TEMPORAL TRENDS OF POLLUTION PATTERNS (CHLORINATED HYDROCARBONS AND BROMINATED FLAME RETARDANTS) IN EGGS OF SEABIRDS FROM NORTHERN NORWAY

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Introduction

Persistent organic pollutants (POPs), such as organochlorines (OCs) and bromiated flame retardants (BFRs), are detected in both the abiotic and biotic Arctic environment[1]. Contaminants originating from industrialized areas reach the remote Arctic areas mainly by atmospheric transport[2,3]. POPs will bioaccumulate through food webs due to their resistance to biodegradation[4]. Consequently, high levels of POPs have been reported in animals at the higher trophic levels, such as the Arctic seabirds[1,5,6]. Due to regulations/ban of POPs levels of most OCs show declining trends in Arctic seabirds[1,7,8]. Little is known about levels congener/isomer patterns and temporal trends of PBDEs and HBCD in the Arctic biota. Increasing concentrations of PBDEs have been reported in Arctic seabird eggs from Canada and the U.S[9,10]. In Europe a stabilization/decrease in PBDE levels were reported from the 1980's until today[11,12]. Studies reporting temporal trends of HBCDs in eggs of seabirds from the European Arctic show contradictory results[9,12].

Hitherto, there have been few studies assessing temporal trends of POP patterns in the environment. The aim of the present study was to investigate temporal trends of POP patterns in seabird eggs. Eggs were collected from herring gulls (*Larus argentatus*), black-legged kittiwakes (*Rissa tridactyla*), and Atlantic puffins (*Fratercula arctica*) in 1983[13], 1993[7] and 2003 at sampling locations along the coast of Northern Norway. The eggs were analyzed for HCB, HCHs, oxychlordane, *p,p*'-DDE, PCBs, BDEs and HBCDs. Eggs of seabirds have previously been recognized as appropriate for long-term monitoring of contaminants in the marine environment[14,15,16]. This is mainly because lipid soluble POPs are transferred along with lipids during egg formation[17]. Accordingly, POP levels in eggs would reflect levels observed in the female bird, and provide important information about temporal trends in seabird colonies.

Materials and methods

Species studied and fieldwork

A total of 156 fresh eggs were collected from herring gulls, black-legged kittiwakes, Atlantic puffins and glaucous gulls in 1983, 1993, and 2003 (Table 1). The Atlantic puffins and black-legged kittiwakes feed mainly on fish such as herring and capelin, whereas the herring gulls have a more varied and opportunistic diet composed of fish, seabird chicks and eggs[18].

Table 1. Number of eggs sampled in 1983, 1993 and 2003 from herring gulls (H. gull), black-legged kittiwakes (kittiwakes) and Atlantic puffins (puffins) from Northern Norway for analyses of BFRs and OCs.

	OCs			BFRs		
Species	1983	1983	1993	2003	1993	2003
Puffin	31	31	10	10	10	10
H. gull	30	30	15	10	9	10
Kittiwake	21	21	25	10	10	10

After sampling, the individual eggs were homogenized and kept frozen (-20°C) until analysis. The OCs were analyzed in 1983, 1993 and 2005[7,13], whereas the brominated compounds in all eggs were analyzed recently (2005).

Chemical analyses

Sample preparation: The Sample preparation was described in detail in Murvoll et al. 2006[19]. Shortly, the egg homogenates were weighed and added the internal standards. The lipids were extracted twice using cyclohexane and acetone (3:2) and an ultrasonic homogenizer. The lipid determination was done gravimetrically. For cleanup (i.e. removal of lipids) the rest of the lipid extracts were treated twice with ultra clean concentrated H_2SO_4.

Detection of OCs and BFRs: OCs were analysed on GC-ECD and BDEs and HBCDs were analysed on GC-MS. Details of detection of OC were given in Sørmo et al. 2006[20] and of BFRs in Murvoll et al. 2006[19].

Calculation of relative contribution: Each group of contaminant (HCB, ∑HCHs, *p,p*'-DDE, ∑PCBs, ∑PBDEs and HBCDs) was calculated as per cent of the sum of all the determined contaminants (∑POPs).

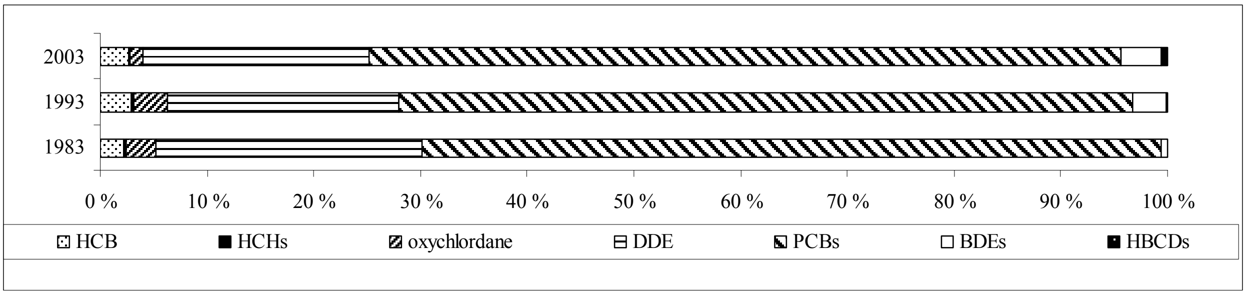
Results and Discussion

PCBs are the dominating contaminants in all three species and in all three years. The relative concentration of ∑PCBs to ∑POPs in herring gull eggs was relatively constant from 1983 to 2003 (approximately 70%). In Atlantic puffin eggs the relative concentration of ∑PCBs to ∑POPs decreased slightly from 70% to 64% from 1983 to 2003. In black-legged kittiwake eggs the relative concentration of ∑PCBs to ∑POPs was below 60% in 1983, and increased to almost 80% in 2003. The increase in the relative proportion of ∑PCBs in black-legged kittiwake eggs coincided with a decrease in the relative proportion of *p,p*'-DDE. Nevertheless, the absolute concentrations of both ∑PCBs and *p,p*'-DDE decreased from 1983 to 2003 in all three species[21]. The total production of PCB on a world-wide basis was estimated to 1320 kt from 1930 to 1992[22]. Production was restricted or banned worldwide in the early 1970s[23]. However, PCBs is still an important contaminant group in the environment, as found in the present study.

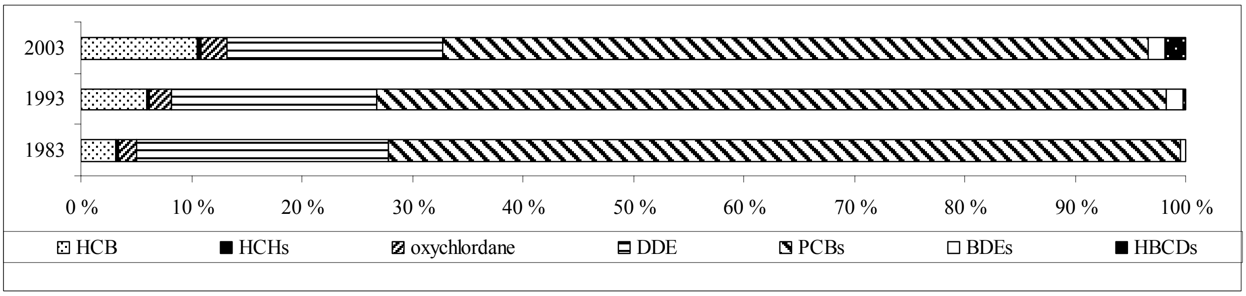
The relative proportion of *p,p*'-DDE to ∑POPs decreased from 1983 to 2003 in all three species. In eggs of herring gulls and black-legged kittiwakes the relative concentrations of *p,p*'-DDE to ∑POPs decreased only slightly from 25 to 21% and from 23 to 20% respectively. In black-legged kittiwake eggs the relative concentration decreased from 30 to 9%. Although decreasing trends of the relative proportion of p,p'-DDE to ∑POPs was found in the present study, *p,p*'-DDE, the main metabolite of *p,p*'-DDT, is the second most important environmental contaminant in the present study. The total production of DDT from 1950 to present was estimated to 2600 kt. DDT was banned in most western countries in the early-1970s, but it may still be produced and used only for disease vector control and according to recommendations and guidelines of the World Health Organization[24]. The decreasing trends of the relative proportion of *p,p*'-DDE to ∑POP correspond with preliminary results assessing the temporal trends of the absolute concentration of *p,p*'-DDE in the eggs of the present study[21].

Lower levels of PBDEs and α-HBCD were found in the seabird eggs of the present study compared to ∑PCBs. However, the relative concentration increased from 1983 to 2003 in all three species. In herring gull eggs the relative concentration of ∑BDEs to ∑POPs increased from 0.6 to almost 4% from 1983 to 2003. In Atlantic puffin and black-legged kittiwake eggs the relative concentration of ∑BDEs to ∑POPs increased from 0.4 to 1.6% and 0.7 to 2.3% from 1983 to 2003, respectively. The relative concentration of HBCDs to ∑POPs increased from 1983 to 1993 in all three species, from 0.2 to 0.6% in eggs of herring gulls, from 0.04 to 1% in eggs of Atlantic puffins, and from 0.1 to 1.3% in eggs of black-legged kittiwakes. These results correspond well with the findings of increasing concentrations of HBCDs and ∑BDEs from 1983 to 2003, and 1983 to 1993, respectively[12]. From 1993 to 2003 the concentrations of ∑BDEs was found to be stabilizing[12]. The total world production of BFRs, such as PBDEs and HBCD, is lower than the total production of PCB and DDT. The estimated production of tetra- and penta-BDEs from 1960 to present was 70 to 120 kt, 500 to 800 kt of octa- and nona-BDEs from 1980 to present and 100 to 200 kt of HBCD from 1980 to present[25]. The PBDEs, and especially the penta- and octa- BDEs, have been shown to be highly toxic[26]. In concert with this, the industry in Japan and the U.S. voluntarily discontinued the production of penta- and octa-BDEs in 1991/2000 and 2005, respectively[27]. Furthermore, the countries within the European Union banned the production and use of penta-BDEs and octa-BDEs in 2004[28]. There is currently no restriction in the production of deca-BDE and HBCD[29]. The relatively high production rate of brominated flame retardants the latest years in contrast to PCB and DDT can explain the increasing concentration in the environment.

A



B



C

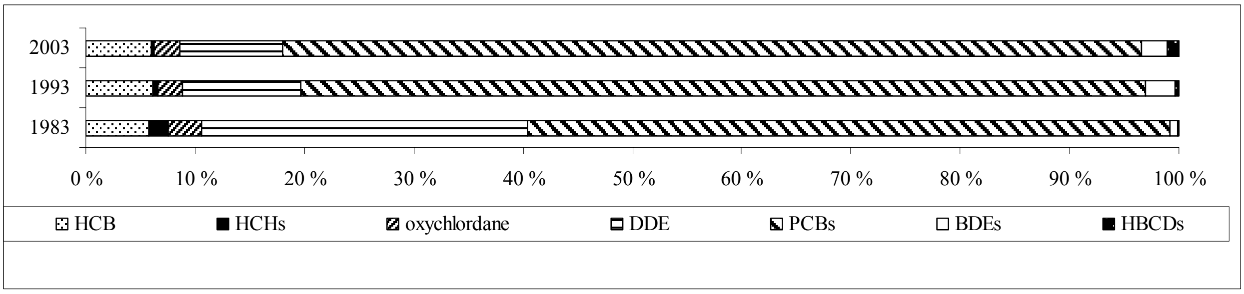


Figure 1: Ratio of POPs (HCB, ∑HCH, *p,p*'-DDE, PCBs, ∑PBDEs and HBCD) in herring gull eggs (A), Atlantic puffin eggs (B) and black-legged kittiwake eggs (C).

Contradictory trends of the relative proportion of oxychlordane and HCB to ∑POPs were found for the different species in the present study. In herring gull eggs the relative proportion of oxychlordane to ∑POPs decreased from 1983 to 2003, whereas stabilizing trends was found for the black-legged kittiwake and the Atlantic puffin eggs during the same time period. The relative contribution of HCB to ∑POPs was increasing in the Atlantic puffin eggs, whereas a stabilizing trend was reported for the other two species. ∑HCHs are the least dominating contaminant in all three species, and as with the other 'legacy' POPs in the present study, the relative contribution of ∑HCHs to ∑POP was decreasing from 1983 to 2003.

In conclusion, "new' contaminants, such as HBCD and BDEs, have become increasingly important as 'legacy' POPs, such as the PCB and DDT, was banned in most countries in the 1990s. Nevertheless, legacy POPs are still the dominating contaminant in seabird eggs from the European Arctic.

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