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Persistent organochlorine compounds in peregrine falcon (*Falco peregrinus*) eggs from South Greenland: Levels and temporal changes between 1986 and 2003

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ABSTRACT

Thirty-seven addled peregrine falcon eggs collected in South Greenland between 1986 and 2003 were analysed for their content of the organochlorine compounds polychlorinated biphenyls (PCBs), dichlorodiphenyl tricloroethane (DDT) and its degradation products, hexachlorocyclohexane (HCH) isomers and hexachlorobenzene (HCB). PCBs and DDT (including metabolites) were by far the most abundant OC groups, with median concentrations of 55 and 40 μg/g lw, respectively. The concentrations were high in an Arctic context, but similar to previously reported levels from Alaska and Norway and slightly lower than concentrations measured in eggs from industrialised regions. Geographical differences may be of importance, considering the migration of peregrine falcons and their prey. ΣHCH and HCB had median concentrations of 0.39 and 0.17 μg/g lw, respectively. On average, DDE accounted for 97% of ΣDDT, but was below critical levels for eggshell thinning. All compound groups showed a weak decreasing trend over the study period, which was statistically significant for HCB and close to being significant for ΣHCH. The weak decrease of ΣPCB and ΣDDT is different from other time trend studies from Greenland, usually showing a more pronounced decrease in the beginning of the study period, followed by a certain stabilisation in recent years.

1. Introduction

The bioaccumulation of organochlorine compounds (OCs) endangered the populations of a top predator, the peregrine falcon (*Falco peregrinus*), in the northern hemisphere and led to its extinction in the most heavily impacted areas of North America and Europe between the 1950s and 1970s. Reduced reproduction rates have mainly been attributed to high concentrations of the insecticide dichlorodiphenyl trichloroethane (DDT) and its degradation product dichlorodiphenyl dichloroethylene (DDE), polychlorinated biphenyls (PCBs) and structurally similar chlorinated chemicals. They have been found to interfere with the calcium metabolism in the birds, leading to reduced eggshell thickness and abnormal behaviour (Lundholm, 1987; Wegner et al., 2005). Furthermore, direct toxic effects on birds include neurotoxicity and decreased reproduction due to endocrine disruption and embryotoxicity (Ambrose et al., 2000). The peregrine falcon has become a high trophic level key species for monitoring of OCs in the environment. However, only few analyses of OC temporal trends have been conducted (Wegner et al., 2005), especially for Arctic populations of the peregrine falcon (Johnstone et al., 1996; Sørensen et al., 2004).

This paper analyses the trends in OC levels over an 18 year time span (1986–2003) in the tundra subspecies of the peregrine falcon (*F. p. tundrius*) in South Greenland. Individuals of this population are likely to be exposed to OCs during their annual movements between the breeding grounds in Greenland (May–September), on the autumn and spring migration through North America and on their wintering grounds in the Caribbean and South America. In Greenland, the birds may be exposed to OCs locally, as the compounds are subject to long-distance transport from their sources to the cold regions of the Arctic. Bioaccumulation and biomagnification of OCs in lipid-rich tissues of Arctic wildlife has been shown in a number of studies (e.g. AMAP, 2004) although concentrations in terrestrial ecosystems have generally been found to be low, in comparison with the more complex food web of the marine ecosystem. The birds of this study nearly exclusively prey on terrestrial passerines during the breeding season in Greenland (Falk et al., 1986; Falk and Møller, 1988). Sources of contamination may be present at their wintering grounds in the Caribbean and South America where phasing out of persistent organochlorine pesticides has generally been slower than in North America and Europe, and renewed use has been deemed necessary to fight malaria. First-year Arctic migrant peregrine falcons have been shown to carry higher OC loads when they return north after their first wintering in South America (Henny et al., 1982).

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The peregrine falcon population in South Greenland has been studied in field surveys since 1981, and addled eggs have been collected since 1986. Recently, information was published on the concentration and long-term trend of brominated flame retardants (BFRs) in peregrine falcon eggs of this population, showing increasing concentrations of some BFRs since 1986 (Vorkamp et al., 2005). Furthermore, the long-term development of eggshell thickness, a proxy for DDT/DDE loads, was studied and indicated gradual, but slow recovery, still far from reaching the natural pre-DDT level (Falk et al., 2006). The present study adds to the existing knowledge by presenting concentrations of OCs in the same eggs which previously were analysed for BFRs. Following up on previous calculations on inter-clutch variation (Vorkamp et al., 2005), the hypothesis of a smaller variation between eggs of the same bird compared with the overall variation was examined, in order to gain some insight into the natural variation among eggs.

The compounds included in this study were 22 PCB-congeners, DDT and its metabolites, α-, β- and γ-hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB). The increased awareness of environmental problems stopped the use of most OCs in industrial production processes and agriculture in the 1970s (AMAP, 2004). PCBs, DDT and HCB are listed in the Stockholm Convention of persistent organic pollutants (POPs), which restricts or prohibits the production, trade and use of these compounds because of their persistence, bioaccumulation, long-range transport and adverse health effects. HCH is covered by the Aarhus Protocol on POPs adopted by the United Nations Economic Commission for Europe (UNECE, 1998), with the ultimate objective to eliminate any discharge, emissions and losses of POPs. Despite the regulation of most OCs, they are still ubiquitously present in the environment. This paper addresses the questions whether or not OC concentrations still reach levels known to cause adverse effects in birds and what the concentration development was between 1986 and 2003.

2. Materials and methods

2.1. Sampling

The eggs originated from peregrine falcons breeding in South Greenland. The population is roughly estimated at 500–1000 pairs (Falk and Møller, 1988). Based on autumn migration counts in the eastern USA, there is a slight evidence for a population increase in the Arctic (Titus and Fuller, 1990). The study area covers the inner parts of the three southernmost municipalities of Southwest Greenland, Nanortalik, Qaqortoq and Narsaq, approx within 60°–61° N and 45°–46° W. The area is low Arctic, with tundra vegetation and willow and birch shrub in the warm, sub-Arctic areas far from the cool outer coast.

The study site was visited annually for field surveys, except in 1993, 1996 and 1997, and addled eggs were collected for contaminant analysis. Several birds are ring marked and could be identified (Table 1). The eggs were frozen on return to Denmark and kept refrigerated until analysis. Prior to analysis, the eggs were weighed and measured, and opened carefully along the egg equator in order to keep two whole egg halves for determination of eggshell thickness.

2.2. Chemical analyses

37 addled eggs collected between 1986 and 2003 were analysed (Table 1). No eggs were collected in 1993, 1996 and 1997 as no field studies were conducted in those years. The analytical method followed the approach previously described for black guillemot eggs (Vorkamp et al., 2004). After homogenisation, about 3.5 g of each egg sample were dried with anhydrous Na_2SO_4, and spiked with recovery standards (CB-3, CB-40, CB-198). In the first sample batch, approximately 6 g of sample was taken. As the OC concentrations were high, the amount of sample was reduced in the following analyses to reduce matrix effects and to keep more of the sample material for other purposes.

Table 1
Overview of the egg samples analysed in this study

ID	Year	Female ID	Lipid (%)	Dry matter (%)
1	1986		7.0	19.7
2	1987	A	9.4	29.0
3	1988	A	18.9	35.3
4	1988[a]	A	22.4	45.2
5	1988[b]		20.3	38.7
6	1989	B	10.7	22.4
7	1990	B	6.3	26.0
8	1990	B	7.3	21.1
9	1990		6.3	22.9
10	1991		7.5	27.5
11	1991		6.8	19.0
12	1991		5.2	17.5
13	1992	C	9.3	18.3
14	1992	B	4.8	23.3
15	1992	B	6.8	17.8
16	1992	B	5.6	15.6
17	1994	C	7.5	22.4
18	1994		3.6	21.1
19	1994		6.7	17.9
20	1994		7.9	20.9
21	1994		5.7	15.6
22	1995	D	6.5	45.4
23	1995	F	6.3	19.0
24	1998	D	5.8	34.2
25	1998	E	7.6	33.2
26	1999	E	3.9	21.7
27	1999	F	6.0	17.3
28	1999	E	4.0	16.2
29	2000	D	3.6	13.3
30	2000	D	2.8	26.2
31	2000	E	3.9	13.7
32	2000	E	4.6	17.6
33	2001		6.5	24.6
34	2002	G	6.9	20.1
35	2002		5.3	15.9
36	2003	G	7.0	20.4
37	2003		6.0	18.2

[a] No data available for PCBs, HCB, HCHs and DDT.
[b] No data available for HCHs.

The samples were Soxhlet extracted using 350 ml of a mixture of *n*-hexane and acetone (4:1, v/v) and concentrated by rotary evaporation. The extracts were purified on a multilayered glass column packed bottom-to-top with 5 g deactivated aluminium oxide containing 10% water, 1 g activated silica (24 h at 160 °C), 5 g activated silica impregnated with 40% concentrated sulphuric acid and 1 cm anhydrous Na_2SO_4, and eluted with 250 ml *n*-hexane. The cleaned extracts were concentrated to about 1 ml by rotary evaporation with *iso*-octane as keeper and under nitrogen. Defined amounts of the internal standards (CB-53, CB-155) were added and the samples were adjusted to a precise volume of 1 ml.

The following individual compounds and congeners were included in the analysis: PCBs: CB-28, CB-31, CB-44, CB-49, CB-52, CB-99, CB-101, CB-105, CB-110, CB-118, CB-128, CB-138, CB-149, CB-151, CB-153, CB-156, CB-170, CB-180, CB-187, CB-188, CB-194 and CB-209. DDTs: p,p′-DDT, p,p′-DDE, p,p′-DDD, o,p′-DDT and o,p′-DDE. HCHs: α-HCH, β-HCH and γ-HCH. HCB. The lipid content was determined according to Smedes (1999), and the dry matter content was calculated based on mass loss after drying at 105 °C until constant weight (within 2% deviation). The compounds were analysed by dual column gas chromatography with electron capture detection (GC-ECD). The technical details on capillary columns, temperature programmes and calibrations are described by Vorkamp et al. (2004). Samples 4 and 5 (Table 1) could not be analysed by GC-ECD because of matrix interferences. No OC data are available for sample 4, while sample 5 was analysed for PCBs, HCB and DDT by GC-MS in the electron impact (EI) mode, using the same capillary column and temperature