuses on the levels and abundance of $MeSO_2$-PCB congeners and PCBs in adipose tissue of four cormorant chicks from each colony.

2. Experimental

Four-to-six weeks-old Cormorant chicks were collected in 1994 from two colonies in the Netherlands, viz. (i) the Biesbosch, situated in the highly contaminated sedimentation area of the River Rhine/Meuse delta where high levels of PCBs and chlorinated pesticides have been found in eggs from the colony and in fish regurgitated by the birds, and (ii) the Brede Water location, known to contain much lower PCB levels in eggs. Four chicks were analysed from each colony.

Subcutaneous adipose tissue was taken from each chick and Soxhlet extracted with n-hexane/acetone (5/2 v/v), according to the method of Jensen et al.[2]) after addition of an internal standard. The extracts were purified and fractionated in a series of clean-up and partitioning steps, schematically presented in Fig. 1. The method for PCB metabolites is a modification of a method for the isolation and identification of $MeSO_2$-PCBs presented in the literature[3]). $MeSO_2$-PCBs were analysed by GC-ECD. Identification was based on retention of authentic standards, which were gifts from the Stockholm University, and SIM-GC-EIMSD. PCBs were analysed by GC-EIMSD.

3. Results and discussion

36 PCB congeners were analysed in adipose tissue from cormorant chicks. Mean levels of total PCBs (sum of 36 congeners) in the Brede Water colony amounted to 11 $\mu g.g^{-1}$ (lipid weight) and were about one-fifth of the mean level of 58 $\mu g.g^{-1}$ observed in the Biesbosch colony. This is in agreement with differences observed in previous findings in eggs collected from the same colonies in 1988. For six congeners (IUPAC nrs. 28, 52, 101, 138, 153 and 180) a total (sum of six PCBs) of 220 and 470 $\mu g.g^{-1}$ (lipid weight) was reported in eggs from Brede Water and Biesbosch, respectively[1]). In yolk-sacs from artificially incubated eggs collected in 1989 in the Biesbosch colony this sum of six congeners amounted to 800 in hatched and 445 $\mu g.g^{-1}$ in unhatched eggs[4]). In fish regurgitated by adult birds from these colonies mean levels were found of 1.3 and 7 $\mu g.g^{-1}$ total PCBs (sum of six), respectively[1]). In the present study this sum of six congeners amounts to 6 and 30 $\mu g.g^{-1}$, respectively. The much lower concentrations found in 1994 in chicks compared to eggs from 1988 can be a result of three different phenomena. First, dilution may have occurred as a result of a stronger increase of lipid intake and/or production compared to PCB accumulation, in the period immediately after hatching. Second, transfer of PCBs from yolk sac to hatchling may be inefficient, as may be inferred from the high concentrations found in yolk sacs of hatchlings in a study with incubated eggs[4]). Thirdly, they reflect that levels of exposure to PCBs in general have gone down during the period 1988-1994.

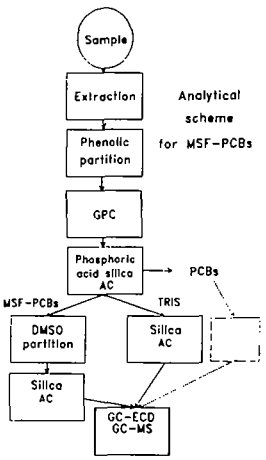

Figure 1. Sample extraction and clean up

PCB congener patterns, expressed as ratios of single congeners concentrations to the concentration of CB 153, reveal that levels of lower chlorinated PCBs are reduced in eggs and hatchlings as compared to regurgitated food. This is most likely a result of PCB metabolism, as is shown below. No difference was found between the congener patterns from the two colonies.

Eleven different $MeSO_2$-PCB congeners were analysed in the adipose tissue from cormorant chicks (Fig.2). These included the 3- and 4-$MeSO_2$-metabolites of CB nrs. 49, 87, 101, 141 and

149, and the 4-$MeSO_2$ of CB 132. Throughout the paper, the following shorthand notation will be used: 3-49, 4-49, etcetera. Mean total $MeSO_2$-PCB concentrations, defined as the sum of the eleven congeners mentioned, amounted to 30 and 70 $ng.g^{-1}$ (lipid weight) in Brede Water and Biesbosch, respectively. The most abundant metabolite observed was invariably the 4-149 congener (Fig. 3), which is consistent with findings for marine mammals[5]). The total concentration of 3-149 and 4-149 amounts to between 20 and 50% of the concentration of their parent compound CB 49. From the 3- and 4-$MeSO_2$-PCB pairs analysed, for CB 149 the concentration of the 4-$MeSO_2$ metabolite predominated its 3-$MeSO_2$ isomer. For CB 87 and CB 101 *para*- and *meta*-isomer abundance was about equal, whereas for CB 49 and CB 141 the *meta*-isomer predominated. The $MeSO_2$-PCB pattern in cormorant chicks is in close agreement with the pattern found in another fish-eating bird, viz. guillemot[6]). Reports for marine mammals show that, with the exception of 4-149, the *meta*-substituted isomers are usually predominant[7])[5]). Differences in metabolite predominance may be caused by differences between species in (activity or structure of) the cytochrome P450 isozymes involved in the biotransformation process.

The ratio of total $MeSO_2$-PCBs to total PCBs is below 0.3%, as can be seen from Table 1. This ratio is much lower than the ratio that is usually observed for mammals[5])[7]) but consistent with the ratios observed in birds and bird eggs[6]). This may be due to lower enzyme activities of birds compared to mammals. Alternatively, transfer of $MeSO_2$-PCBs from adult birds to yolk sac and subsequently to hatchlings may be hampered by physiological barriers. This study indicates that 4-6 weeks-old hatchlings have lower PCB concentrations than what is found in total eggs or yolk sac. Yolk sac to hatchling transfer may constitute a barrier for PCBs as was discussed above. Low $MeSO_2$-PCB to PCB ratios would thus reflect a similarly low ratio in the mother birds. Unfortunately we do not avail of $MeSO_2$-PCB data in parent cormorants. Alternatively, however, the route from mother via yolk sac to hatchling may constitute some selective barriers for the PCB metabolites. The $MeSO_2$-PCB patterns observed in this study do not differ much from those observed in muscle of adult guillemots or guillemot eggs[6]), which may be taken as a tentative indication of non selective transfer to the hatchling. To further investigate this, analysis of mother, eggs and hatchlings from one species would be necessary.

Table 1. Range of total PCBs and total $MeSO_2$-PCBs in Cormorant chicks ($ng.g^{-1}$ lipid weight) from two Dutch colonies

$\Sigma MeSO_2$-PCB	
Brede Water	Biesbosch
20 - 40	50 - 130
ΣPCB	
Brede Water	Biesbosch
3500 - 14000	40000 - 70000

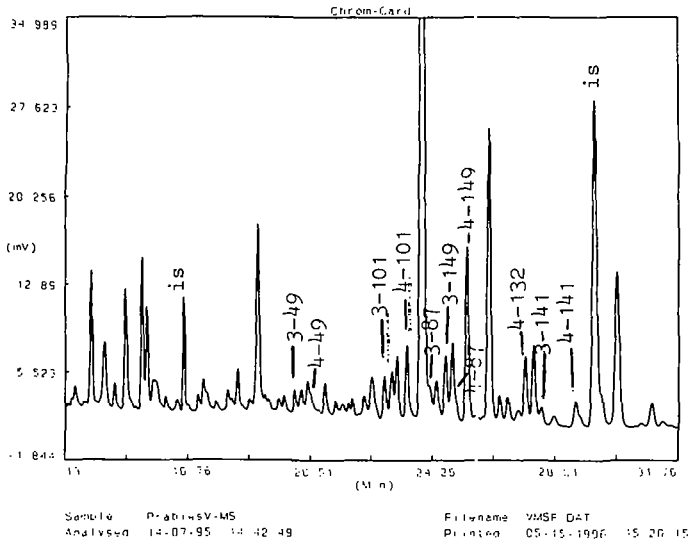

Figure 2. ECD-chromatogram of the $MeSO_2$-PCB fraction of an extract of adipose tissue from a cormorant chick from the Biesbosch colony

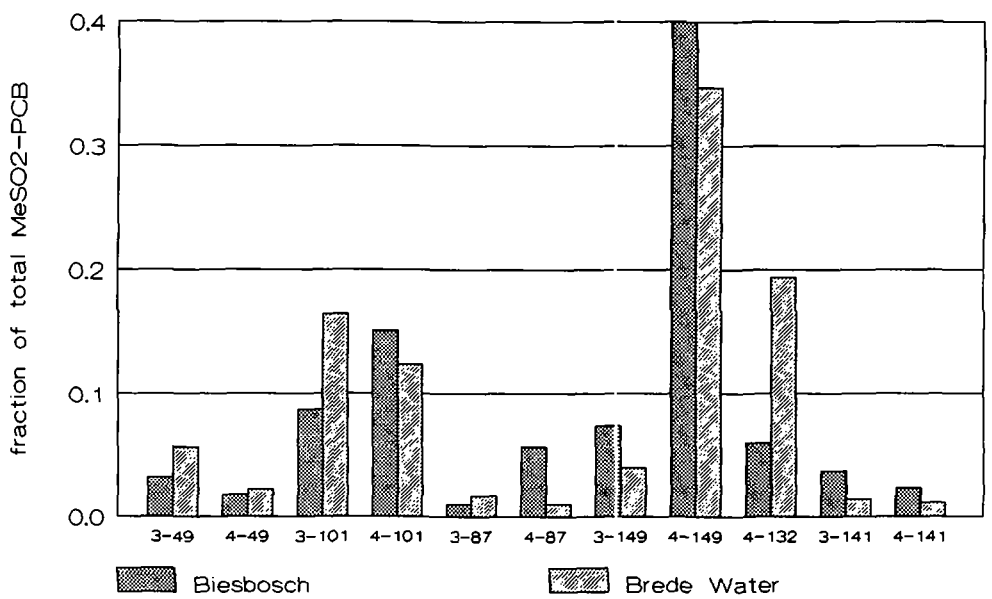

Figure 3. Congener pattern of $MeSO_2$-PCBs metabolites in Cormorant chicks (relative to total sum of 11 metabolites)

4. Conclusions

$MeSO_2$-PCB metabolites are found in Cormorant chicks at levels of several tens of $ng.g^{-1}$. Relative to total PCB concentrations these levels correspond to between 0.05 and 0.3%. This ratio is much lower than the ratio found in marine mammals, but corresponds to those found for other birds. The observed pattern of metabolite congeners in cormorant chicks resembles that of guillemot, but is different from that observed in adipose tissue of marine mammals.

5. Acknowledgements

Piet den Besten from RIZA, Theo Boudewijn from Bureau Waardenburg and Bert van Hattum and Pim Leonards from the Free University organised the survey, including the sampling campaign.

6. References

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