Toxaphenes and other Organochlorines in Dippers (*Cinclus cinclus* L.) from Southern Norway

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1. Introduction

Birds are often used as indicator organisms for assessing the contamination status of pristine and polluted areas. Due to their high trophic position, seabirds are particularly well suited as monitors of organic pollutants such as chlorinated hydrocarbons[1-4]. Since the organochlorine (OC) content in eggs is closely connected to the concentrations in the female bird, analysing eggs allows a detailed investigation of the distribution of OCs in birds without killing the animals[5-7].

In previous investigations it could be shown that dippers (*Cinclus cinclus* L.) are excellent indicators to assess the distribution of persistent pollutants in pristine riverine habitats[8-10]. The dipper is a non-migrating passerine and very closely connected to its food area [11-13]. The levels and composition of pollutants in eggs and tissues of dippers reflect bioaccumulation and transformation processes in the food chain water - insect larvae - small freshwater fish - dipper of a riverine area. The pristine habitats dippers need as a living space are known to be very sensitive. The monitoring of pollutants in such sensitive areas is needed for effective measures aimed at reducing pollutant levels in the ecosystem.

To assess the contamination status of riverine environments in Southern Norway, dipper eggs from several locations were collected and analysed for their content of α- and γ-hexachlorocyclohexane (HCHs), hexachlorobenzene (HCB), eight polychlorinated biphenyl congeners (PCBs), as well as the two toxaphene congeners Tox 26 (198-603) and Tox 50 (198-643, nomenclature according to Ochme, M. and R. Kallenborn[14]).

2. Experimental

In spring 1993 eight deserted dipper eggs were collected at six pristine riverine areas in Aust-Agder county, the southernmost part of Norway (Table 1), and stored at -30°C until analysis. Approximately 0.5 g of dipper egg was homogenised with 2-4 g of sodium sulphate. The homogenate was filled into a glass column (40 cm x 3 cm id.) for extraction and an internal standard was added. The lipids, including the OCs, were extracted by a slow flow of 100 ml cyclohexane (0.5 ml/min). Further clean-up was carried out by gel permeation chromatography using a column (30 cm x 2.5 cm id.) filled with biobeads SX-3 and cyclohexane/ ethylacetate (1:1) as mobile phase. The eluate was concentrated to 500 µl and fractionated on a deactivated alumina column with a gradient of n-hexane and methyl-t-butyl ether (MTBE) as mobile phase: 0 - 50 ml (100% n-hexane), 50 -

100 ml (50:50, n-hexane : MTBE), 100 - 150 ml (25:75, n-hexane : MTBE). All analysed OCs were collected in one fraction ranging from 10 - 130 ml. Quantification was performed using a gas chromatograph connected to a low resolution mass spectrometer (GC-LRMS) in the negative ion chemical ionisation mode (NICI).

Table 1 Sampling sites for the dipper eggs

Location	Abbreviation	Number of eggs
Tredal	TR	2
Fugletveit	FT	2
Røysedal	RL	1
Røstad	RS	1
Hardbakken	HB	1
Kylland	KL	1

3. Results

The HCHs, HCB, the PCBs and both toxaphene congeners could be detected above the detection limit in all dipper egg samples from Southern Norway. Table 2 lists the concentrations normalised on a fresh weight basis.

Table 2 Concentrations of selected organochlorines in dipper eggs from Southern Norway in units of ng/g fresh weight

Compounds	Locations							
	TR1	**TR2**	**RL**	**RS**	**FT1**	**FT2**	**HB**	**KL**
α-HCH	1.3	0.5	0.7	0.7	0.7	0.7	1.8	0.6
γ-HCH	2.6	1.2	2.4	1.2	2.5	2.2	2.8	0.9
HCB	6.3	2.6	2.0	0.4	4.1	4.0	11.0	2.4
PCB-101	3.3	1.4	1.0	1.5	2.8	2.6	4.8	1.7
PCB-118	3.0	1.6	1.1	1.4	2.3	2.4	4.2	1.6
PCB-105	0.3	0.1	0.1	0.1	0.2	0.2	0.2	0.1
PCB-153	43.5	21.8	17.3	22.0	58.6	58.9	77.1	17.8
PCB-138/163	52.1	25.8	21.7	30.2	70.1	72.7	94.5	21.4
PCB-156	3.0	1.5	1.3	1.7	3.7	3.9	5.4	1.2
PCB-180	26.4	12.0	9.3	13.0	38.3	38.1	52.3	10.1
Tox-26 (198-603)	0.5	0.3	0.4	0.4	0.8	1.1	2.4	0.2
Tox-50 (198-643)	0.4	0.2	0.3	0.3	0.8	0.9	2.9	0.3

The PCBs are the most abundant of the OCs quantified in the eggs. Their levels are approximately five times higher than the concentrations of HCB, HCHs, and the toxaphene congeners, which all tend to be in the same range between 0.5 and 10 ng/g fresh weight.

Toxaphene was measured for the first time in Norwegian dipper eggs. The two quantified toxaphene congeners (198-603 and 198-643) are those which also in other studies were found to be accumulating in food chains[15]. The concentrations of these two congeners in the eggs are between 0.16 and 2.9 ng/g fresh weight.

4. Discussion

All investigated OC compounds are known to be subject to long range atmospheric transport. HCHs, HCB and PCBs have been used in Norway in the past and may still be in use in small

quantities. Therefore both, long range transport and application within Norway, are potential sources for these contaminants in the analysed eggs. Toxaphene, however, has never been used as an insecticide in Norway and its source thus has to be long-range transport from application areas elsewhere. This insecticide was produced in huge amounts world-wide and has for example been used on cotton in the USA and Russia[16]. The fact that the concentrations of toxaphene are in the same range as those of HCB and HCHs, even though it never has been used locally, shows that long range transport, atmospheric deposition and subsequent bioaccumulation are sufficient to explain the levels of these OCs in Norway.

As should be expected from the close proximity of the sampling sites, the concentrations and composition of the OCs in the eight dipper eggs were quite similar. The egg from the site Hardbakken however had clearly higher concentrations of toxaphene than the other seven eggs. This egg showed also the highest concentrations of all the other quantified substances, suggesting biological reasons for this anomaly rather than the vicinity of a local point source.

In the two cases where two eggs were available from one location, the results were reasonably close. Even for eggs from the same bird, one would not necessarily expect identical results. It could be shown that the concentration levels of OCs in herring gull eggs decline from the first to the last egg[3].

Ormerod and Tyler reported data for various OCs in dipper eggs collected in Wales and Ireland[10]. Table 3 compares the concentrations in the eggs from the three locations. Only those chemicals are listed for which concentrations have been reported in both studies.

Table 3 Concentrations of selected organochlorines in dipper eggs from three European countries (geometric means in units of ng/g fresh weight).

	S-Norway	Wales	Ireland
year of sampling	1993	1992	1992
no. of samples	8	15	18
γ-HCH	1.8	2.5	3.1
HCB	2.9	3.7	1.2
PCB-118	2.0	2.5	40
PCB-153	33.8	39.1	2.5
PCB-138/163	41.7	23.6	5
PCB-180	20.4	6.8	1.2
reference	this study	[10]	[10]

The comparison reveals that the patterns of the PCB distribution is different. In the Welsh and Irish eggs PCB 153 was the most dominant congener, while in the Norwegian samples PCB-138/163 was the congener with the highest concentration (Table 3). This indicates that the investigated riverine environments in Ireland are influenced by different local sources of organochlorines than the Norwegian and Wales catchments. Part of the differences may also be explained by differences in the food habits and in the ecological structure of the dipper habitats.

5. References

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