

POPs IN MARINE BIRDS FROM THE EASTERN BARENTS SEA (RUSSIA): COMPARATIVE ANALYSIS OF DATA SET FROM 1992 AND 2002

Savinov V¹, Gabrielsen GW², Savinova T¹, Alekseeva L³, Polder A⁴, Skaare JU^{4,5}, Koryakin A⁶

¹Akvaplan-niva, Polar Environmental Center, N-9296, Tromsø, Norway, ²Norwegian Polar Institute, Polar Environmental Centre, N-9296, Tromsø, Norway, ³Centre for Environmental Chemistry, S.P.A. Typhoon, Obninsk, Russia, ⁴The Norwegian School of Veterinary Science, Department of Pharmacology, Microbiology and Food Hygiene, Division of Pharmacology and Toxicology, P.O. Box 8146 Dep., N-0033 Oslo, Norway, ⁵National Veterinary Institute, P.O. Box 8156 Dep., N-0033 Oslo, Norway, ⁶Kandalaksha State Nature Reserve, Kandalaksha, Russia.

Abstract

Residue levels of establish persistent organic pollutants: polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), DDT family compounds, hexachlorocyclohexanes (HCHs), and chlordane related compounds (CHLs) in hepatic tissue of seabirds (Brünnich's guillemot, Common guillemot, Black-legged kittiwake, Razorbill and Atlantic puffin) collected in 1992 and 2002 on islands of the Eastern Barents Sea have been compared. During the decade period, statistically significant decrease in residue levels of all analysed contaminants was found in liver of Brünnich's guillemots, Razorbills, Kittiwakes (HCB and Σ DDT excluded) and Atlantic puffins (HCB and Σ HCH excluded). In liver of Common guillemots, only Σ PCB concentration measured in 2002 was significantly lower compared to those found in 1992. The levels of the other organochlorines did not differ significantly. Decline in hepatic concentrations during the study period made up 37-73% (Σ PCB), 40-65% (Σ DDT), 49-50% (HCB), 57-71% (Σ CHL) and 92-95% (Σ HCH) of levels found in 1992.

Introduction

Production and usage of the most establish persistent organic pollutants (POPs) were generally banned during 1980s-1990s¹. However their residues are present in the components of terrestrial and aquatic ecosystems until now. Seabirds are indicators of the state of the marine environment since they are closely connected to the stocks of marine fish and invertebrates. The main goal of present study was to determinate possible changes in environmental conditions of the Eastern Barents Sea through comparison of POPs residue levels in tissues of seabirds collected in 1992 and 2002.

Materials and Methods

Fieldwork. Brünnich's guillemots (*Uria lomvia*), Common guillemots (*Uria aalge*), Black-legged kittiwakes (*Rissa tridactyla*), Razorbills (*Alca torda*) and Atlantic puffins (*Fratercula arctica*) were caught on islands of the Seven Islands Archipelago (Barents Sea) in the summer 1992 and 2002 (Figure 1). Hepatic tissues of seabirds were sampled and kept frozen at -20° until analyses.

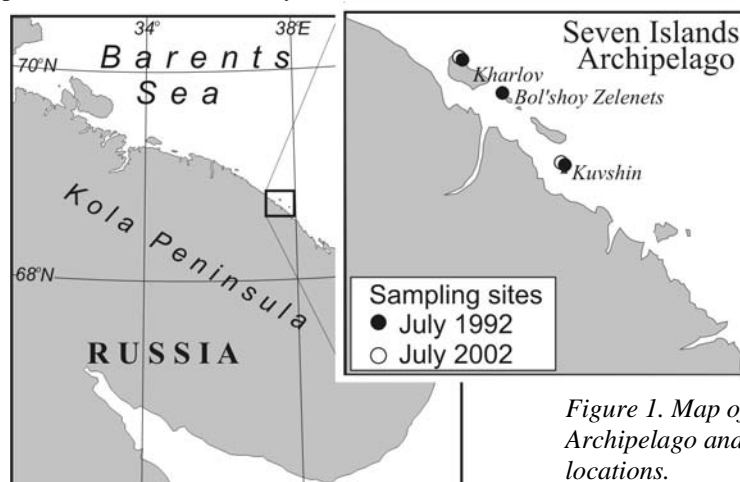


Figure 1. Map of the Seven Islands Archipelago and sampling site locations.

Chemical analyses. Samples were analysed for polychlorinated biphenyls (PCBs), DDT family compounds, Hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and chlordane related compounds (CHLs). Analyses of samples collected in 1992 were conducted at Institute of Pharmacology and Toxicology, Norwegian Veterinary College (Oslo, Norway) using methods described by Brevik² with modifications³. The laboratory's analytical quality was approved in several intercalibration tests, including the ICES/IOC/OSPARCOM inter-comparison exercises on the analysis of PCBs in marine media and analytical quality assurance test WHO/INEP. Samples collected in 2002 were analyzed 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 and GC conditions are presented in⁴. The quality assurance included: analysis of reference materials (NIST cod liver 1588), blanks, duplicates every 5 samples, spike and surrogate recovery.

Statistical analyses. The hypothesis of normal distribution was tested using Shapiro-Wilk's W Test on log-transformed data. The t-test was used to evaluate the differences between mean when this hypothesis was not rejected; otherwise Mann-Whitney U test was applied for evaluation. Null hypothesis (equality of means) was rejected at the 95% significance level ($p < 0.05$). Statistically significant differences between mean organochlorine concentrations found in hepatic tissues of female and male were not found for all bird species studied, therefore sex of the birds has not been taken into account in calculations of means.

Lipid base log-transformed concentrations were used for comparison mean organochlorine concentrations in tissues of birds measured in 1992 and 2002. Outliers and extreme values (Figure 2) were excluded.

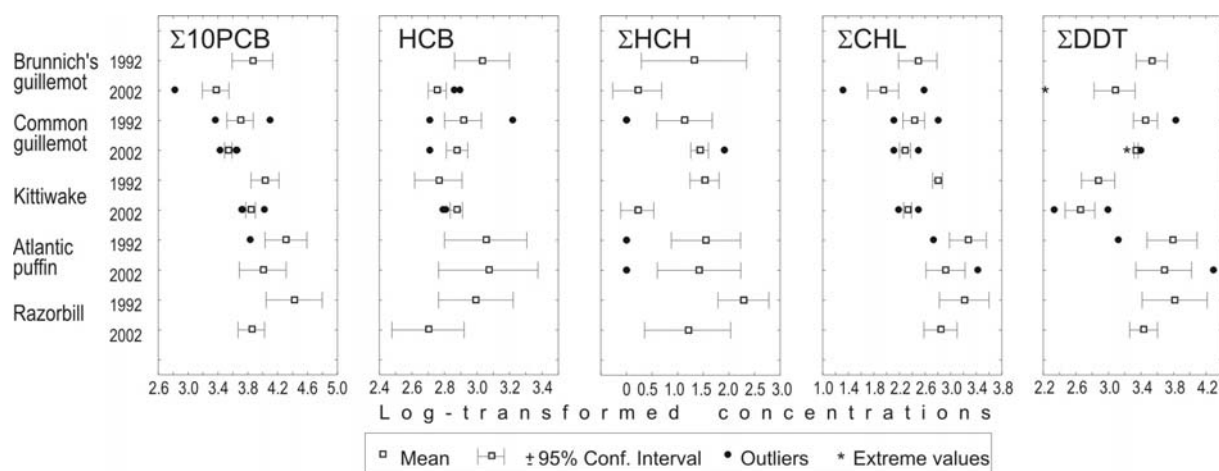


Figure 2. Non-outliers ranges of organochlorine concentrations (ng/g lipid weight) in hepatic tissues of seabirds

Results and Discussion.

Arithmetic mean concentrations of organochlorines in hepatic tissues of seabirds are presented in Table 1.

PCBs were the major organochlorine contaminants in all samples. In 2002, the highest $\Sigma 10\text{PCB}$ (sum of PCB-28, 31, 101, 105, 118, 138, 153, 156, and 180) concentrations (from 4611 ng/g up to 30000 ng/g lipid wt) were found in liver of Atlantic puffins. In hepatic tissues of Brunnich's guillemots and Common guillemots, ΣPCB concentration ranging from 655 ng/g to 4505 ng/g lw; average levels of ΣPCB in these bird species were the lowest. Residue levels of $\Sigma 10\text{PCB}$ found in liver of Kittiwakes and Razorbills were quite similar and varied within ranges of 5111 – 10486 ng/g lw and 5175-11936 ng/g lw, respectively. Mean $\Sigma 10\text{PCB}$ concentrations in hepatic tissues of these bird species differed significantly from those found in both Atlantic puffins and guillemots.

Residue levels of Σ 10PCB in seabirds in 2002 significantly differed from those found in the same bird species collected in 1992 (Table 2). During the 1992-2002 period, decline in Σ PCB concentrations made up 29%-73% of 1992 level. PCB patterns in tissues of the same bird species collected in 1992 and 2002 were quite similar. However relative amounts of PCB-118 in liver of Brünnich's guillemots and Common guillemots collected in 2002 were markedly lower than in samples collected in 1992.

Table 1. Organochlorine residue levels (ng/g lipid weight) in hepatic tissues of seabirds from the Seven Islands Archipelago in 1992 and 2002. Arithmetic mean and standard deviation (S.D.). N = number of samples.

Compounds	Year	Brünnich's		Common		Kittiwake		Atlantic puffin		Razorbill	
		1992	2002	1992	2002	1992	2002	1992	2002	1992	2002
	N	5	10	9	10	5	10	7	6	5	5
HCB	Mean	1115	579	868	769	594	751	1341	1431	1048	534
	S.D.	333	109	332	152	133	89	849	1082	364	216
α -HCH	Mean	23	1.1	3.2	2.2	2.5	<0.05	10	<0.05	<0.05	<0.05
	S.D.	34	3.6	4.9	3.0	3.6		18			
β -HCH	Mean	26	11	24	23	28	1.8	56	57	245	24
	S.D.	34	36	22	22	7.3	3.9	57	73	134	16
γ -HCH	Mean	2.7	0.5	<0.05	5.9	7.1	0.6	<0.05	2.2	<0.05	1.4
	S.D.	3.7	1.6		4.2	16	1.9		5.4		3.1
Σ HCH	Mean	52	13	28	31	37	2.4	66	60	245	26
	S.D.	66	41	25	20	20	5.5	54	73	134	16
Oxychlordane	Mean	243	92	199	178	482	187	743	637	246	133
	S.D.	137	64	111	51	61	43	459	622	125	69
<i>trans</i> -Chlordane	Mean	<0.03	7.0	5.9	12	15	12	2.7	58	15	125
	S.D.		21	9.0	13	1.7	13	7.2	32	15	65
<i>cis</i> -Chlordane	Mean	<0.03	4.4	<0.03	<0.03	<0.03	0.6	459	2.9	365	7.9
	S.D.		10				1.9	222	4.0	290	4.2
<i>trans</i> -Nonachlor	Mean	33	1.8	10	11	48	16	583	221	990	378
	S.D.	36	5.7	13	12	31	13	462	215	513	180
<i>cis</i> -Nonachlor	Mean	69	11	84	<0.01	85	<0.01	451	105	352	119
	S.D.	72	10	40		22		272	100	267	56
Σ CHL	Mean	345	116	298	201	629	221	2239	1023	1967	763
	S.D.	179	103	156	55	96	45	1264	806	1186	367
<i>p,p'</i> -DDE	Mean	3509	1434	2889	2173	649	474	6666	4612	6626	2802
	S.D.	1187	656	1469	152	284	263	3423	3055	3765	1048
<i>o,p'</i> -DDD	Mean	<0.03	<0.03	<0.03	1.5	<0.03	<0.03	61	0.2	153	1.6
	S.D.				4.8			91	0.6	141	2.4
<i>p,p'</i> -DDD	Mean	62	<0.03	40	0.7	<0.03	<0.03	118	11	274	12
	S.D.	67		35	2.3			125	10	219	7.3
<i>o,p'</i> -DDT	Mean	<0.08	<0.08	<0.08	0.7	<0.08	4.0	<0.08	596	107	<0.08
	S.D.				2.2		3.6		1170	239	
<i>p,p'</i> -DDT	Mean	<0.08	0.5	197	19	141	41	460	1160	619	6.0
	S.D.		1.5	100	57	90	33	291	2434	312	5.6
Σ DDT	Mean	3572	1435	3126	2195	791	519	7304	6381	7779	2827
	S.D.	1198	656	1577	176	292	289	3739	6502	4278	1055
Σ 10PCB	Mean	7951	2644	5652	3494	11216	7011	24469	12338	30922	7372
	S.D.	3505	1210	3168	562	3502	1550	13659	9446	15844	2702

In 2002, the highest Σ DDT (sum of *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT) residue levels ranging from 2332 ng/g to 10479 ng/g lw were found in liver of Atlantic puffins. Mean Σ DDT concentration in hepatic tissue of this bird species significantly differed from those found in all other bird species studied. In all samples, *p,p'*-DDE prevailed in Σ DDT composition; relative amounts of this compound made from 72% up to

100% of Σ DDT. Statistically significant decrease in Σ DDT level during the 1992-2002 period was found for Brünnich's guillemots (65%), Atlantic puffins (54%) and Razorbills (58%).

Table 2. Organochlorine residue levels (ng/g lipid weight) in hepatic tissues of seabirds from the Seven Island Archipelago in 1992 and 2002. Geometric means, outliers excluded. Significantly ($p=0.05$) differing values are marked by bold type.

Species	Contaminants (ng/g lipid wt). Year.									
	Σ 10PCB		Σ DDT		HCB		Σ CHL		Σ HCH	
	1992	2002	1992	2002	1992	2002	1992	2002	1992	2002
Brünnich's guillemot	7243	2692	3402	1192	1074	533	306	88	21	1.6
Common guillemot	4886	3468	2559	2228	796	788	261	194	19	24
Kittiwake	10725	6761	748	445	579	780	624	212	33	1.6
Atlantic puffin	24677	10003	7841	3606	1131	1172	2029	664	65	50
Razorbill	26381	7037	6507	2704	985	500	1634	696	193	16

Among samples collected in 2002, the highest HCB residue levels (523-3493 ng/g lw) were found in liver of Atlantic puffins. In the other four bird species, HCB concentrations did not make more than 950 ng/g lw and were significantly lower compared to puffins. Statistically significant decrease in HCB contamination levels during the 1992-2002 period was found for Brünnich's guillemots (50%) and Razorbills (49%) while mean HCB concentration in liver of Kittiwakes collected in 2002 was significantly higher compared to 1992 (Table 2).

Razorbills and Atlantic puffins were the most contaminated with chlordane-related compounds. In 2002, hepatic Σ CHL concentrations (sum of oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and *cis*-nonachlor) in birds of these species ranged from 413 ng/g to 2573 ng/g lw. Mean concentrations calculated for these two bird species did not differ significantly however they were significantly higher compared to the other bird species studied. Statistically significant decrease in Σ CHL residue level during the study period was found for all bird species studied with the exception of Common guillemots. The decrease made from 57% to 71%. Oxychlordane making up to 89% of Σ CHL prevailed in all samples collected in 1992 and 2000 with the exception of Razorbills, in hepatic tissues of which average relative amounts of this compound were 13% (in 1992) and 17% (in 2000) whereas *cis*-nonachlor contribution into Σ CHL made up 50% in average in both 1992 and 2002 hepatic samples of Razorbills.

With regards to hepatic Σ HCH levels (sum of α -, β - and γ -HCH) bird species combined into three homogeneous groups. These groups are Kittiwakes and Brünnich's guillemots, Common guillemots and Razorbills, and Atlantic puffins. The highest Σ HCH concentrations (up to 203 ng/g lw in 2002) were found in liver of Atlantic puffins. Geometric mean Σ HCH concentration in hepatic tissues of this bird species was significantly higher compared to the other four bird species investigated. Statistically significant decrease in Σ HCH concentration during the study period was found for Brünnich's guillemot, Kittiwakes and Razorbills (Table 2). B-HCH prevailed in all samples analysed.

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