

Chlorinated hydrocarbons and polybrominated diphenyl ethers in glaucous gulls (*Larus hyperboreus*) from Barentsburg (West Spitsbergen)

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Introduction

The glaucous gull is the main avian predator in the Arctic ecosystem; it is particularly vulnerable to contaminant exposure due to low metabolic capacity. Their diet includes mainly small crustaceans, mollusks (mainly mussels), polychaetes and fish. In the nestling period, they feed also on eggs and young birds of the other species¹. Considerable numbers of glaucous gulls were found dead on Svalbard. Detailed analysis of their tissues demonstrated extremely high concentration of PCBs and global pesticides^{2,3}. However, only limited information is available on toxaphene and polybrominateddiphenyl ether levels in glaucous gulls from Svalbard archipelago⁴.

Materials and Methods

In August 2001, 20 adult glaucous gulls (13 female and 7 male) were collected in Barentsburg area (Figure 1). Traditional ornithological measurements were carried out for each bird. Governor of Svalbard (Sysselmannen på Svalbard) issued permission for bird sampling.

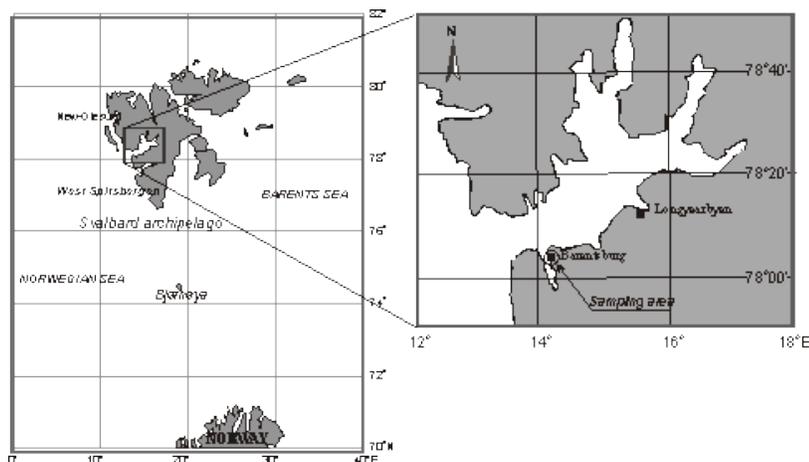


Figure 1. Map of Svalbard archipelago and area of glaucous gulls sampling in 2001

Liver samples were sampled and kept frozen at -20°C until analyses. Samples were analysed for organochlorine contaminants (OCs): PCBs, DDT family, chlorobenzenes (CBz), hexachlorocyclohexanes (HCHs), chlordane related compounds (CHL), endosulfanes, endrine, methoxychlor, mirex, toxaphenes, and also polybrominated diphenyl ethers (PBDEs). Toxaphene (homologues and individual chlorobornane congeners) and PBDEs were analysed at National Water Research Institute (Burlington) using a modification of the method⁵. All other OC analyses, were conducted at the Centre of Environmental Chemistry, S.P.A. "Typhoon" (Obninsk, Russia) using a Hewlett Packard Model 5790A GC equipped with a ⁶³Ni electron capture detection system. Detailed method description, including GC

conditions, is published elsewhere⁶. The quality assurance included: analysis of reference materials (NIST cod liver 1588), blanks, duplicates, spike and surrogate recoveries.

Total TCDD-equivalent of PCBs was calculated using TCDD toxic equivalency factors (TEFs) according to⁷. The body condition index (BCI) was calculated as (body weight/wing length). Liver somatic index (LSI) was calculated as (liver weight/body weight) x 100%. Factor analysis was used for revealing of correlation structure of contaminant concentrations. Lipid base log-transformed contaminant concentrations were used for Spearman rank order correlation and factor analyses. The statistical analysis was carried out using STATISTICA Ver.4.5 (StatSoft).

Results and Discussion. Levels of persistent organic pollutants in hepatic tissue of glaucous gulls are presented on Table 1. Significant differences between concentrations of all contaminants analyzed in tissues of male and female birds were not found.

Table 1. Persistent organic pollutant concentrations (ng/g wet weight) and lipid contents (%) in hepatic tissues of glaucous gull from Barentsburg area, 2001. Arithmetic means \pm standard deviation (Mean \pm S.D.), geometric means (GM) and median

Compounds	Female, N=13			Male, N=7			GM	Median
	Mean	\pm S.D.	GM	Median	Mean	\pm S.D.		
Σ CB _Z	25.7	\pm 16.8	20.9	21.9	25.8	\pm 8.87	24.3	30.7
Σ HCH	1.71	\pm 1.07	1.20	1.43	2.40	\pm 2.08	1.87	1.54
Σ CHL	345	\pm 386	181	225	215	\pm 183	130	135
Endosulphanes	0.24	\pm 0.24	0.12	0.21	1.12	\pm 2.45	0.28	0.17
Σ DDT	205	\pm 86.4	191	190	441	\pm 393	299	264
Endrine	0.67	\pm 0.54	0.38	0.52	0.85	\pm 0.59	0.70	0.86
Methoxychlor	1.20	\pm 1.39	0.27	0.57	0.60	\pm 0.65	0.14	0.51
Mirex	4.22	\pm 3.73	2.36	3.49	3.19	\pm 1.70	2.60	3.61
Σ Toxaphene	83.4	\pm 53.1	30.9	87.3	133	\pm 131	98.5	91.5
Σ PCB	856	\pm 403	784	804	1372	\pm 721	1175	1628
Σ PBDE	21.1	\pm 25.3	13.9	17.3	15.9	\pm 7.30	14.2	15.6
Lipid, %	3.72	\pm 0.74	3.65	3.57	3.71	\pm 0.55	3.68	3.55

Σ CB_Z = sum of 1.3.5-TCB, 1.2.4-TCB, 1.2.3-TCB 1.2.3.4-TetCB, PentCB and HCB, Σ HCH

= sum of α -, β - and γ -HCH, Σ CHL = sum of *cis*- and *trans*-chlordane, *trans*-nonachlor, oxychlordane, and heptachlor, Σ DDT = sum of *o,p*²-DDE, *p,p*²-DDE, *o,p*²-DDD, *p,p*²-DDD, *o,p*²-DDT and *p,p*²-DDT, Σ Toxaphene = sum of *hexa*-, *hepta*-, *octa*- and *nona*-homologues, Σ PCB = sum of 55 PCB congeners, Σ PBDE = sum of PBDE-17, 28, 47, 66, 71, 77, 85, 99, 100, 138, 153, 154, 183, 190 and 209.

Σ PCBs, Σ DDT, Σ CHL and Σ CB_Z were the most abundant persistent OC contaminants in hepatic tissue of both male and female glaucous gulls. The others OCs investigated (hexacholocyclohexanes, endosulphanes, endrine, methoxychlor and mirex were found in almost every sample; however their concentrations did not exceed 7 ng/g ww (Table 1).

Σ PCB concentrations ranged from 368 to 2410 ng/g wet weight; common geometric mean (calculated for all gulls analyzed) was 903 ng/g ww. This level is 2.4 times as higher than Σ PCB concentration in liver of the same species from New-Olesund (north-western part of the West Spitsbergen, Figure 1) (373 ng/g ww) but two times lower than in glaucous gulls from Bjørnøya (one of the islands of Svalbard archipelago located southward off West Spitsbergen, Figure 1) (1844 ng/g ww) found in 1991⁸. Following PCB congeners were the most abundant into Σ PCB (Figure 2). Total concentration of these congeners was approximately 95% of Σ PCB. Total TEQ values ranged from 39 to 533 pgTEQ/g ww and from 78 up to 2004 pgTEQ/g ww for female and male gulls accordingly. Contribution of PCB-126 into Total TEQ was 84-96%

Σ DDT was the second most abundant OC contaminants. Σ DDT levels ranged from 122 to 408 ng/g ww and from 81 to 1115 ng/g ww in hepatic tissues of female and male birds accordingly. Common geometric mean (223 ng/g ww) was two time higher than in glaucous gulls from New-Olesund (114 ng/g ww) and 1.4 time lower than in the same bird species from Bjørnøya (314 ng/g ww) in 1991⁸. Contribution of *p,p*²-DDE into Σ DDT was 85-95%.

ΣCHL concentrations ranged from 13 to 1181 ng/g ww and from 15 to 481 ng/g ww in liver of female and male birds accordingly. Common geometric mean (161 ng/g ww) was 5 and 1.4 times higher compared to ΣCHL concentration found in glaucous gulls from New-Olesund (32.9 ng/g ww) and Bjørnøya (117 ng/g ww), accordingly, in 1991⁸. Contribution of oxychlorodane into ΣCHL was 92-100%.

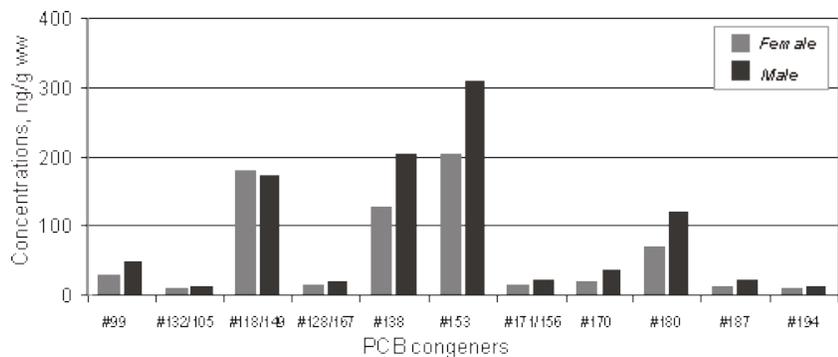


Fig.2. PCB congener patterns in hepatic tissues of glaucous gull from Barentsburg, 2001. PCB congeners accounting less than 1% of ΣPCB in each sample are not shown.

ΣCBz residue levels ranged from 7.6 to 58.4 ng/g ww. HCB contribution into ΣCBz was 75-97%. Common geometric mean of HCB (18.9 ng/g ww) was similar to those found in glaucous gulls from New-Olesund (16.2 ng/g ww), but was 2.7 times lower than in the same bird species from Bjørnøya (50.6 ng/g ww) in 1991⁸.

ΣToxaphene levels ranged from 6.5 to 163 ng/g and from 37 to 421 ng/g ww in hepatic tissue of female and male glaucous gulls accordingly. *Octa-* and *hepta-*toxaphenes were predominated; their contributions in ΣToxaphene were 75% and 17%, accordingly. Among individual chlorobornane congeners analysed (Parlars 26, 31, 32, 38, 39, 40/41, 42, 44, 50, 56, 58 and 62 also B7-1001 and B8-1412), the highest concentration were found for Parlar-38 (common geometric mean 8.8 ng/g ww, range 1.7-50 ng/g ww) and Parlar-44 (geometric mean 4.1 ng/g ww, range 0.5-49 ng/g ww). Parlars 39, 56 and 62 were not detected; geometric mean and median concentrations of the others chlorobornane congeners did not exceed 1 ng/g ww, while median concentration of Parlars 26 and 50 found in glaucous gulls from Longyerbyen (Figure 1) in 1995 were 16.3 and 21.6 ng/g ww accordingly⁴.

ΣPBDE hepatic concentrations in female and male glaucous gulls ranged from 3.5 to 100 ng/g ww and from 6.1 to 27 ng/g ww accordingly. Among PBDEs, the highest concentrations were found for PBDE-47, followed by #100, #99, #209, #153 and #154 (Figure 3), while levels of the others individual PBDEs were lower than 0.4 ng/g ww (PBDE-17, 28, 66, 183 and 190) or below detection limit (PBDE-71, 77, 85). It is important to mention that despite the average concentration of PBDE-209 (0.95 ng/g ww) was not very high in comparison to some other PBDEs, its level in some individuals reached 7.5 and 86.5 ng/g ww. The last mentioned value is the highest PBDEs concentration found during the present studies.

Similar study was conducted on Bjørnøya in 1995⁴. Out of ten PBDE congeners analysed in liver of glaucous gulls only PBDE-47 and 99 were detected. Median concentration of PBDE-47 (2.3 ng/g ww) was 3.6 times lower than found in gulls from West Spitsbergen during the present study (median concentration 8.3 ng/g ww) while PBDE-99 levels were similar.

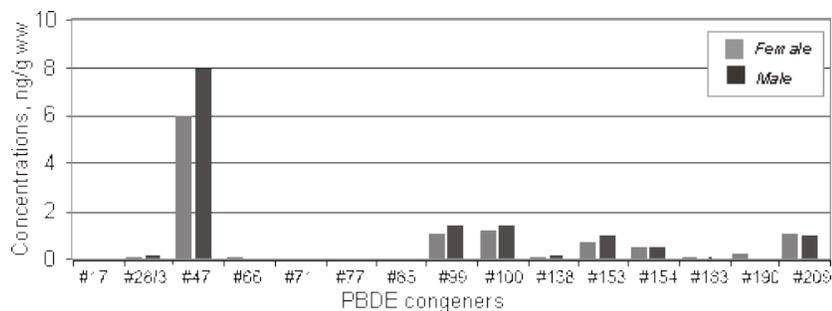


Fig.3. PBDE congener patterns in hepatic tissues of glaucous gull from Barentsburg, 2001.

Relationships between biological characteristics and contaminant levels.

According to correlation analysis, significant relationships ($p < 0.1$) were found for BCI vs PBDE-28 ($r = 0.411$, $p = 0.072$), BCI vs PBDE-153 ($r = 0.380$, $p = 0.098$), BCI vs Σ DDT ($r = 0.423$, $p = 0.063$), BCI vs HCB ($r = 0.477$, $p = 0.034$), BCI vs Σ PCB ($r = 0.582$, $p = 0.008$), BCI vs *nona*-toxapenes ($r = 0.435$, $p = 0.063$) also LSI vs PBDE-138 ($r = -0.432$, $p = 0.0574$), LSI vs *o,p'*-DDE ($r = -0.577$, $p = 0.008$) and LSI vs HCB ($r = -0.448$, $p = 0.0475$).

Correlation structure of contaminant levels

In the result of the factor analysis, four first common factors accounted 75.6% of the total variance were found. These factors had significant positive loadings on following contaminants: Factor 1 (26.7% of total variance) – Σ DDT, mirex, Σ CBz, Σ PCB and Σ Toxapene; Factor 2 (20.6%) – Σ HCH and β -endosulphane; Factor 3 (14.8%) – α -endosulphane and metoxychlor; Factor 4 (13.5%) Σ PBDE and endrine.

This is the first information on individual PBDE congener levels in organs of marine birds from the West Spitsbergen. A group of 17 PBDE congeners, including *deca*-BDE, was screened. Currently BDE-47 is the most abundant congener, following by BDE-100, 99 and more important *deca* BDE-209, which reflects contemporary application of brominated flame retardants in adjacent environment.

Acknowledgements

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