New and updated time trends of persistent organic pollutants and their effects on eggs of peregrine falcons (Falco peregrinus) from South Greenland

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Scientific Report from DCE – Danish Centre for Environment and Energy No. 249 2017

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Abstract: Peregrine falcons *(Falco peregrinus)* accumulate persistent organic pollutants (POPs) to high concentrations. DDT and its metabolites caused severe effects on reproduction and population survival in the past. In this study, we addressed the following organic pollutants in eggs of peregrine falcons from South Greenland: Polychlorinated biphenyls (PCBs), DDT and its metabolites, hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), chlordane-related pesticides, toxaphene, polychlorinated naphthalenes (PCNs), several groups of brominated flame retardants (polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), hexabromobiphenyl (BB) 153, "novel" flame retardants), dechlorane plus and perfluorinated alkylated substances (PFASs). The concentrations were generally high in a bioaccumulation context, i.e. in the µg/g range for the organochlorine POPs. Some eggs reached critical levels for DDE, but those were generally eggs from the 1980s. Time trend analyses covering the period 1986-2014 showed decreasing concentrations for the organochlorine POPs, including PCNs, with the exception of α-HCH and toxaphene. BB-153 and some perfluoroalkyl sulfonates (PFSAs) decreased as well, while significant increases were found for BDE-209 and some of the long-chain perfluoroalkyl carboxylic acids (PFCAs). The "novel" flame retardants were detectable in the peregrine falcon eggs, but concentrations were comparably low (i.e. < 5 ng/g lipid weight) and only seemed to increase for dechlorane plus. The eggshell thickness increased significantly over the study period and was predicted to reach the pre-DDT level by 2034. However, breeding success of the South Greenland peregrine population has lately been low, possibly related to climate factors.

Keywords: Birds of prey, brominated flame retardants, DDT and DDE, eggshell thickness, migratory birds, perfluorinated alkylated substances

Layout: Graphic Group, AU Silkeborg

Front page photo: Female Peregrine falcon with geolocator tag attached to its left leg (see page 10). Knud Falk has taken all photos in this report

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Contents

1 Sammenfatning

Vandrefalken *(Falco peregrinus)* er en rovfugl, der forekommer på alle kontinenter på nær Antarktis og hovedsageligt lever af andre fugle. Vandrefalke, der opholder sig på Grønland i ynglesæsonen om sommeren, trækker langs gennem Nordamerika til vinterlokaliteten i Latinamerika. Dens høje placering i den terrestriske fødekæde medfører en ophobning af svært nedbrydelige, organiske kontaminanter (persistent organic pollutants, POPs). Et kendt eksempel er DDT, som sammen med nedbrydningsprodukterne DDE og DDD bevirkede tynde æggeskaller, med alvorlige konsekvenser for reproduktionen og populationerne.

Formålet med dette projekt var at undersøge en række POP'er og nye organiske kontaminanter i vandrefalkeæg fra Sydgrønland indsamlet i perioden mellem 1986 og 2014, samt udviklingen i æggeskaltykkelsen. Projektet er en fortsættelse af den tidligere undersøgelse "Persistent organic pollutants (POPs) in the Greenland environment – long-term temporal changes and effects on eggs of a bird of prey" (Sørensen et al., 2004). Det nye projekt har udvidet tidligere tidsserier for polychlorerede biphenyler (PCB), DDT og nedbrydningsprodukterne, hexachlorcyclohexan (HCH), hexachlorbenzen (HCB), chlordan-relaterede pesticider, toxaphen, flammehæmmerne polybromerede diphenyl ethere (PBDE), hexabromcyclododecan (HBCDD) og hexabrombiphenyl (BB)-153 samt skaltykkelsen. Derudover er der etableret nye tidsserier for polychlorerede naphthalener (PCN), perfluorerede alkylerede substanser (PFAS) og forskellige alternative halogenerede flammehæmmere, inkl. dechloran plus.

PCB'erne og DDT-gruppen (specielt nedbrydningsproduktet DDE) udgjorde fortsat de højeste koncentrationer i æggene fra de grønlandske vandrefalke og lå fortsat på µg/g niveau. Indholdet i enkelte prøver overskred tærskelværdier for effekter, dog var det primært de ældste prøver fra 1980'erne. Koncentrationen var faldende for PCB'er, DDT og andre organochlorforbindelser, med undtagelse af α-HCH og toxaphen. Deres trends var positive, dog ikke signifikante. Generelt var variabiliteten stor mellem de enkelte prøver, hvilket sandsynligvis relaterer sig til vandrefalkenes lange træk til vinterområder i Sydamerika. Her kan kontaminanteksponeringen variere betydeligt, både mellem enkelte lande/regioner og mellem by- og landområder. Vandrefalken opsøger i reglen det samme vinter-territorium år efter år, således at der nemt kan opstå individforskelle i kontaminanteksponering.

I lighed med andre organochlorforbindelser var indholdet af PCN'er på et højt niveau i vandrefalkene (median 21 ng/g lipidvægt), i forhold til andre arter, men koncentrationen var faldende. Til gengæld er der fundet en signifikant stigning for den bromerede flammehæmmer BDE-209, som først er blevet tilføjet til Stockholm Konventionen i 2017. Andre PBDE'er og HBCDD er også steget, men ikke signifikant. Et signifikant fald i koncentrationen blev til gengæld fundet for BB-153, hvis produktion ophørte i USA i 1970'erne. De alternative flammehæmmere blev fundet i generelt lavere koncentrationer end PBDE'erne (< 5 ng/g lipidvægt), men kunne også påvises i de gamle prøver fra 1980'erne. Dechloran plus viste en stigende (dog ikke statistisk signifikant) tendens, mens 2,4,6-tribromphenyl 2,3-dibromopropyl ether (DPTE eller TBP-DBPE) faldt i koncentrationen i undersøgelsesperioden. Undersøgelser på den beslægtede

amerikanske tårnfalk *(Falco sparverius)* viste en række effekter for miljørelevante PBDE- og HBCDD-koncentrationer, heriblandt adfærdsændringer.

PFOS var klart det vigtigste enkeltstof i PFAS-gruppen (median 65 ng / g vådvægt), men uden signifikant koncentrationsændring igennem undersøgelsesperioden. Til gengæld var indholdet af perfluoralkylsulfonaterne PFHxS og PFHpS faldende, mens nogle af de lang-kædede perfluoralkylcarboxylater (PFCA) blev fundet i signifikant stigende koncentrationer. PFOS-koncentrationen lå på et niveau, der har vist effekter i andre fuglearter.

Æggeskallerne er blevet tykkere med tiden, samtidig med at koncentrationen for DDT og nedbrydningsprodukterne har været faldende. Der er derfor grund til at formode, at det faldende indhold af DDT, DDE og DDD betyder en mindre påvirkning af falkene og dermed en æggeskalstykkelse, der nærmer sig præ-DDT niveauet. En fremskrivning viste, at præ-DDT niveauet vil kunne nås omkring 2034. Dette er senere end for europæiske rovfugle, som generelt var tilbage på præ-DDT niveauet efter årtusindskiftet. Selvom skaltykkelsen ligger over det kritiske niveau og har været stigende, har de grønlandske vandrefalke haft ringere ynglesuccess siden ca. 2010, muligvis relateret til klimafaktorer. Derudover kan andre, mere subtile kontaminant-relaterede effekter være mulige forklaringer, heriblandt cocktail-effekter af de mange kontaminanter, som hver især ligger tæt på kendte effektniveauer. Dette er dog ikke undersøgt i projektet, som primært har undersøgt koncentrationer og tidstrend for en lang række regulerede og ikke-regulerede organiske kontaminanter.

2 Preface

2.1 Background

This report presents the results of the study "New and updated time trends of persistent organic pollutants and their effects on eggs of peregrine falcons *(Falco peregrinus)* from South Greenland". It builds on the project "Persistent organic pollutants (POPs) in the Greenland environment – Long-term temporal changes and effects on eggs of a bird of prey" conducted in 2003/2004 by the same project group. The first project included the chemical analysis of the following groups of POPs in peregrine falcon eggs collected in South Greenland between 1986 and 2003:

- Polychlorinated biphenyls (PCBs)
- Chlorinated pesticides, i.e. DDT and its degradation products, hexachlorocyclohexanes (HCH), hexachlorobenzenes, chlordane-related pesticides and toxaphene
- Brominated flame retardants, i.e. polybrominated diphenyl ethers (PBDEs), brominated biphenyl (BB)-153 and hexabromocyclododecane (HBCDD).

In addition, the eggshell thickness in these and other peregrine falcon eggs from Greenland was determined. By including eggshells from West Greenland, this covered the time period of 1972-2003. The eggshell thickness increased over the course of the study period, but was still below pre-DDT levels. All POPs were found to occur at high concentrations compared with their bioaccumulation in other wildlife species. While most organochlorine compounds showed decreasing concentrations, brominated flame retardants were found to increase. The results of this first project were published in one scientific report (Sørensen et al., 2004) and four scientific publications (Vorkamp et al., 2005; Falk et al., 2006; Vorkamp et al., 2009; 2014a).

The current project is based on new sample material, i.e. peregrine falcon eggs collected in South Greenland between 2004 and 2014. The compounds listed above as well as the eggshell thickness were determined in these new samples. In addition, all samples covering the time period 1986-2014 were analysed for the following compounds:

- "Novel" flame retardants which might have replaced PBDEs.
- Polychlorinated naphthalenes (PCNs)
- Perfluorinated alkylated substances (PFASs).

The report includes five chapters for each of these compound groups where the "novel" flame retardants were combined with the PBDEs and HBCDD. It further contains an introduction to the peregrine falcon population in South Greenland, a brief description of the methods applied in the study and a presentation and discussion of the results of the eggshell measurements.

2.2 Objectives

The primary objective of this study was to follow the long-term variation in contaminant accumulation and effects in the peregrine falcon. In combination

with the samples and data available from the first project, the study specifically aimed to

- establish new time series of bioaccumulating contaminants with known or anticipated toxicity ("novel" flame retardants, PCNs, PFASs),
- extend the existing time series of POPs (PCBs, chlorinated pesticides, PBDEs, HBCDD),
- update the existing time series for eggshell thickness.

Based on these data, a further objective of this study was to assess potential toxicological impacts on the peregrine falcon. Finally, the contaminant time series were to be analysed in relation to the regulations taken under the Stockholm Convention on POPs. Most of the compounds included in this study have been added to the Stockholm Convention at different time points over the last 15 years. DecaBDE, the fully brominated PBDE congener, was added to the Stockholm Convention in 2017 and perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS) are under review for the Stockholm Convention, while the "novel" flame retardants are not currently considered for global regulation. Thus, the results obtained in this project will give additional information for the risk assessment of these compounds, with regard to their bioaccumulation in a terrestrial top-predator and their temporal development.

2.3 Acknowledgements

The study was funded by the Danish Cooperation for Environment in the Arctic (DANCEA) of the Danish Environmental Protection Agency (MST-112-00197).

The authors thank Birgit Groth for managing the sample bank and for performing the chemical analyses. Challenges in the analysis of the newly included compounds were solved skillfully. The authors further acknowledge Inga Jensen for the analysis of the PFAS compound group and Annegrete Ljungqvist for general assistance with the project.

The egg samples have been collected in more than four decades with financial support from private and public funds; in addition to those listed in Falk et al. (2006) they include the W.A. Burnham Memorial Fund and Grønlandsbanken.

3 The peregrine falcon

3.1 Introduction

The peregrine falcon (*Falco peregrinus)* is a crow-sized (0.6 - 1.2 kg) bird of prey with an almost global distribution, only absent in the Antarctic and a range of oceanic islands and "isolated" countries like New Zealand and Iceland (Cade, 1982). As a top predator the peregrine falcon is exposed to POPs through the food chain and ever since the undesirable side effects of pesticides – eggshell breakage and mortality of adults and embryos – were first documented in the peregrine (Ratcliffe, 1958, 1970), it has served as a key species in monitoring the levels and changes in pollutant loads in many parts of the world. This includes the "classical" POPs (Cade et al., 1988; Furness and Greenwood, 1993; Ratcliffe, 2000; Vorkamp et al., 2009; 2014a) as well as emerging problem substances (Guerra et al., 2012; Lindberg et al., 2004; Vorkamp et al., 2005).

From the early 1940s the widespread use of DDT and other organochlorine pesticides caused severe declines in the peregrine populations in North America and Europe and by the 1970'ies the species was extinct in large areas (Cade et al., 1988; Wegner et al., 2005); other birds of prey were similarly affected. Following the ban of some of the most critical POPs the populations recovered since around 1980. By now the peregrine is re-occupying most of the former distribution range, although in some regions (e.g. eastern Europe) the population density is still far from pre-DDT levels. There are even signs of northward range expansion in the high Arctic, where climate change effects open a slightly longer "summer window" allowing the flexible peregrine falcon to squeeze in a breeding season in new areas (Burnham et al., 2012).

Most recently, though, new challenges have also emerged in the Arctic, including lowered reproduction partly caused by climate change-induced increased rainfall variability affecting chick mortality (Anctil et al., 2014; Franke et al., 2011 - see further below); other, yet undetermined, factors may also be at play in causing a new and large inter-annual variation in peregrine reproduction.

Spurred by the pesticide-induced sudden population crash in the 1960s and 1970'ies, peregrine population surveys were initiated in many areas. Some surveys developed into long term monitoring programmes gathering further evidence of local variation in impacts as well as general ecology. Several of the monitoring programmes cover the circumpolar Arctic (Figure 1) and the species is now included as one of the few terrestrial predators in the *Arctic Terrestrial Biodiversity Monitoring Plan* under the Arctic Council (Christensen et al., 2013) where the practical modalities are now under development.

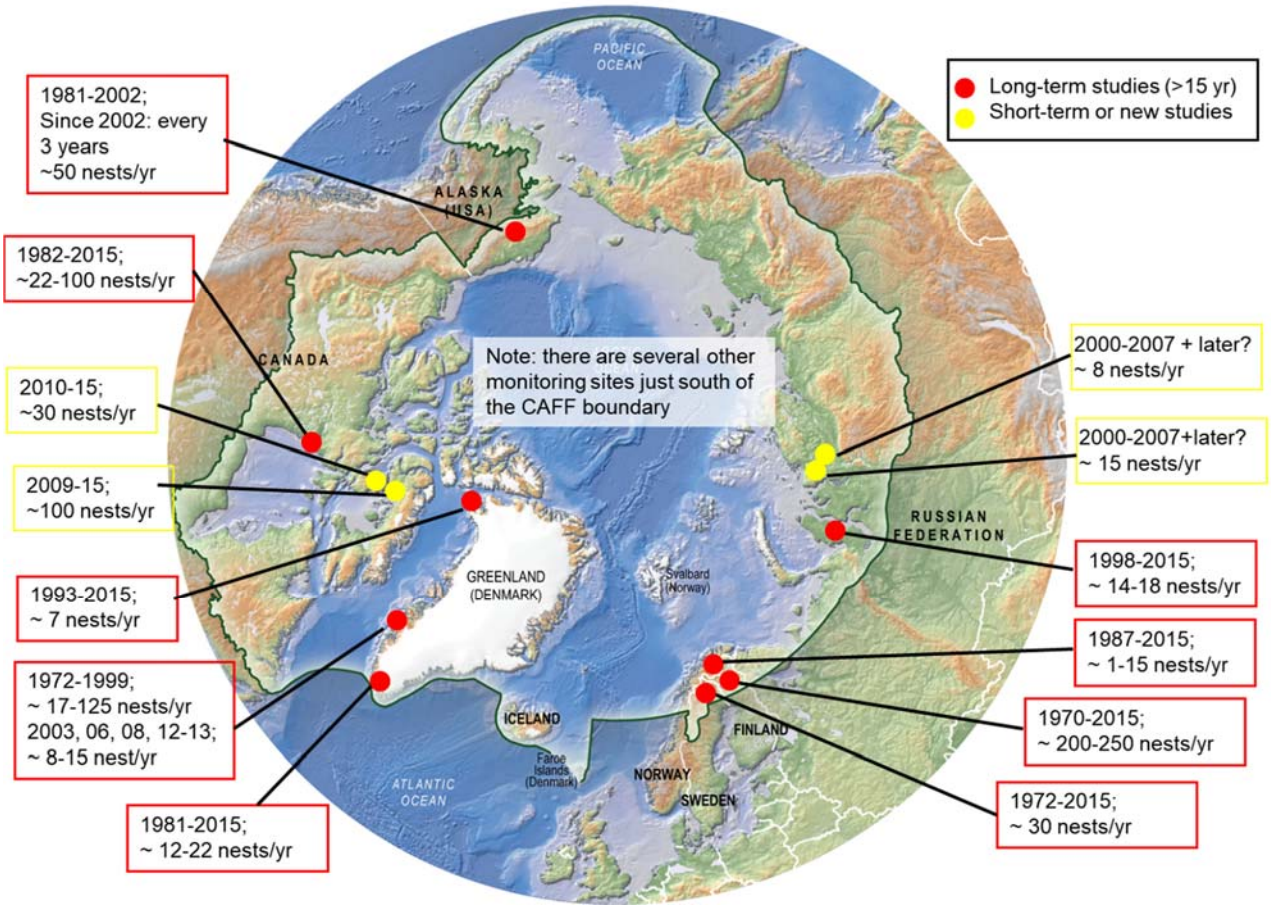


Figure 1. Preliminary overview of main terrestrial peregrine falcon monitoring sites within the Conservation of Arctic Flora and Fauna (CAFF) boundary (green line); source: information compiled from internet sources and mail correspondence with principal investigators (Falk and Møller unpubl.).

3.2 Peregrine falcon ecology

3.2.1 Migration and winter range

The peregrine falcons in Greenland belong to the *tundrius* subspecies which inhabits the Arctic tundra of North America from Alaska to Greenland. In Greenland the peregrine breeds (and is expanding) as far north as 77°N in West Greenland (Burnham et al., 2012), and on the cooler east coast a breeding pair has been found as far north as 72°N (R. Burton pers. comm. 2005), with highest densities in the relatively mild south and south-western parts of the country. Greenland holds an estimated population of 500-1000 pairs (Falk and Møller, 1988; Boertmann, 1994).

The *tundrius* subspecies is a long-distance migrant with main wintering areas in Latin America. Ring recoveries indicate that Greenland females tend to winter in the Caribbean region and northern South America (to Paraguay and northern Argentina) although some females may winter as far north in the US as 39°N (Lyngs, 2003; Burnham et al., 2012; Falk and Møller unpubl.). This also applies to adult breeding females from this study: Preliminary results based on geolocator data from three adults breeding females tagged in South Greenland indicate that they remained stationary for about five months in The Dominican Republic, Costa Rica (in three winters) and Venezuela, respectively. However, one ringed breeding female was recovered as far south as 30°S (Falk and Møller unpubl.). The general wintering areas for males appears to be much further south between 2° and 26°, or even 34°S (Lyngs, 2003; Mattox and Restani, 2014).

With the advent of electronic tracking devices over the past decades, further details on the migration timing, routes and wintering areas of individual birds have been revealed. There is increasing evidence that at least the adult females are faithful to their wintering territory, as suggested by satellite tracking; for instance a West Greenland bird returned to a wintering site in the Gulf of Mexico in two successive years (McGrady et al., 2002) and a North Greenland female wintered in the same place two winters in succession (Burnham et al., 2012; K. Burnham pers. comm). A female from the South Greenland study population went to Costa Rica all three winters we have tracked her, and a female from near Igloolik, Nunavut, wintered two years in a row in southern Mexico (A. Franke and M. Prostor, pers. comm. 2016). Even more convincing, a female breeding on Baffin Island in Nunavut has returned to the same wintering site in Chile eight years in succession so far (Falcon Research Group - http://www.frg.org/ accessed October 2016). Observations from other parts of the world (other subspecies) also provide evidence that adult peregrines show fidelity to their wintering areas.

This is significant in relation to how the individual birds are exposed to pollutants from specific environments and sites. For example, the wintering area of one of the females providing samples to the pollutant analyses included in this report wintered on the highly urbanised Venezuelan coastline around the capital Caracas. In contrast, five different females from northern Greenland were utilising open areas with scattered forests, farmland, residential areas and wetlands - but all of them in areas with "human disturbance" (Burnham et al., 2012).

The autumn migration takes Greenlandic peregrines across the Davis Strait to Canada and then the majority of birds follow the Atlantic Flyway of North America (East coast) while some use the Mississippi and Central Flyways towards the Caribbean and Latin America (Burnham et al., 2012; Mattox and Restani, 2014). In spring the pattern is reversed, but with less concentration of birds following the Atlantic Flyway; individuals may choose different autumn and spring routes, and also shift routes between years (Falcon Research Group, http://www.frg.org/ accessed October 2016). Migration speed varies (including some stopover days) but on average migrating females move 100 - 270 km/day and with peak distances of more than 1300 km in a single day when crossing oceans like the Gulf of Mexico (Burnham et al., 2012).

So, during a year the adult female peregrines from Greenland spend:

- approximately 5 months (November - March) relatively stationary in their winter territories in Latin America;
- about 6 weeks spring migration (April – May), with days to weeks on stopover sites in North America before arriving in breeding areas in mid-May;
- about 4.5 months (May - late September) in Greenland around the breeding site and utilising a core home range (hunting area) of an estimated 72-183 km^2 (Burnham et al., 2012),
- approximately 5-6 weeks (late September - late October) on migration, including at stopover sites; four birds tracked as they left the South Greenland study area departed between 20 September and 2 October.

3.2.2 Feeding ecology

Peregrines feed almost exclusively on birds (97-100%, Sherrod, 1978), usually captured in flight in open habitats. In the inland habitats supporting most peregrines in Greenland the main prey is terrestrial passerines supplemented by a few rock ptarmigans *(Lagopus muta)* (Burnham and Mattox, 1984; Falk et al., 1986; Rosenfield et al., 1995) and, in some pairs, the occasional waterbird like merganser *(Mergus merganser)*, black guillemot *(Cepphus grylle)* or gull *(Larus sp.)* (Falk and Møller unpubl.). The relatively few coastal pairs may rely much more on seabirds, e.g. little auks *(Alle alle)* in Northwest Greenland (Burnham et al., 2012).

The four common small passerine species that make up the bulk of adult as well as chick diet in South Greenland are themselves migrants. The Northern wheatear winters in sub-Saharan West Africa (Bairlein et al., 2012) while the other three small species breeding in Southwest Greenland winter in south-eastern Canada and north-eastern US; a few snow buntings can winter in urban areas in Southwest Greenland (Lyngs, 2003).

On migration through North America the peregrines may prey on almost any bird species; the recorded menu of peregrines in North America (not only Arctic migrants) includes hundreds of bird species weighing from 20 g to 3 kg (Sherrod, 1978). Where observations of diet on migration and staging areas have been recorded – mostly along the eastern coast of USA and the central flyway in central North America (e.g. Hunt et al., 1975; Dekker, 2009) – diet appears to include more aquatic species, including shorebirds, laughing gull *(Leucophaeus atricilla)*, small ducks but still with significant contributions of terrestrial passerines, woodpeckers, pigeons and starlings. In urban environments, pigeons and starlings but also gulls (harbours) are among favourite prey species. On the wintering grounds in Latin America, little is known on their diet although "abundant food in the form of passerines, pigeons and doves" in Chilean wintering are mentioned in the description of wintering peregrine ecology by the Falcon Research Group (http://www.frg.org/ accessed March 2016).

3.2.3 Breeding ecology and reproduction

Peregrines breed on ledges on cliffs where they are safe from mammalian predators. The cliff or "site" is the centre of the territory that tends to be occupied every year, although some less favourable territories/sites may only be used irregularly. Pairs tend to stay together on the same cliff year after year until one of the mates dies or is replaced by another peregrine. Most breeders only last a few years – mean breeding lifespan is 2.0 and 2.2 years for females and males, respectively, in West Greenland (Restani and Mattox, 2000) and more than 20% of the breeding females are replaced annually (Falk and Møller unpubl.). However, a few birds may breed for many years: in South Greenland 3 females bred 10 years or more on their respective sites (Falk and Møller unpubl.).

The high turnover among the breeders is balanced by a high breeding success of 1.9 young per occupied territory (averaged over 1981-2016, Falk and Møller unpubl.). However, breeding success measured by different parameters is variable and in some years, including most recent years, fall at or below "critical thresholds" (USFWS, 2003) as displayed in Fig. 2 and 3 – the latest drop causing some concern.

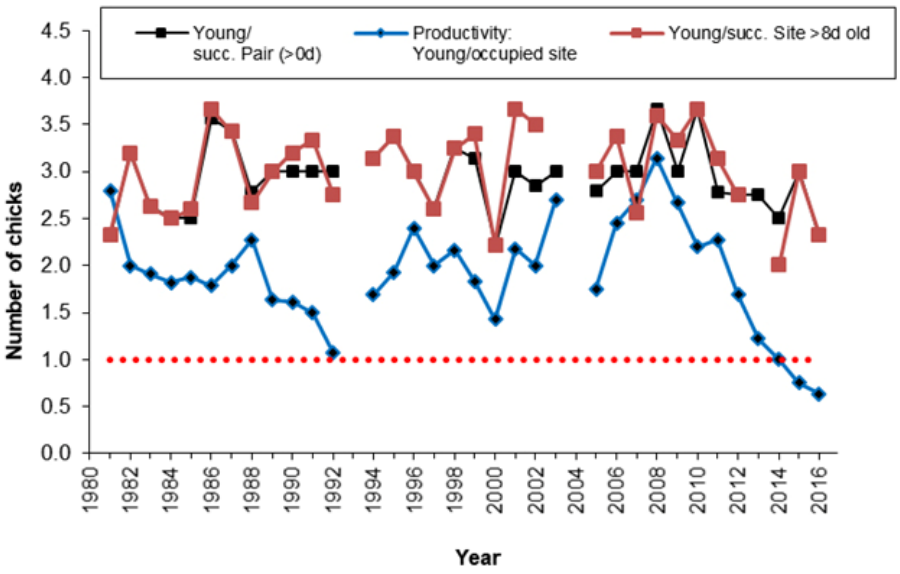


Figure 2. Annual production during the entire monitoring programme – measured as number of young/successful pair (full broods, young of any age, black line); young/successful pair (young reached at least 8 days of age, red line); number of young per occupied site ("productivity," blue line) – for all sites checked each year; the red line is the critical limit for productivity that "will initiate a special review" according to USFWS (2003).

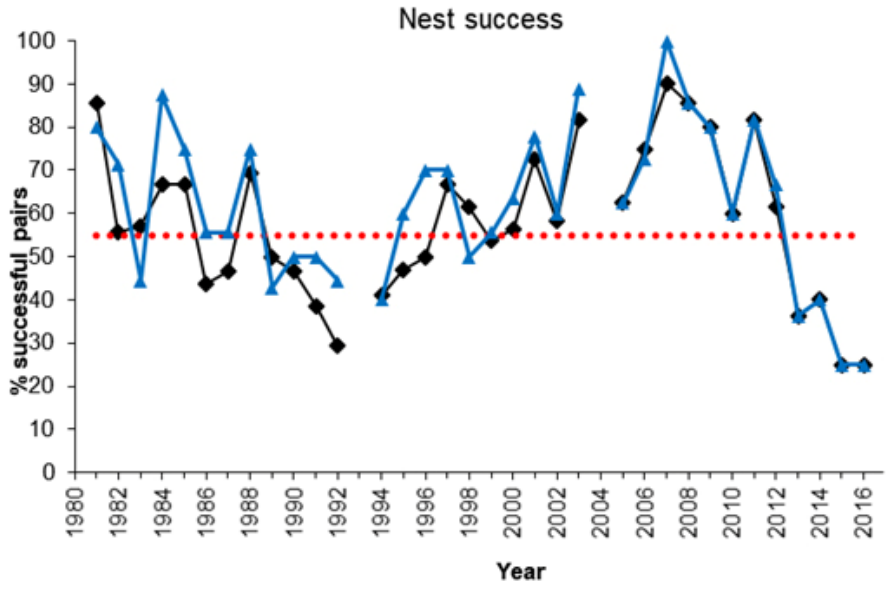


Figure 3. Nest success: proportion of occupied historical sites that produced young; black line is all sites, blue line is comparable "monitoring sites" only (smaller sample size 1981-2002). The red line is the threshold where there "would be cause for concern in the short term" (USFWS, 2003).

Climate change is beginning to affect the Arctic peregrine falcons in different ways:

- The northern limits of breeding range are gradually expanding in the high Arctic, including in northernmost West Greenland (Burnham et al., 2012).
- In Arctic Canada breeding success and overall production has declined over past decades; one critical factor identified is the increased frequency of days with heavy rainfall (>8 mm / 24h) in the breeding season, in particular when peregrine nests contain small young (Anctil et al., 2014).
- In South Greenland the timing of breeding has been gradually, but non-significantly, earlier over the 35 year study period (Falk and Møller unpubl.).

3.3 Additional points for interpreting contaminant analyses

The contaminant loads in the birds build up over the year, and the egg loads may represent the female's uptake from mainly the 5 months in winter areas and the approximately 2 months on varying diet during migration and in the pre-

breeding season in Greenland. In Greenland, the relatively clean diet the last few weeks prior to egg laying may dilute the winter loads since analyses of DDE and PCBs in the falcons' prey species in Greenland in the early 1970s revealed lower levels of POPs than found in other populations (Burnham and Mattox, 1984). How much the contaminant contents in the eggs represent wintering grounds versus the local terrestrial environment in Greenland depends on the half-life of each compound in the falcons – factors that are largely unknown.

The study area in South Greenland covers the main sheep-farming district where low-lying areas are increasingly (but still small scale) claimed for winter fodder (hay) production and also some vegetables for local marketing. Although a few pest species occur, no pesticides are used in the local farming (A. Kanuthsen, Greenland Ministry of Fisheries, Hunting and Agriculture, pers. comm. 2016; Lehman et al., 2016). The study area includes the Narsarsuaq airport which was established in 1941 as a US Air Force base and used for military purposes until 1958. Since DDT was introduced on the global market as an insecticide from around 1940, it was most likely (according to anecdotal evidence) used to fight the dense mosquito populations at the Narsarsuaq base area. Hence, with its long half-life there could in theory remain a localized DDT source in the study area.

4 Methods

4.1 Study design

This study combines existing data, obtained in the previous project about contaminants in peregrine falcon eggs (samples from 1986-2003) and their effects on eggshell thickness (Sørensen et al., 2004), with new analyses. Thus, the approach in this project combines three groups of samples and analyses, as outlined in Table 1. In addition, the measurements of eggshell thickness of the previous project (Falk et al., 2006) have been continued, now covering the time period 1981-2014 for eggs from South Greenland. Further data on eggshell thickness are available from West Greenland, covering in total the time period of 1972-2003 (Falk et al., 2006).

Table 1. Study design including existing data (Sørensen et al., 2004) and new analyses. PCBs: Polychlorinated biphenyls, DDT: Dichlorodiphenyltrichloroethane, HCH: Hexachlorocyclohexane, HCB: Hexachlorobenzene, PBDEs: Polybrominated dipenyl ethers, BB-153: 2,2',4,4',5,5'-hexabromobiphenyl, HBCDD: Hexabromocyclododecane, PFASs: Perfluorinated alkylated substances, PCNs: Polychlorinated naphthalenes, NFRs: "Novel" flame retardants.

Study	Time period	Compound groups	Number of samples	Description
Sørensen et al. (2004)	1986-2003	PCBs, DDT and degradation products, HCH, HCB, chlordane-related compounds, toxaphene, PBDEs, BB-153*, HBCDD	37	Previous project
This study	2004-2014	PCBs, DDT and degradation products, HCH, HCB, chlordane-related compounds, toxaphene, PBDEs, HBCDD	11	Extension of old time series
This study	1986-2014	NFRs, PCNs, PFASs	41	New time series

*N=22.

The peregrine falcon eggs had been collected outside of this study, in ongoing long-term field studies in South Greenland (www.vandrefalk.dk). Those monitoring studies included the collection of addled eggs when available, as detailed in the previous project (Sørensen et al., 2004). The eggs were collected with annual permits from Greenland authorities and transferred to Denmark with CITES export and import permits. Subsequently, they were registered, weighed and measured in Denmark, and their content was stored at -20°C in the dark until analysis. The analyses in the previous project were performed in 2003/2004, while the samples of this study were analysed in 2014/2015. The chemicals and procedures chosen for analysis are introduced in detail in the following chapters.

4.2 Selection of samples

For the extension of the old time series, all samples were analysed that had become available since the previous project. In total, these were eleven samples, extending the previous time series of 1986-2003 to 2014 (Table 1).

Table 2. Samples selected for the previous project, the extension of the old time series and the new time series. Identical letters indicate eggs of the same bird.

Year	Sample number	Bird	Previous project	Extension of old time series	New time series
1986	01-1593		x		x
1987	01-1608	A	x		x
1988	01-1609	A	x		
1988	01-1610	A	x		x
1988	01-1597		x		
1989	01-1617	B	x		x
1990	01-1618	B	x		x
1990	01-1619	B	x		x
1990	01-1623	C	x		
1990	01-1624	C			x
1991	01-1598		x		
1991	01-1611		x		x
1991	01-1629		x		x
1992	01-1620	B	x		x
1992	01-1621	B	x		x
1992	01-1622	B	x		x
1992	01-1601	D	x		
1994	01-1602	D	x		x
1994	01-1630		x		x
1994	01-1631		x		x
1994	01-1632		x		x
1994	01-1633		x		x
1995	02-1785	E	x		x
1995	01-1603	F	x		
1998	01-1604	F	x		
1998	01-1613	G	x		x
1999	01-1626	E	x		x
1999	01-1614	G	x		x
1999	02-1789	G	x		x
2000	01-1615	G	x		x
2000	01-1616	G	x		x
2000	01-1606	F	x		
2000	01-1607	F	x		x
2001	01-1645	H	x		
2002	02-1788	I	x		x
2002	02-1790	H			x
2002	02-1787		x		x
2003	03-0542		x		x
2003	03-0543	I	x		x
2005	05-0593			x	x
2005	05-0594	J		x	x
2006	2007-3222	J		x	x
2007	2007-3221	H		x	x
2008	2012-11315			x	x
2011	2012-11316			x	x
2012	2012-11317			x	x
2013	2013-12538	K		x	x
2013	2013-12539	K		x	x
2013	2013-12540			x	x
2014	2014-13070			x	x

For the new time series, the ideal approach would have been to re-analyse the 37 samples of the previous project plus the eleven new samples. Besides budget obstacles, this was not entirely possible because some samples had been used completely, and for others, little material was left, with implications for detection limits. Still, it was possible to select samples covering the sampling period of 1986-2014, as detailed in Table 2. The table also gives information about eggs of the same bird. The same 41 samples were analysed for the three new compound groups of NFRs, PCNs and PFASs.

4.3 Chemical analysis

Several different methods were used for the determination of the wide spectrum of compounds analysed in this study. Descriptions of the chemicals selected for this study and their analytical methods are therefore given in each of the subsequent chapters about specific compound groups.

For the extension of the time series, the same analytical methods were used as in the previous project, with the exception of hexabromocyclododecane (HBCDD). In the previous project, HBCDD had been analysed by a Dutch laboratory using gas chromatography with mass spectrometry (GC-MS), which yielded ΣHBCDD. The state of the art today is the isomer-specific analysis by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS), which was applied in this study.

The brominated flame retardants BB-153 and BDE-154 co-elute on most GC-columns (Covaci et al., 2003). In the previous project, a subset of 22 samples was re-analysed using a newly developed method which enabled the separation of BB-153 and BDE-154 (Vorkamp et al., 2005), but the remaining 15 samples of the previous project reflect a sum of BB-153 and BDE-154. The separation of the two compounds was achieved for all the eleven new samples.

For the analysis of polychlorinated biphenyls (PCBs), DDT and its degradation product, hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB) a new instrument had been implemented since the previous project. As part of the laboratory's accreditation, an internal validation document concluded satisfactory results for all compounds analysed on the new instrument, with the exception of o,p'-DDT and p,p'-DDT, which showed lower precision and accuracy than before. The contribution of these compounds to ΣDDT is small: On average they account for 1.2% of ΣDDT in the peregrine falcon eggs. For the analysis of toxaphene, the supplier of analytical standards had changed between the two projects because the original supplier did not offer these toxaphene congeners any longer.

The analyses of PCBs, DDT, HCH, HCB and PBDEs followed the laboratory's accredited methods for these compounds without being explicitly run as accredited analyses. Recovery rates were determined for each sample. The eleven new samples were analysed in one batch, including one duplicate analysis, one blank and two samples of the laboratory's reference material. The new time series formed another batch, including one duplicate analysis, one blank, spiked control samples as well as spiked and non-spiked duplicates of the laboratory's reference material. Detection limits and other compound-specific information are given in the following chapters.

4.4 Supporting parameters

Dry matter and lipid content were determined for all samples. The dry matter content was determined according to Danish Standard 204, i.e. drying at 105°C until constant mass. As the dry matter content had changed since the previous project, the dry matter content was re-determined for all the samples included in the new time series. Considering the same samples, the dry matter content was now on average about 30% higher than in the previous project.

The lipid determination in the previous project followed the method by Smedes (1999). The same method was applied to determine the lipid content in the new samples for the extension of the old time series. The lipid content might also have changed during the storage of the samples since the previous project. For this reason, the lipid content was re-analysed in the samples of the new times series.

4.5 Eggshell thickness

The determination of the eggshell thickness used the same methodology as that of the previous project, as described in detail by Falk et al. (2006). The measurements included shell fragments from hatched eggs as well as whole eggs after opening them in the laboratory. They are described in detail in chapter 10. In this analysis, mean shell thickness was estimated for 184 clutches (at least 20 fragments available per clutch) and for 56 whole eggs from 44 clutches.

4.6 Time trend analysis

It was decided prior to the beginning of this study that comparability should be ensured with the AMAP Core Programme, the Danish/Greenland environmental monitoring under the Arctic Monitoring and Assessment Programme (AMAP). The AMAP Core Programme has monitored many of the same compounds measured in this study in marine species in Greenland and thus produced time series covering a comparable time period (Rigét et al., 2016). In addition, the AMAP Core Programme includes a screening element for new contaminants, which recently covered the same "novel" flame retardants as studied in the peregrine falcon eggs (Vorkamp et al., 2015a). Thus, the methods for chemical analyses are identical with those of the AMAP Core Programme.

The statistical time trend analysis is different now from that of the previous project, in order to match the methods of the AMAP Core Programme. It was recently described by Rigét et al. (2016): Based on annual medians or means (here: arithmetic means), the variation over time is divided into a linear and a non-linear component. The linear component is tested by log-linear regression, while a 3-point running smoother is used for the non-linear component. The non-linear component is tested by analysis of variance (ANOVA). The approach was originally described by Nicholson et al. (1998).

In case of several eggs per year, the concentrations were first averaged for eggs from the same bird. Then a mean concentration was calculated for each bird over several years. Concentrations below detection limits were replaced with half the detection limit in the time trend analysis. The same approach was chosen for the trend analysis of eggshell thickness: Eggshell fragments were averaged for each year, as were eggshell thicknesses for whole eggs. As these were not significantly different, data from fragments and whole eggs were combined, and a mean eggshell thickness was calculated for each year.

5 Polychlorinated biphenyls (PCBs)

5.1 Introduction

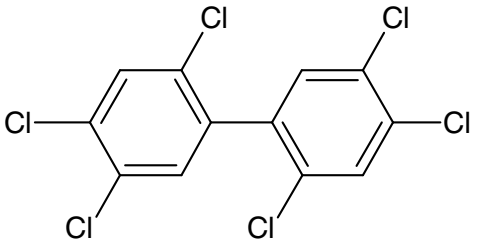
Polychlorinated biphenyls (PCBs) are aromatic compounds with up to ten hydrogen atoms substituted by chlorine. This leads to 209 PCB congeners in the ten homologue groups of mono- to decachlorinated biphenyls. PCBs have only been used as mixtures of several congeners, but with widely varying composition and degree of chlorination. Of the 209 congeners, 130 have been identified in commercial PCB mixtures at concentrations above 0.05% (IARC, 2015). PCBs were produced in quantities of at least 1.3 million tons in several industrial countries (Breivik et al., 2002) and used as dielectric fluid in capacitors and transformers, as hydraulic fluids and as additives to a number of products, e.g. rubber, caulk and joint sealants, insulation, cutting oil and wire and cable coating (IARC, 2015). The chemical structure of CB-153, the congener with the most pronounced biomagnification (Norstrom and Muir, 1994), is shown in Figure 4.

Because of their persistence, bioaccumulation and health risks, PCBs were phased out in most western countries in the 1970s and 1980s. PCBs were among the "dirty dozen", the first twelve compounds and compound groups with global regulation under the Stockholm Convention on Persistent Organic Pollutants (POPs). PCBs are included in Annex A (elimination) and Annex C of the Stockholm Convention, to account for the unintentional formation of PCBs in thermal processes and incomplete chemical reactions. Best available techniques and best environmental practice should be applied to minimize PCB emissions from unintended production (UNEP, 2009a). In the USA, which have not ratified the Stockholm Convention, PCBs are controlled under the Toxic Substances Control Act (TSCA) of 1976, which bans the manufacture, processing, distribution in commerce and use of PCBs above a threshold of 50 ppm (Head, 2005).

PCBs are omnipresent in the environment and found in remote areas like the polar regions (AMAP, 2004; Schiavone et al., 2009), the deep sea (Booij et al., 2014) and high mountain lakes (Schmid et al., 2011). The Danish / Greenland AMAP Core Programme has monitored PCBs in Greenland biota since its beginning in 1994 and documented decreasing concentrations (Vorkamp et al., 2011; Rigét et al., 2016). PCBs have previously been analysed in the peregrine falcon eggs from South Greenland for the time period of 1986 to 2003, as summarized below.

Adverse effects of PCBs and their metabolites include neurotoxicity, immunosuppression, effects on thyroid and retinol, reproductive effects and carcinogenicity (AMAP, 2004; IARC, 2015). PCBs have been implicated in the decline of peregrine falcons in some populated areas, caused by, among others, behavioural changes and reduced reproduction because of endocrine disruption and embryo toxicity (Ambrose et al., 2000; Wegner et al., 2005).

Figure 4. Chemical structure of CB-153 (2,2',4,4',5,5'-hexachlorobiphenyl).



5.2 Results of the previous project

In the previous project, 37 peregrine falcon eggs were analysed covering the years 1986 to 2003 (Sørensen et al., 2004; Vorkamp et al., 2009). As expected, the ΣPCB concentrations were high, with median and mean values of 55 and 62 µg/g lipid weight (lw) (3.1 and 4.6 µg/g wet weight, ww). These concentrations were slightly lower than those of peregrine falcon eggs from industrialised areas, but similar to results from Alaska and Norway (Ambrose et al., 2000; Herzke et al., 2002). On a lipid weight basis, the concentrations in peregrine falcon eggs were higher than those in polar bears *(Ursus maritimus)* from East Greenland, the top predator of the marine food chain (Norstrom et al., 1998; Dietz et al., 2013). CB-153, CB-180 and CB-138 were the main congeners, on average accounting for 30, 20 and 15% of ΣPCB.

The concentration of ΣPCB decreased over the study period, but the trend was not significant. It was discussed whether a substantial decrease in PCB concentrations could have taken place prior to the sampling period, as studies from Germany had shown the main PCB decrease between the 1970s and the beginning of the 1990s (Wegner et al., 2005). On the other hand, the exposure situation might be fundamentally different for the peregrine falcons from South Greenland which migrate to Central and South America. In the wider Caribbean region, for example, PCBs were widely used and were still present in some transformer oils in 2002 (Fernandez et al., 2002; UNEP, 2002). ΣPCB declined less steeply than ΣDDT. For most individual PCB congeners, the time trend results were not different from those of ΣPCB. Three congeners (CB-101, CB-149, CB-151) had a positive slope, but it was not significant.

5.3 Analytical methods

Eleven eggs collected in 2005 to 2014 were analysed in the current project, as detailed in chapter 4. The analytical methods were identical with those of the previous project (Vorkamp et al., 2009), ensuring data comparability in the extended time series. The PCB congeners included in the analysis are summarised in Table 3.

The PCBs were Soxhlet extracted with hexane:acetone (4:1). The extracts were cleaned on a multi-layer column consisting of deactivated aluminium oxide, silica (with and without H_2SO_4) and sodium sulfate. They were evaporated to 1 mL and analysed by dual column gas chromatography (GC) with electron capture detection (ECD). As described in chapter 4, the analytical method and QA/QC measures followed the procedures of the accredited organochlorine analysis. The limits of detection are included in Table 3.

Table 3. Summary of PCB congeners included in this project.

PCB congener	Full name	CAS number	Limits of detection* (ng/g wet weight)
CB-28	2,4,4'-Trichlorobiphenyl	7012-37-5	0.34
CB-31	2,4',5-Trichlorobiphenyl	16606-02-3	0.89
CB-44	2,2',3,5'-Tetrachlorobiphenyl	70362-45-7	0.38
CB-49	2,2',4,5'-Tetrachlorobiphenyl	41464-40-8	0.42
CB-52	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	0.85
CB-99	2,2',4,4',5-Pentachlorobiphenyl	38380-01-7	0.32
CB-101	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	0.44
CB-105	2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	0.72
CB-110	2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	0.41
CB-118	2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	0.41
CB-128	2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3	0.80
CB-138	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	0.39
CB-149	2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0	0.41
CB-151	2,2'3,5,5',6-Hexachlorobiphenyl	52663-63-5	0.39
CB-153	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	0.43
CB-156	2,3,3',4,4',5-Hexachlorobiphenyl	38380-08-4	0.43
CB-170	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	0.32
CB-180	2,2'3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	0.46
CB-187	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	0.40
CB-194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7	0.37
CB-209	Decachlorobiphenyl	2051-24-3	0.36

* for 3.5 g sample. The sample intake varied between 3.06 and 3.75 g.

5.4 Results and discussion

5.4.1 Concentrations of polychlorinated biphenyls

All PCB congeners were above detection limits in all samples. Table 4 summarises the mean and median concentrations of ΣPCB, CB-153 and CB-52 for the entire data set and the two subsets of 1986-2003 and 2004-2014.

Table 4: Summary of results (in µg/g lipid weight) for ΣPCB, CB-153 and CB-52 in peregrine falcon eggs from South Greenland in the previous project (1986-2003; Vorkamp et al., 2009) and the current project (2004-2014).

	ΣPCB		CB-153		CB-52	
	Median	Mean	Median	Mean	Median	Mean
1986-2003	54.6	62.2	14.8	18.7	0.0117	0.0184
2004-2014	34.8	43.4	11.7	14.0	0.0298	0.0445
1986-2014	52.6	57.8	14.5	17.6	0.0166	0.0245

CB-52 is of minor importance for ΣPCB, however, it is one of the few PCB congeners with higher concentrations in the 2004-2014 data set than in the old samples (two-tailed t-test on ln-transformed data, $p<0.05$). The other congeners with a significantly different concentration in the two data sets are CB-49, CB-101 and CB-110, in all cases these concentrations are higher in the more recent samples (2004-2014). No significant difference was observed for ΣPCB or any of the other congeners.

Table 4 shows that ΣPCB for the whole data set (1986-2014) is similar to ΣPCB of the previous study, which included most of the 48 samples (Sørensen et al.,

2004; Vorkamp et al., 2009). This means that the comparisons with other studies will still reach the same conclusions as described in section 5.2. Few studies on PCBs in peregrine falcon eggs have been published since the previous project, as summarised in Table 5. The PCB concentrations in the peregrine falcon eggs from Norway and the American east coast were higher than the corresponding concentration in our study (Gjershaug et al., 2008; Clark et al., 2009). For the Norwegian study, the longer time period has to be borne in mind, as levels in the 1970s probably were higher than those in subsequent samplings. The Californian data were similar to the results of the peregrine falcon eggs from Greenland (Park et al., 2009).

Following an empirical relation between levels of p,p'-DDE in blood plasma and eggs of peregrine falcon (Jarman et al., 1994) and assuming that this relation also is valid for ΣPCB, the ΣPCB concentration in blood can be converted to an approximate concentration in eggs. For the Canadian studies, this would correspond to ranges of about 2.1-4.2 µg/g ww and 3.4-6.8 µg/g ww, i.e. the same level as the Norwegian and the Greenland result.

Table 5. Studies published since 2008 on PCB concentrations in peregrine falcons. ww: wet weight, lw: lipid weight.

Sample type	Location	Year	ΣPCB concentration	Reference
Blood plasma (nestlings)	Great Lakes, Canada	2004/2005	Geometric mean: 0.35 µg/g ww	Fernie and Letcher (2010)
Blood plasma (females)	Nunavut, Canada	2004-2006	Geometric mean: 0.57 µg/g ww	Franke et al. (2010)
Egg	East coast, USA	1993-1999	Geometric mean: 7.62 µg/g ww [a)]	Clark et al. (2009)
Egg	California, USA	1986-2007	Median: 52.3 µg/g lw	Park et al. (2009)
Egg	Norway	1970-2005	Median: Appr. 6 µg/g ww [b)]	Gjershaug et al. (2008)

[a)] adjusted for dehydration loss, [b)] taken from figure.

5.4.2 Time trends of polychlorinated biphenyls

As described in chapter 4, the trend analysis is different from that of the previous project (Vorkamp et al., 2009). While the former project used linear regression of ln-transformed data, the current method works with a log-linear and a non-linear component. ΣPCB decreases significantly ($p<0.05$) for lipid-normalised and wet weight concentrations (Figure 5). The trend of ΣPCB is strongly influenced by that of its main component, CB-153, which also decreased significantly (Table 6). Decreasing PCB concentrations have been found in most monitoring programmes, including the AMAP Core programme (Rigét et al., 2016). However, the main decrease was generally observed shortly after the ban of PCBs and prior to those time series which were first set up in the 1990s. For example, the ringed seal *(Phoca hispida)* and polar bear time series, which date back to the 1980s, show a clear decrease in the beginning of the time series, but stabilization or even increasing concentrations in the last few years (Vorkamp et al., 2011, Rigét et al., 2016).

In line with these observations in the Arctic, decreases of PCB levels have also been documented for peregrine falcon eggs from South Greenland. Among the more recent studies, ΣPCB in peregrine falcon eggs from Norway decreased over the study period of 1965-2005, in fact, more clearly than PCBs in corresponding time series for golden eagles *(Aquila chrysaetos)*, white-tailed sea eagles *(Haliaeetus albicilla)* and merlin *(Falco columbarius)* (Gjershaug et al., 2008). Park et al. (2009), on the other hand, did not find significant changes in the PCB concentrations in peregrine falcon eggs from California over the study period of 1986 to 2007.

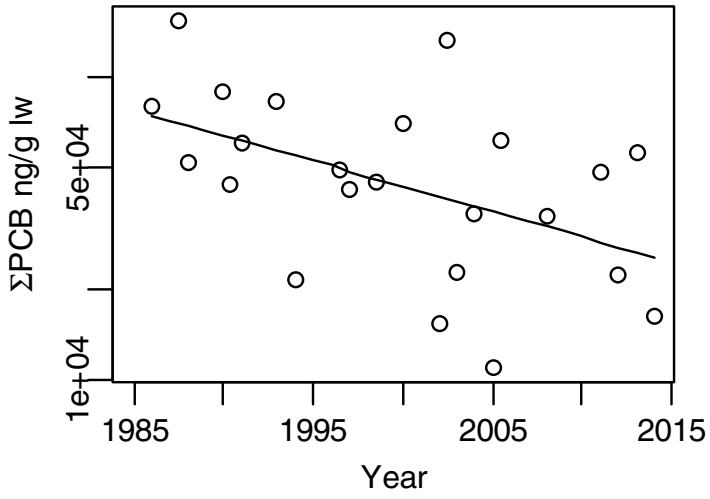


Figure 5. Concentration (in ng/g lipid weight) of ΣPCB in peregrine falcon eggs from South Greenland (1986-2014).

Although ΣPCB decreased, a few individual congeners increased, as indicated by the mean and median concentration in Table 4. Figure 6 shows the temporal trend for CB-52. However, none of the increasing trends are significant. It seems surprising that the lower chlorinated congeners, which generally have shorter half-lives than the higher chlorinated congeners (Ritter et al., 2011), do not decrease as clearly. Recently, the unintentional formation of lower chlorinated PCB congeners in some industrial processes has been discussed and might be a factor to consider in the understanding of the time trends (Vorkamp, 2016). The highly chlorinated PCB congeners show the steepest decrease in the peregrine falcon eggs (Table 6), as exemplified by CB-180 in Figure 6.

Table 6. Examples of the PCB time trend analysis, based on concentrations in ng/g lipid weight. Statistically significant results (p<0.05) are written in italics. ΣPCB is comprised of 21 congeners (**Table 3**).

Congener	Linear component		Non-linear component		Annual change (%)
	F	P	F	p	
CB-28	0.3	0.59	-0.37	1	-1.2
CB-52	0.47	0.5	0.29	0.93	+1.2
CB-101	4.28	0.05	-0.36	1	+3.9
CB-118	4.22	0.05	-0.62	1	-3.2
CB-138	*6.39*	*0.02*	-0.51	1	*-4.0*
CB-153	*5.07*	*0.04*	-0.50	1	*-3.3*
CB-180	*9.51*	*< 0.01*	-0.14	1	*-4.5*
ΣPCB	*6.70*	*0.02*	-0.46	1	*-3.8*

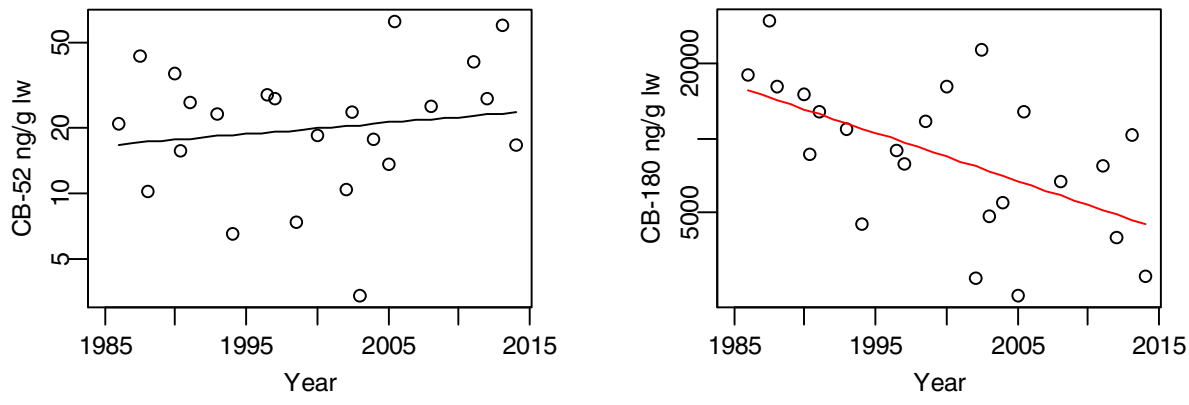


Figure 6. Concentrations (in ng/g lipid weight) of CB-52 and CB-180 in peregrine falcon eggs from South Greenland (1986-2014).

5.4.3 Discussion of the results in relation to the Stockholm Convention

As described above, most time trend studies on PCBs have documented decreasing concentrations in the environment. This is in line with the results for ΣPCB in the peregrine falcon eggs. PCBs were among the "dirty dozen" included in the Stockholm Convention in 2004, requiring national implementation plans for the phase-out of PCBs in all ratifying countries. National regulations in the countries of highest PCB usage (Breivik et al., 2002) had preceeded the Stockholm Convention, likely causing the PCB decrease observed since the 1970s / 1980s.

Some time series, in particular those of lower chlorinated PCB congeners, did not show the same trend of decreasing concentrations in the peregrine falcon eggs. Although reasons remain speculative, the unintentional formation of certain PCB congeners might have gained importance relative to the original industrial use of PCBs (Vorkamp, 2016). This emission pathway is recognized by the Stockholm Convention, as PCBs are also included in Annex C. If other studies confirm a contribution to environmental PCB concentrations from these sources, they might benefit from more research and regulatory awareness.

5.4.4 Toxicological considerations

A critical level of 40 µg / g ww has been used for ΣPCB in relation to successful reproduction of the peregrine falcon (Johnstone et al., 1996 and references therein). The maximum concentration of ΣPCB in our data was 27 µg / g ww, which is below this threshold, but in the same order of magnitude. However, the maximum concentration was found in a peregrine falcon egg from 1988. In combination with the generally decreasing trends (Table 6), the risk of PCB-related population effects is probably lower now than it was in the past.

The peregrine falcons are exposed to relatively high concentrations of many compounds with potential adverse effects, for which interactions and combined effects can occur. It has been pointed out in previous discussions of effects that PCBs are usually correlated to DDE, making it difficult to single out effects of specific compounds in wild birds (Wiemeyer et al., 1984). In a study on ospreys *(Pandion haliaetus)* and red kites *(Milvus milvus)*, a no-observed-adverse-effect-concentration (NOAEC) of 4 µg / g ww was used (Jimenez et al., 2007), which would be exceeded by 40% of the samples of our study. This threshold is among the lowest PCB levels in a compilation of effect levels for falconiform birds (Hela et al., 2006).

5.5 Conclusions

PCB concentrations in peregrine falcon eggs have remained high, i.e. in the µg / g range, and are comparable to levels of PCBs in peregrine falcons from more populated areas. The concentrations of ΣPCB and the main PCB congeners had decreased significantly since the 1980s, but no significant concentration changes were observed for some of the lower chlorinated PCB congeners, such as CB-52. New PCB sources might play a role in this unexpected lack of a temporal trend, but reasons for this observation are currently speculative. The PCB levels were below toxic thresholds reported for peregrine falcons, but by less than a factor 2 for the highest concentration. Nearly half the samples exceeded critical thresholds found for other birds of prey. While the decreasing time trends suggest a lower PCB-related risk today than in the past,

the concurrent exposure to many persistent organic pollutants at high concentrations might lead to combinatory effects not yet understood by the current state of knowledge.

6 Organochlorine pesticides

6.1 Introduction

The organochlorine pesticides in this study include DDT and its degradation products, hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), chlordane-related pesticides and toxaphene. Although chemically diverse (Figure 7), their production and use history is similar. Being introduced in the middle of the 20th century and finding extensive use, these pesticides were recognized as persistent organic pollutants from the 1960s onwards, leading to bans in agriculture in most western countries in the 1970s and 1980s. DDT was first used during the 2nd World War for disease control and became an increasingly used agricultural insecticide afterwards. The discovery of its insecticidal action was awarded with the Nobel Prize of Physiology and Medicine in 1948. The book "Silent Spring" (Rachel Carson) from 1962 raised public awareness of adverse effects of DDT and other organochlorine pesticides, including effects on birds. The cumulative world production of DDT was estimated at 2 million tons (ATSDR, 2002).

HCB, a fully chlorinated aromatic hydrocarbon, was introduced in 1945 as a fungicide. It has also been used in the production of pyrotechnics and rubber chemicals and it can be a by-product in the production of chlorinated solvents (Moermond and Verbruggen, 2012). HCH is a fully chlorinated aliphatic hydrocarbon. It consists of several isomers of which only γ-HCH (lindane) has insecticidal properties. HCH was originally used as technical HCH, a mixture of five isomers, of which γ-HCH only accounted for 11-18% (UNEP, 2006). Technical HCH was phased out in most western countries and Japan in the 1970s and replaced by lindane (γ-HCH), but it continued to be used in other parts of the world (UNEP, 2007). About 10 million tons of technical HCH are estimated to have been released into the environment between 1948 and 1997 (Li, 1999).

The chlordane-related compounds included in this study are a selection of five out of 120 or more individual compounds of technical chlordane. Chlordane was used as an insecticide and termiticide, mainly in the USA and Japan (Jaward et al., 2005; EFSA, 2007). The total global production volume was estimated at 70 000 tons until the mid-1980s (Dearth and Hites, 1991). Toxaphene was introduced in the late 1940s and produced at a global quantity of 1.3 million tons (Voldner and Li, 1993). It was used as an insectide, but also for controlling fish populations (de Geus et al., 1999), mainly in the USA, Central America and the former Soviet Union (Voldner and Li, 1993). Like chlordane, toxaphene is a complex mixture of many individual compounds of which six have been selected for this study.

All compounds except HCH were among the initial "dirty dozen" of the Stockholm Convention, meaning global bans since 2004. However, DDT is listed in Annex B ("restriction") with acceptable purpose for disease vector control. As of 2007, DDT was still being produced in India and North Korea, in a quantity of about 4500 tons (van den Berg, 2009). HCH was added to the Stockholm Convention in 2009, specifically α-, β- and γ-HCH. Comparably to PCBs, the organochlorine pesticides of this study are omnipresent in the environment including the Arctic (AMAP, 2004). Unlike PCBs, no current emission sources are known for these organochlorine pesticides, beyond the exemptions of the Stockholm Convention and secondary sources resulting from

the compounds' persistence in the environment. Several studies have reported an earlier offset and a more rapid decrease of DDT in biota compared with PCBs (Bignert et al., 1998).

The organochlorine pesticides of this study have all been included in the Danish / Greenland AMAP Core Programme since its introduction. They were also previously analysed in peregrine falcon eggs from South Greenland, for the period 1986-2003, as summarized below. In general, organochlorine pesticides have received most attention in studies on birds of prey as DDT and its metabolites in particular affect shell thickness (Lundholm, 1987; Peakall and Kiff, 1979, 1988). The other organochlorine pesticides have been studied to a lesser extent and were generally found in levels of 1-2 orders of magnitude below those of ΣDDT and ΣPCB (Jarman et al., 1993, Augspurger and Boynton, 1998; Herzke et al. 2002).

Besides their impact on eggshell thickness and the associated reproductive failure in a range of raptors and seabird species, all organochlorine pesticides of this study have been evaluated to be carcinogenic in animals (IARC, 1987; 1991; 2001). In humans, exposure to organochlorine pesticides has also been associated with immunotoxicity, neurotoxicity, neurodegenerative disorders, infertility and spontaneous abortion (Mrema et al., 2013).

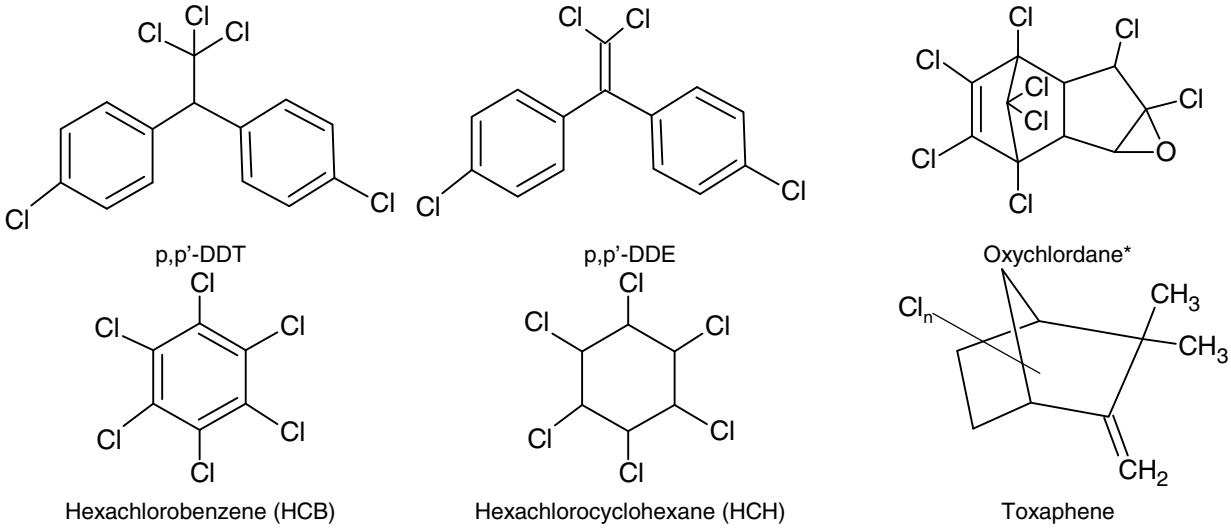


Figure 7. Chemical structures of some organochlorine pesticides included in this study. *Oxyclordane is the stable transformation product of many chlordane-related pesticides.

6.2 Results of the previous project

The approach in the previous project was the same as for PCBs: Organochlorine pesticides were analysed in 37 peregrine falcon eggs from the years 1985 to 2003 (Sørensen et al., 2004; Vorkamp et al., 2009; 2014a). p,p'-DDE had the highest concentrations of all individual compounds, with a median concentration of 39 µg / g lw (2.4 µg / g ww). These levels were similar to those in peregrine falcon eggs from Alaska and Norway, but lower than those of the Canadian Arctic, Germany and non-Alaska USA, for the same study periods (Jarman et al., 1993; Johnstone et al., 1996; Ambrose et al., 2000; Herzke et al., 2002; Wegner et al., 2005). The same pattern was found for HCB, HCH and chlordane-related pesticides, however, these had been studied to a lesser extent. In contrast to the similarities of these organochlorine pesticides to results from Norway (Herzke et al., 2002), toxaphene concentrations were roughly ten times higher in the peregrine falcon eggs from Greenland, suggesting differences in exposure which are more pronounced for toxaphene than for other organochlorines.

HCB, cis-chlordane and trans-chlordane were the only compounds with a significantly decreasing trend during the study period of 1986-2003. The decreasing trend of ΣHCH was close to being significant (p=0.051). Toxaphene, on the other hand, showed non-significantly increasing trends for four out of the six congeners (Vorkamp et al., 2014a). As discussed for PCBs, several studies observed the main decrease of ΣDDT in the environment immediately after its ban in the 1970s (Bignert et al., 1998; Wegner et al., 2005). Results from the 1970s confirmed much higher DDE levels in peregrine falcons from Greenland than found in this study (Walker et al., 1973). The critical DDE level of 15-20 µg / g ww given in the literature (Peakall, 1969) was not exceeded in any of the eggs of the previous study. However, a no-observed adverse effect level (NOAEL) of 3 µg / g ww (Herzke et al., 2002) was exceeded in 42% of the eggs.

6.3 Analytical methods

The same 11 eggs were analysed for organochlorine pesticides as for PCBs (Chapter 5). The extraction and clean-up method was identical with that of the PCB analysis. DDTs, HCB and HCHs were determined together with PCBs, in the same dual GC-ECD run, while chlordane-related pesticides and toxaphene were analysed by gas chromatography and mass spectrometry with electron capture negative ionisation (GC-MS-ECNI). Both types of instrumental analysis had also been applied in the previous project, ensuring data comparability in the same manner as described for PCBs (Vorkamp et al., 2009; 2014a).

Although not included in laboratory's accredited methods, the determination of chlordane-related pesticides and toxaphene used the same QA / QC methods as applied for the compound groups included in the laboratory's accredited methods for biota (PCBs, DDTs, HCB, HCHs). A summary of the individual compounds and their limits of detection is given in Table 7.

Table 7. Summary of the organochlorine pesticides included in this project.

Compound	CAS number	Limits of detection* (ng/g wet weight)
p,p'-DDT	50-29-3	0.39
p,p'-DDE	72-55-9	0.43
p,p'-DDD	72-54-8	0.43
o,p'-DDT	789-02-6	0.45
o,p'-DDE	3424-82-6	0.39
Hexachlorobenzene (HCB)	118-74-1	1.00
α-Hexachlorocyclohexane (α-HCH)	319-84-6	0.83
β-Hexachlorocyclohexane (β-HCH)	319-85-7	0.43
γ-Hexachlorocyclohexane (γ-HCH)	58-89-9	0.86
Cis-chlordane	5103-71-9	0.018
Trans-chlordane	5103-74-2	0.019
Cis-nonachlor	5103-73-1	0.033
Trans-nonachlor	39785-80-5	0.018
Oxychlordane	27304-13-8	0.036
Toxaphene Parlar 26 (CHB-26)	142534-71-2	0.018
Toxaphene Parlar 40 (CHB-40)	166021-27-8	0.018
Toxaphene Parlar 41 (CHB-41)	165820-16-6	0.018
Toxaphene Parlar 44 (CHB-44)	165820-17-7	0.088
Toxaphene Parlar 50 (CHB-50)	66860-80-8	0.018
Toxaphene Parlar 62 (CHB-62)	154159-06-5	0.089

* for 3.5 g sample. The sample intake varied between 3.06 and 3.75 g.

6.4 Results and discussion

6.4.1 Concentrations of organochlorine pesticides

Considering the eleven new samples of this project, the median concentrations increased in the order ΣHCH < HCB < ΣToxaphene < ΣChlordane < ΣDDT. Figure 8 shows the median concentrations of the compound groups together with those of the main individual compound of each group. Studying a similar suite of organochlorine pesticides, Herzke et al. (2002) also found that p,p'-DDE accounted for about 90% of all organochlorine pesticides in peregrine falcon eggs.

Of the five compounds and compound groups (ΣDDT, HCB, ΣHCH, ΣChlordane and ΣToxaphene), only ΣDDT had significantly different mean concentrations between the old and the new data set (two-tailed t-test on ln-transformed data, $p<0.05$). The mean concentrations of HCB and ΣChlordane were significantly different in a one-tailed test ($p=0.048$ and $p=0.034$; respectively), but not in a two-tailed test. Table 8 shows these mean values for each of the data sets as well as for all samples covering the period of 1986 to 2014. The overall mean is closer to the mean of the old data set because of the differences in sample number. Individual compounds contributing to ΣDDT, ΣHCH ΣChlordane and ΣToxaphene also differed significantly between the two data sets (two-tailed t-test on ln-transformed data, $p<0.05$).

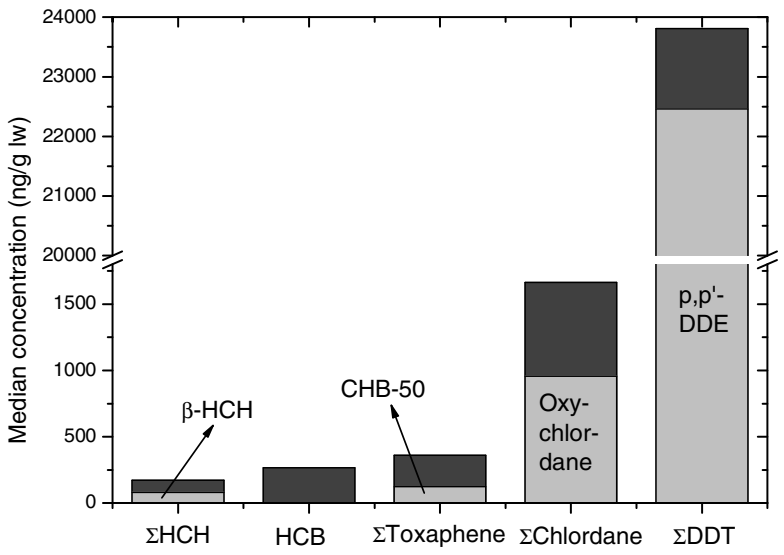


Figure 8. Median concentrations (ng/g lw) of organochlorine pesticide groups and their main individual compounds in peregrine falcon eggs from South Greenland (1986-2014).

Table 8. Mean concentrations (µg/g lw) of ΣDDT, HCB, ΣHCH, ΣChlordane and ΣToxaphene peregrine falcon eggs from South Greenland in the previous project (1986-2003; Vorkamp et al., 2009; 2014a) and the current project (2004-2014). Numbers in italics indicate a significant difference (two-tailed t-test on ln-transformed data, $p<0.05$).

	N	ΣDDT	HCB	ΣHCH	ΣChlordane	ΣToxaphene
1986-2003	36	*40.0*	0.389	0.173	2.13	1.27
2004-2014	11	*23.8*	0.266	0.174	3.67	0.629
1986-2014	47	38.4	0.376	0.173	3.32	1.13

As the average summed concentrations of ΣHCH, ΣChlordane and ΣToxaphene as well as the HCB concentration are similar for the two data sets the comparisons with other studies will reach the same conclusions as de-

scribed previously (Sørensen et al., 2004; Vorkamp et al., 2009; 2014a). Regarding more recent studies on organochlorines in peregrine falcon eggs and roughly comparable sampling periods, ΣDDT and ΣToxaphene were similar to results from Norway (Gjershaug et al., 2008) (Table 9). Individual DDT compounds in our study appear lower than in peregrine falcon eggs from the east coast of the USA, with the exception of p,p'-DDT (Clark et al., 2009). Likewise, chlordane-related pesticides have lower concentrations in our study, while the concentration of HCB is slightly higher (Table 9).

Two studies have analysed blood of peregrine falcons (Franke et al., 2010; Fernie and Letcher, 2010). Using the empirical egg-blood conversion factor established for p,p'-DDE in peregrine falcons (Jarman et al., 2014), our concentrations are comparable to those of adult females from Nunavut, Canada (Franke et al., 2010). Nestlings sampled at the Great Lakes generally had somewhat lower blood concentrations if compared to converted blood concentrations in the adult peregrine falcons from Greenland, only p,p'-DDT had approximately the same level (Fernie and Letcher, 2010). The high values reported in the eastern US suggest that the peregrine falcons from Greenland can be exposed to contaminants in this region as they pass through on their migration routes.

Table 9. Geometric mean concentrations (ng/g wet weight), unless specified otherwise, of organochlorine pesticides in peregrine falcon studies published since 2008 and corresponding values of this study.

Compound	Sample type	Location	Year	Concentration	Reference	This study
ΣDDT	Egg	Norway	1970-2005	Median: Appr. 3000 [a]	Gjershaug et al. (2008)	2135 [b]
p,p'-DDE	Blood plasma (females)	Nunavut, Canada	2004-2006	230	Franke et al. (2010)	103-207 [c,d]
p,p'-DDE	Blood plasma (nestlings)	Great Lakes, Canada	2004/2005	2.7	Fernie and Letcher (2010)	103-207 [c,d]
p,p'-DDE	Egg	East coast, USA	1993-1999	4260	Clark et al. (2009)	2068 [b]
p,p'-DDT	Blood plasma (nestlings)	Great Lakes, Canada	2004/2005	1.16	Fernie and Letcher (2010)	1.5-3.0 [c,d]
p,p'-DDT	Egg	East coast, USA	1993-1999	7.9	Clark et al. (2009)	19 [b]
p,p'-DDD	Egg	East coast, USA	1993-1999	24	Clark et al. (2009)	5.8 [b,e]
o,p'-DDT	Egg	East coast, USA	1993-1999	10	Clark et al. (2009)	0.83 [b,e]
HCB	Blood plasma (nestlings)	Great Lakes, Canada	2004/2005	0.13	Fernie and Letcher (2010)	1.3-2.6 [c,d]
HCB	Egg	East coast, USA	1993-1999	10	Clark et al. (2009)	29 [b]
ΣChlordane	Blood plasma (nestlings)	Great Lakes, Canada	2004/2005	1.37	Fernie and Letcher (2010)	7.6-15 [c,d]
Oxychlordane	Egg	East coast, USA	1993-1999	340	Clark et al. (2009)	86 [b]
Cis-nonachlor	Egg	East coast, USA	1993-1999	26	Clark et al. (2009)	20 [b]
Trans-nonachlor	Egg	East coast, USA	1993-1999	140	Clark et al. (2009)	43 [b]
ΣToxaphene	Egg	Norway	1970-2005	Median: Appr. 50 [a]	Gjershaug et al. (2008)	40 [b]

[a] Taken from figure. [b] 1986-2014. [c] 2004-2014. [d] Re-calculated according to Jarman et al. (1994), assuming a conversion factor of 6-12 between blood and eggs. [e] Concentrations below detection limits were replaced with half the detection limit in the calculation of geometric means.

6.4.2 Time trends of organochlorine pesticides

Being the predominant organochlorine pesticide in terms of concentrations and likely toxicological effects, p,p'-DDE showed a significantly decreasing

trend over the whole study period (Figure 9). The time trend of ΣDDT is similar to that of p,p'-DDE, but slightly steeper, probably due to the pronounced decrease of p,p'-DDD.

Lower concentrations of p,p'-DDE compared with results from the 1970s had already been observed in the previous project (Walker et al., 1973; Vorkamp et al., 2009). Decreases of p,p'-DDE since the early 1980s have also been reported for peregrine falcons from Nunavut, Canada (Franke et al., 2010). Like ΣPCB, ΣDDT has been found to decrease in most of the time series established under the AMAP Core Programme (Rigét et al., 2016). The main decrease took place in the 1970s and 1980s.

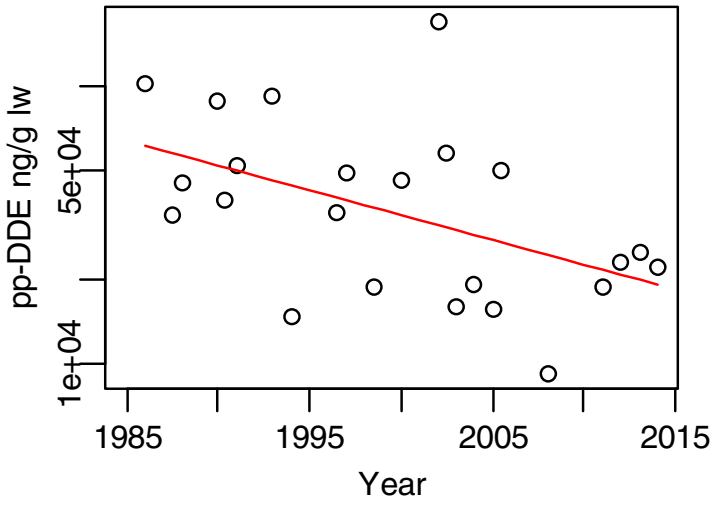


Figure 9. Concentrations (in ng/g lipid weight) of p,p'-DDE in peregrine falcon eggs from South Greenland (1986-2014).

The significantly decreasing trend of HCB (Table 10) confirms the results of the previous project (Vorkamp et al., 2009). Both β- and γ-HCH decreased significantly. α-HCH showed no significant trend. This observation in the largely terrestrial peregrine falcon contrasts the HCH developments in eggs of the marine black guillemots from Greenland, where β-HCH showed a non-significant increase, while α- and γ-HCH decreased significantly (Rigét et al., 2016). The different physical-chemical properties of the HCH isomers can lead to different exposure situations, for example from volatilization from soil or water, especially in a changing climate (Bossi et al., 2013).

Of the chlordane-related pesticides, oxychlordane, *cis*- and *trans*-chlordane were found to decrease significantly over the study period of 1986-2014. Consequently, ΣChlordane had changed from a non-significant decrease in the previous project to a significant decrease. A clear decrease of oxychlordane had also been observed in peregrine falcon eggs from Alaska (Ambrose et al., 2000). In the AMAP Core Programme, ΣChlordane was found to decrease significantly in about half the time series, while the other half showed no trend (Rigét et al., 2016). This is in line with previous analyses of all Arctic time trends also showing decreases or no trends (Rigét et al., 2010).

The updated time trends for toxaphene show a significant non-linear component for CHB-44 and CHB-62 indicating a decreasing trend. The trends for CHB-44 and CHB-50 in particular are strongly influenced by low concentrations in the oldest sample from 1986. If this sample was removed from the data set, CHB-44 would have a significantly decreasing log-linear trend with an annual change of -7.1%. For CHB-50, the current positive trend would be

reversed into a non-linear decreasing trend, with an annual change of -2.3%. Toxaphene was found to decrease in eggs of tawny owl *(Strix aluco),* a strictly terrestrial predator, in Norway from 1986 to 2004, by approximately a factor of four (Bustnes et al., 2007). The AMAP Core Programme has also generally shown decreasing concentrations of ΣToxaphene (Vorkamp et al., 2015b; Rigét et al., 2016). However, in the Canadian Arctic monitoring programme, some recent increases of toxaphene have been reported (Muir et al., 2013).

Table 10. Examples of the time trend analysis of organochlorine pesticides, based on concentrations in ng/g lipid weight. Statistically significant results ($p < 0.05$) are written in italics.

Compound	Linear component		Non-linear component		Annual change (%)
	F	P	F	P	
p,p'-DDE	*6.7*	*0.02*	1.4	0.29	*-4.1*
ΣDDT	*7.6*	*0.01*	0.25	0.93	*-4.4*
HCB	*5.4*	*0.03*	0.97	0.48	*-5.0*
ΣHCH	2.9	0.10	0.75	0.61	-2.6
ΣChlordane	*6.7*	*0.02*	0.30	0.92	*-4.3*
ΣToxaphene	0.18	0.67	1.7	0.18	-1.1

6.4.3 Discussion of the results in relation to the Stockholm Convention

Together with PCBs and other POPs, DDT (and its degradation products), HCB, chlordane-related pesticides and toxaphene were among the "dirty dozen" initially regulated by the Stockholm Convention. Analogously to PCBs, DDT had been banned in several countries prior to the Stockholm Convention. p,p'-DDE still has the highest concentration of the individual compounds analysed in the peregrine falcon eggs. However, the concentrations have decreased significantly over the study period of 1986-2014 and thus more clearly than those of ΣPCB. This is the case although DDT is regulated under Annex B of the Stockholm Convention (restriction). Up to the mid-1990s DDT was still used to combat malaria (> 1000 tonnes annually) in countries where the peregrine falcons from Greenland winter (PAHO, 1994).

Of the HCH isomers, only β- and γ-HCH decreased significantly. Air monitoring in Greenland and other studies indicated that volatilization of α-HCH from seawater is a major source of atmospheric concentrations, which increases in importance with the extent of receding seaice (Bossi et al., 2013). ΣToxaphene does not show decreasing concentrations, as also found in the previous project (Vorkamp et al., 2014a). Although the use and phase out history of toxaphene is similar to that of the other organochlorine pesticides and no current emission sources are known, its elimination seems to proceed more slowly compared with some of the other compounds of the "dirty dozen".

6.4.4 Toxicological considerations

The critical level of DDE for eggshell thinning is 15-20 µg/g ww (Peakall, 1969; Peakall and Kiff, 1988) resulting in a eggshell thinning of 17-20%. With a maximum concentration of 9.1 µg/g ww in this study, none of the peregrine falcon eggs reached this threshold. As mentioned above, a NOAEL of 3 µg/g ww (Herzke et al., 2002) was exceeded by 42% of the eggs of the previous study. None of the eleven eggs analysed in the current project had a concentration above 3 µg/g ww for p,p'-DDE. Thus, considering the whole study period of 1986-2014, only 34% of the eggs had concentrations above 3 µg/g

ww. However, two eggs from 2005 and 2006, respectively, had a concentration of p,p'-DDE of 2.9 µg/g ww. A lowest observed effect concentration (LOEC) of 2 µg/g ww has been reported for p,p'-DDE in prairie falcon *(Falco mexicanus)*, above which impacts on the population were observed (Fyfe et al., 1988). This value is exceeded by nearly half of our peregrine falcon eggs (49%), with multiple eggs having a concentration close to 2 µg/g ww. As further discussed in chapter 10, the shells of the peregrine falcon eggs studied here are still thinner than they were before the introduction of DDT. For HCB, a critical level of 4 µg/g ww has been reported (Johnstone et al., 1996), but all HCB concentrations of this study were clearly below this concentration.

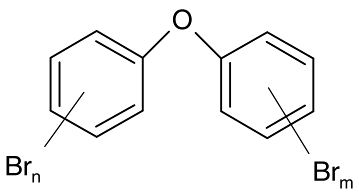
6.5 Conclusions

All organochlorine pesticides included in this study could be detected at relatively high levels in the peregrine falcon eggs, with p,p'-DDE being the clearly predominant compound. The concentrations of organochlorine pesticides were comparable to results from Norway and Canada, but appeared lower than those recently published for peregrine falcon eggs from the east coast of the USA. p,p'-DDE is amongst the organochlorine pesticides with a significantly decreasing trend over the study period of 1986-2014. Furthermore, HCB, ΣChlordane and the HCH isomers except α-HCH decreased significantly, which is in line with other time trend studies in biota. Toxaphene on the other hand did not show any clear trend, for currently unknown reasons since its use and phase out history is similar to that of the other organochlorine pesticides. Despites its decreasing trend, a substantial number of samples still exceeds the levels of p,p'-DDE associated with subtle effects. As evidenced by eggshell measurements in this project, the shell thickness has not yet returned to its pre-DDT level. Furthermore, the exposure of the peregrine falcons to a cocktail of multiple high concentration chemicals can have unexplored effects.

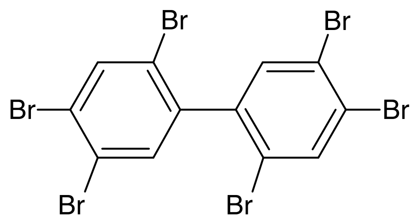
7 Brominated flame retardants

7.1 Introduction

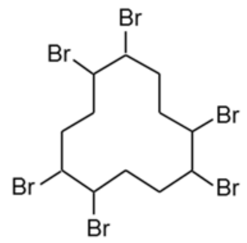
The history of brominated flame retardants (BFRs) is linked to that of petroleum-based (and thus flammable) polymers. Both additive and reactive BFRs exist, of which the first are mixed with the polymers and the latter form covalent bonds. The release of reactive flame retardants from products into the environment is generally found to be smaller than that of additive flame retardants (de Wit, 2002). This study only includes additive flame retardants: Polybrominated diphenyl ethers (PBDEs), brominated biphenyl 153 (BB-153), hexabromocyclododecane (HBCDD) (Figure 10) and several so-called novel flame retardants (NFRs), as specified below (Figure 11).



PBDEs

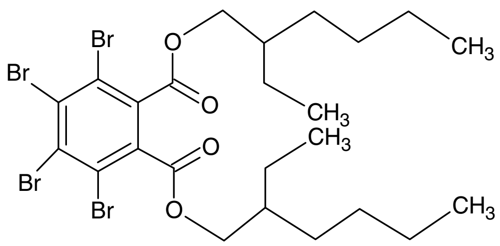


BB-153

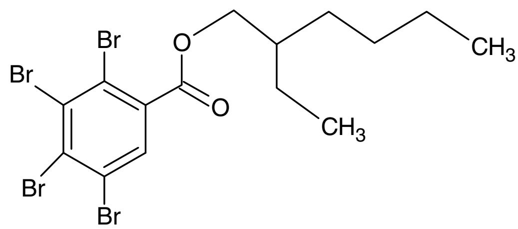


HBCDD

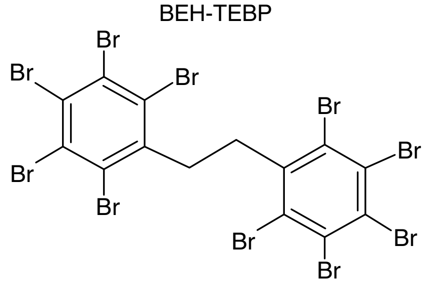
Figure 10. Chemical structures of polybrominated diphenyl ethers (PBDEs), polybrominated biphenyl (BB)-153 and hexabromocyclododecane (HBCDD).



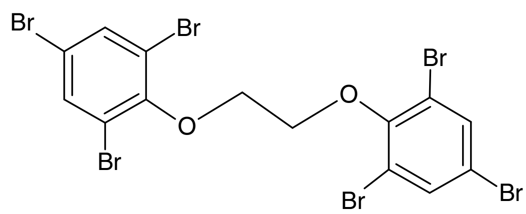
BEH-TEBP



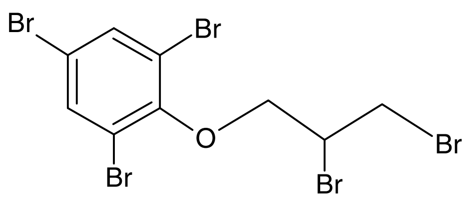
EH-TBB



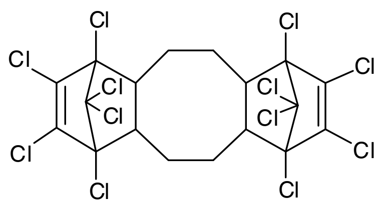
DBDPE



BTBPE



DPTE / TBP-DBPE



DDC-CO

Figure 11. Chemical structures of bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), 2,4,6-tribromophenyl 2,3-dibromopropyl ether (DPTE or TBP-DBPE) and dechlorane plus (DDC-CO).

Being brominated analogues to PCBs, mixtures of polybrominated biphenyls (PBBs) were used as flame retardants, mainly in the 1970s. The Michigan incident in 1973, when a PBB mixture was mistaken for an animal feed supplement and fed to cattle in Michigan, USA, ceased the PBB production in the USA shortly thereafter (Carter, 1976). In Europe, the DecaBB product, primarily consisting of the fully brominated congener, was still produced until 2000. Our study only included the congener BB-153, a hexabrominated congener, which is the most recalcitrant and bioaccumulative one, analogously to CB-153 in the PCB group (de Boer et al., 1998). Hexabromobiphenyl was added to the Stockholm Convention in 2009 (UNEP, 2009b).

PBDEs were used in three commercial mixtures (Penta-, Octa- and DecaBDE), which differ in composition and application fields. Cumulative global production amounts of Penta-, Octa- and DecaBDE since the 1970s were about 100 000, 110 000 and 1.25 million tons, respectively (Abassi et al., 2015). According to these estimates, about 95 and 45% of Penta- and DecaBDE, respectively, were used in North America. Penta- and OctaBDE were added to the Stockholm Convention in 2009, which effectuated a global ban (UNEP, 2009c). DecaBDE was added in 2017 (UNEP, 2017).

The commercial HBCDD mixture consists of several isomers, the most important ones being γ-HBCDD (75-89%), α-HBCDD (10-13%) and β-HBCDD (1-12%). HBCDD is mainly used as a flame retardant in polystyrene, for example in building insulations. Unlike PBDEs, HBCDD was used to a higher degree in Europe than in North America (de Wit et al., 2010). HBCDD was included in the Stockholm Convention in 2013, but with an exemption for its use in expanded and extruded polystyrene, provided the material is labelled accordingly (UNEP, 2013).

With the regulations of PBDEs and HBCDD, unregulated NFRs might be used increasingly although very little factual information is available on their identities, production volumes and use numbers (Covaci et al., 2011). Based on their recent detection in high trophic level animals of the marine environment of Greenland (Vorkamp et al., 2015a), the following NFRs were chosen for the analysis in peregrine falcon eggs:

- Bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB). These compounds have been used in combination in the Firemaster 550® and Firemaster BZ-54® flame retardants, probably as a replacement of PentaBDE (Stapleton et al., 2008). BEH-TEBP has also been used individually, as a flame retardant and plasticizer. BEH-TEBP is the brominated analogue to di(2-ethylhexyl) phthalate (DEHP), a suspected endocrine disrupter (Latini, 2005).

- Decabromodiphenyl ethane (DBDPE) was introduced in the 1990s and has the same applications as DecaBDE (Kierkegaard et al. 2004). DBDPE is produced in the USA and in China, but not in Europe (Covaci et al., 2011; Dungey and Akintoye, 2007).

- 1,2-Bis(2,4,6-tribromophenoxy)-ethane (BTBPE) is used as a replacement of OctaBDE (Hoh et al., 2005). It has been produced in the USA since the 1970s (Hoh et al., 2005), but no information is available on recent production volumes. BTBPE is listed as a low production volume chemical in the European Union (Covaci et al., 2011).

- 2,4,6-Tribromophenyl 2,3-dibromopropyl ether (DPTE or TBP-DBPE) is chemically related to BTBPE as both molecules possess a 2,4,6-tribromophenoxy moiety. No information is available on its current production, but the compound can be purchased on internet sites. The compound was found in higher concentrations than PBDEs, i.e. several hundred ng/g in harp seal from the Arctic (von der Recke and Vetter, 2007).

- Dechlorane plus (DDC-CO) is a chlorinated additive flame retardant used since the 1960s, mainly in thermoplastic materials (Feo et al., 2012). It consists of two stereoisomers, *syn*- and *anti*-DDC-CO, in a ratio of about 1:3 (Hoh et al., 2006). Production sites in the USA and China have been mentioned (Hoh et al., 2006; Wang et al., 2010), while no production takes place in Europe (ECHA, 2007).

Several studies from Europe and North America have addressed BFRs in peregrine falcon eggs (e.g. Chen et al., 2008; Johansson et al., 2011) and generally reported concentrations which are lower than those of organochlorine pesticides and PCBs, but high in the context of BFR accumulation in wildlife. These studies have focused on PBDEs, with some additional information on HBCDD or BB-153. PBDEs and HBCDD are also included in the AMAP Core Programme.

7.2 Results of the previous project

As described for PCBs and organochlorine pesticides, 37 peregrine falcon egg samples were analysed in the previous project, covering the years 1985 to 2003 (Sørensen et al., 2004; Vorkamp et al., 2005). The previous project included PBDEs, BB-153 and HBCDD, but none of the novel flame retardants. The ΣPBDE concentration was among the highest reported for Arctic wildlife at the time, with a median of 1900 ng/g lw and a range of 300-12900 ng/g lw (Vorkamp et al., 2005). However, the ΣPBDE median concentration was < 5% of the respective concentrations of ΣPCB or ΣDDT. The PBDE levels were comparable to, but slightly lower than those available from Sweden at the time (Lindberg et al., 2004). A remarkable result was the presence of BDE-209 in the samples, although only accounting for 0.77% of ΣPBDE (based on medians). All PBDE congeners showed increasing concentrations over time, but they were only statistically significant for BDE-99, BDE-100, BDE-153 and BDE-209 (Vorkamp et al., 2005).

BB-153 was only determined in a subset of 22 eggs. The median concentration was 550 ng/g lw, thus exceeding median concentrations of individual PBDE congeners (except BDE-153) (Vorkamp et al., 2005). In contrast to the PBDEs, BB-153 decreased over time, however, the trend was not statistically significant. ΣHBCDD was detected in about half of the eggs, and the median concentration was 2.4 ng/g lw (range 0.1-230 ng/g lw), which appeared lower than results from Sweden (Lindberg et al., 2004). The time trend also showed a decreasing tendency, however, it was not statistically significant and, because of the lower detection frequency, based on fewer samples.

7.3 Analytical methods

The same 11 eggs as for PCBs and organochlorine pesticides (2004-2014) were also analysed for PBDEs, BB-153 and HBCDD. In addition, the whole time series of 41 eggs (1986-2014) was analysed for the NFRs.

For PBDEs and BB-153, the extraction and clean-up method was identical with that of the PCB analysis. In the column clean-up, a second fraction consisting of hexane:dichloromethane (1:1) was eluted, containing the HBCDD isomers. As mentioned in chapter 4, the method for the determination of HBCDD had changed compared with the previous project. Then, a Dutch laboratory had analysed HBCDD by GC-MS, a technique which does not separate the individual isomers, but only produces a result for ΣHBCDD. In the current project, the analysis by high performace liquid chromatography with tandem mass spectrometry (HPLC-MS / MS) allowed an isomer-specific analysis. Consequently, the old and new results are not directly comparable, and a time trend over the entire time period is only possible for ΣHBCDD. For PBDEs and BB-153, the analytical method is identical with that of the previous project (GC-MS-ECNI).

The analytical method of the NFRs is based on the method for PBDEs, with modifications. As the compound BEH-TEBP is not stable during the acid treatment applied in the clean-up step, the extracts are split for separate clean-up and lipid removal for BEH-TEBP (by gel permeation chromatograph with subsequent adsorption on silica) and the remaining compounds (by adsorption chromatography on aluminium oxide and silica with and without sulphuric acid). The latter used hexane:dichloromethane (1:1) instead of hexane. All compounds were analysed by GC-MS-ECNI, but two different GC columns were used, one for DBDPE and BEH-TEBP, the other one for the remaining compounds. Table 11 gives the detection limits of all compounds.

Table 11. Summary of the brominated flame retardants (and dechlorane plus) included in this project. The HBCDD isomers were determined by HPLC-MS/MS, the other compounds by GC-MS-ECNI.

Compound	Acronym	CAS number	Limit of detection* (ng/g wet weight)
2,2',4-Tribromodiphenyl ether	BDE-17	147217-75-2	0.090
2,4,4'-Tribromodiphenyl ether	BDE-28	41318-75-6	0.090
2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	5436-43-1	0.088
2,2',4,5'-Tetrabromodiphenyl ether	BDE-49	243982-82-3	0.090
2,3',4,4'-Tetrabromodiphenyl ether	BDE-66	189084-61-5	0.090
2,2',3,4,4'-Pentabromodiphenyl ether	BDE-85	182346-21-0	0.090
2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	60348-60-9	0.090
2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	189084-64-8	0.090
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	68631-49-2	0.18
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	207122-15-4	0.090
2,2',3,4,4',5,5'-Heptabromodiphenyl ether	BDE-183	207122-16-5	0.18
Decabromodiphenyl ether	BDE-209	1163-19-5	0.28
2,2',4,4',5,5'-Hexabromobiphenyl	BB-153	59080-40-9	0.11
α-Hexabromocyclododecane	α-HBCDD	134237-50-6	0.017
β- Hexabromocyclododecane	β-HBCDD	134237-51-7	0.017
γ-Hexabromocyclododecane	γ-HBCDD	134-237-52-8	0.017
Bis(2-ethylhexyl)tetrabromophthalate	BEH-TEBP	26040-51-7	0.020 **
2-Ethylhexyl-2,3,4,5-tetrabromobenzoate	EH-TBB	183658-27-7	0.039 **
Decabromodiphenyl ethane	DBDPE	84852-53-9	0.078 **
1,2-Bis(2,4,6-tribromophenoxy)-ethane	BTBPE	37853-59-1	0.039 **
2,4,6-Tribromophenyl 2,3-dibromopropyl ether	DPTE/TBP-DBPE	35109-60-5	0.0039 **
Syn-dechlorane plus	*Syn*-DDC-CO	13560-89-9	0.0039 **
Anti-dechlorane plus	*Anti*-DDC-CO	13560-89-9	0.0036 **

* for 3.5 g sample. The sample intake varied between 3.06 and 3.75 g.

** for 2.5 g sample. The sample intake varied between 0.028 and 2.90 g, after splitting the extracts for separate clean-up of the BEH-TEBP fraction.

7.4 Results and discussion

7.4.1 Concentrations of brominated flame retardants

PBDEs, BB-153 and HBCDD were widely detectable in the peregrine falcon eggs (Figure 12). The PBDE congeners BDE-17 and BDE-28 are not included in Figure 12 as more than half of the samples had concentrations below detection limits.

The highest concentration was found for BDE-153, with a median concentration of 670 ng/g lw. The predominance of BDE-153 in peregrine falcon eggs is different from the BDE-47 dominated pattern generally found in marine animals (e.g. Vorkamp et al., 2004a) and was also observed in other studies of brominated flame retardants in peregrine falcon eggs (e.g. Chen et al., 2008; Park et al., 2009). It can likely be attributed to the long half-life of BDE-153 (Drouillard et al., 2007) and to debromination of BDE-209 (Holden et al., 2009). However, considering only the eleven new samples (2004-2014), BDE-99 and BDE-153 have very similar median concentrations of 1010 and 990 ng/g lw. Whether this is a real change in the PBDE pattern or an artefact because of the low sample number of this subset of samples, is not clear. The predominance of BDE-99 is unexpected given that BDE-153 is the most recalcitrant of the PBDE congeners and BDE-99 is one of the main constituents of the commercial PentaBDE product banned globally in 2009 (La Guardia et al., 2006; UNEP, 2009c). Results from Sweden showed the opposite trend, i.e. lower percentages of BDE-99 and higher percentages of BDE-153 over time (Johansson et al., 2011). BDE-209 was detected in all samples, at an overall median concentration of 15 ng/g lw.

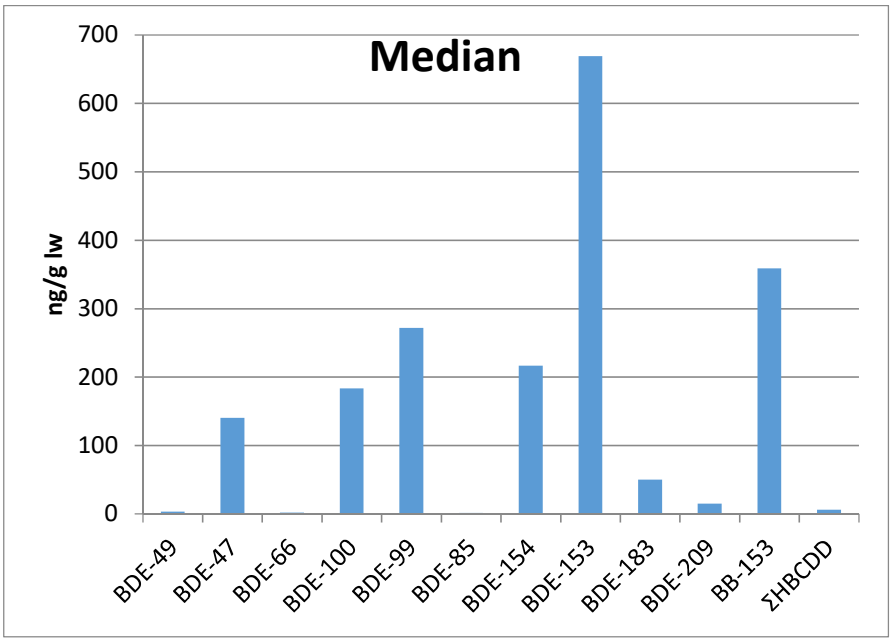


Figure 12. Median concentrations (in ng/g lipid weight) of the main PBDE congeners and ΣHBCDD in 48 peregrine falcon eggs from South Greenland, collected between 1986 and 2014. BB-153 was only determined in 34 samples. BDE-154 is likely biased towards higher concentrations because of co-elution with BB-153 in 14 samples.

The ΣPBDE median concentration for all eggs is 1910 ng/g lw, with a range of 270-12900 ng/g lw. The ΣPBDE median concentration of the new samples alone is 3500 ng/g lw, but given their low number, they do not contribute much to the overall median concentration. For BB-153 and ΣHBCDD, the median concentrations of all eggs were 360 and 6.0 ng/g lw. Considering the eggs of the second project alone, the median concentration of ΣHBCDD is 50 ng/g lw, but determined with a different analytical method than before.

Table 12 summarises recent examples of PBDE, BB-153 and HBCDD concentrations from the literature, to provide comparisons of our results with other studies. The populations in the studies listed in Table 12 are non-migratory, i.e. representing the local and regional pollution to a higher extent than the peregrine falcons of our study. While the ΣPBDE concentration in the peregrine falcon eggs from Greenland is higher than in eggs from Spain and Germany, it is lower than in eggs collected in the USA and Canada (Potter et al., 2009; Newsome et al., 2010; Guerra et al., 2012). The studies from the USA highlighted large differences between concentrations in peregrine falcon eggs from rural and urban areas.

Table 12. Examples of recently published mean concentrations (ng/g lipid weight), unless specified otherwise, of polybrominated diphenyl ethers (PBDEs), brominated biphenyl 153 (BB-153) and hexabromocyclododecane (HBCDD) in peregrine falcon eggs and corresponding values of this study.

Compound	Location	Year	Concentration	Reference	This study
ΣPBDE	Germany	2014	480	Vetter et al. (2016)	4095 [a)]
ΣPBDE	Canada	2007-2009	8300	Guerra et al. (2012)	2170 [b)]
ΣPBDE	Spain	2007-2009	950	Guerra et al. (2012)	2170 [b)]
ΣPBDE	Sweden	1974-2007	1848	Johansson et al. (2011)	2238 [c)]
ΣPBDE	USA (urban)	1986-2007	12300	Newsome et al. (2010)	2238 [c)]
ΣPBDE	USA (rural)	1986-2007	4742	Newsome et al. (2010)	2238 [c)]
ΣPBDE	USA	1993-2002	Median: 201 ng/g wet weight	Potter et al. (2009)	Median: 94 ng/g wet weight [d)]
BB-153	Canada	2007-2009	330	Guerra et al. (2012)	160 [b)]
BB-153	Spain	2007-2009	20	Guerra et al. (2012)	160 [b)]
BB-153	USA	1993-2002	Median: 21.6 ng/g wet weight	Potter et al. (2009)	Median: 28 ng/g wet weight [d)]
ΣHBCDD	Germany	2014	12.4	Vetter et al. (2016)	90 [a)]
ΣHBCDD	Canada	2007-2009	3700	Guerra et al. (2012)	34 [b)]
ΣHBCDD	Spain	2007-2009	480	Guerra et al. (2012)	34 [b)]
ΣHBCDD	UK	1973-2002	421	Leslie et al. (2011)	17.2 [e)]

[b)] 2013-2014, N=4. [b)] 2007-2009, N=2. [c)] 1986-2007, N=41. [d)] 1986-2002, N=35. [e)] 1986-2002, N=32; only samples from the first project.

The concentrations published for ΣHBCDD vary considerably between publications and thus locations. Leslie et al. (2011) found for peregrine falcon eggs from the UK that the isomer pattern of HBCDD varied as well: Although α-HBCDD was the main isomer in most eggs, some eggs only contained β-HBCDD or similar amounts of β- and γ-HBCDD. This is clearly different from our results where ΣHBCDD nearly exclusively consisted of α-HBCDD. The presence of β- and γ-HBCDD in the samples from the UK might reflect a proximity to the use of technical HBCDD (Law et al., 2008).

Compared with PBDEs, BB-153 and HBCDD, the concentrations of the NFRs are consistently lower (Figure 13). BEH-TEBP and DBDPE are not included in Figure 13 because of their low detection frequency. BEH-TEBP was detected in five samples, while DBDPE was below detection limits in all samples. DPTE, syn- and anti-DDC-CO, on the other hand, were detected in 100% of the samples.

The low detection frequency of DBDPE is in line with the findings of Guerra et al. (2012) who analysed DBDPE in peregrine falcon eggs from Spain and Canada, but only detected it in one out of 25 samples. In a previous study involving dechlorane plus (DDC-CO), the same birds from Spain and Canada

had been separated into aquatic and terrestrial habitats (Guerra et al., 2011). Considering the terrestrial birds, the ΣDDC-CO median concentration was 0.6 and 43 ng / g lw for birds from Spain and Canada, respectively (Guerra et al., 2011), which is lower and higher, respectively, than the concentration in the eggs from Greenland. DPTE was found in peregrine falcon eggs from Germany with a mean concentration of 33 ng / g lipid weight (Vetter et al., 2016), which clearly exceeded the level in our study. Vetter et al. (2016) explained that DPTE was still being used in Germany, with the potential implication of higher concentrations close to local sources.

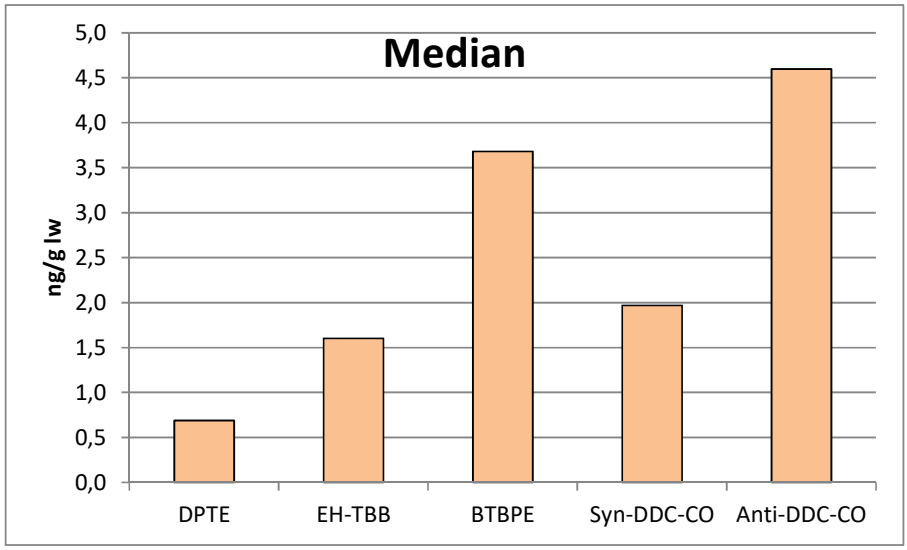


Figure 13. Median concentrations (in ng/g lipid weight) of the "novel" flame retardants analysed in peregrine falcon eggs from from South Greenland (1986-2014). BEH-TEBP and DBDPE are not shown because of low detection frequencies.

7.4.2 Time trends of brominated flame retardants

ΣPBDE increased over the new study period of 1986-2014, but the increase was not statistically significant. Regarding the individual congeners, no time trend could be calculated for BDE-17, BDE-28 and BDE-49 because of their low detection frequencies. The remaining PBDE congeners showed a positive trend (with the exception of BDE-66) for the lipid-normalised concentrations, as they did in the previous project (Vorkamp et al., 2005). However, the trend was only statistically significant for BDE-209, with an annual change of +7.2% ($p=0.01$). Unlike the BDE congeners, BB-153 showed a significantly decreasing trend of -8.0% per year ($p<0.01$). The concentration developments of BDE-209 and BB-153 are shown in Figure 14. Thus, the trends observed for these congeners in the previous project had now only changed in their rates, not in their directions.

Time trend studies on peregrine falcon eggs from Europe indicated a shift to decreasing concentrations of BDE-209 about 10-20 years ago (Johansson et al., 2011; Leslie et al., 2011). Different exposure situations can be expected, since these peregrine falcons reflect PBDE use patterns in Europe. Increasing trends of BDE-209 were found in US studies as of 2006 / 2007, more pronounced for the east coast than for California (Chen et al., 2008; Park et al., 2009), but no recent updates are available. For the other PBDE congeners, the Swedish time trend found a maximum in the mid- to late 1990s, which matched the temporal use pattern of PBDEs in Europe (Johansson et al., 2011). In accordance with our results, the peregrine falcon eggs from the east coast of the USA did not show a significant trend (Chen et al., 2008), while ΣPBDE increased significantly in peregrine falcon eggs from California (Park et al., 2009). None of these time trend studies included BB-153.

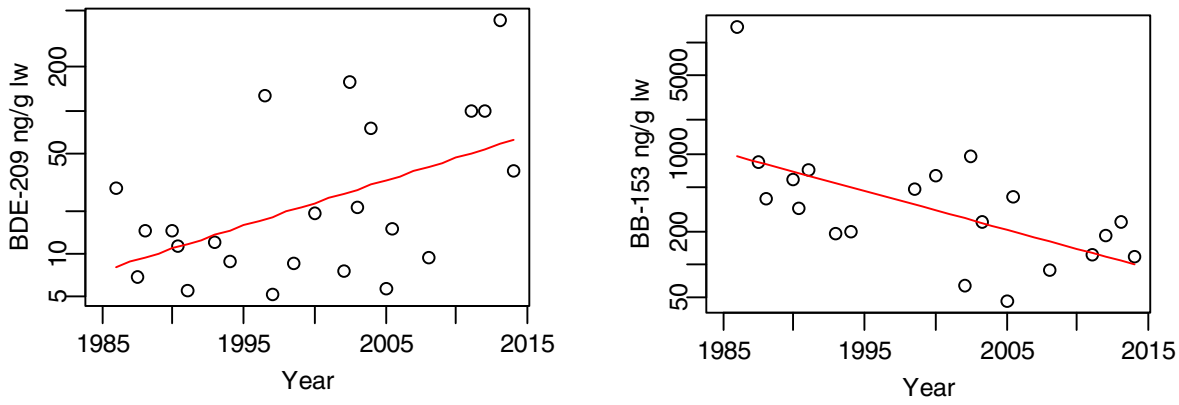


Figure14. Concentrations (in ng/g lipid weight) of BDE-209 (left) and BB-153 (right) in peregrine falcon eggs from South Greenland (1986-2014).

HBCDD showed a non-significant increasing trend, which suggests that the trend observed in the former project had been reversed. In the case of HBCDD both the chemical and the statistical method were changed, reducing the comparability between the results of the former and the current project. However, also regarding the new results alone (2004-2014), ΣHBCDD seems to increase. A significant increase of HBCDD was also found in the peregrine falcon eggs from Sweden as of 2007, with indications of a shift to decreasing concentrations, i.e. in a similar way as observed for BDE-209 (Johansson et al., 2011). The UK study did not find a trend for HBCDD over the time period of 1973-2002 (Leslie et al., 2011), and HBCDD was not included in the US time trend studies by Chen et al. (2008) and Park et al. (2009).

The AMAP Core Programme includes time trends for PBDEs in ringed seal *(Phoca hispida)* (blubber) from East and West Greenland as well as HBCDD in ringed seals (blubber) and glaucous gull *(Larus hyperboreus)* (liver) from East Greenland (Vorkamp et al., 2012; Rigét et al., 2016). No trend is available for BDE-209 because of too many results below detection limits. For the remaining PBDEs, the time trend from East Greenland suggests a maximum between 2000 and 2005, which is not apparent in the ringed seals from West Greenland, where concentrations still seem to increase. Thus, the time trend from West Greenland is similar to the results for the peregrine falcons from South Greenland, although the exposure situation of a non-migratory species is different. HBCDD possibly peaked between 2005 and 2010 in the ringed seals and glaucous gulls from Greenland, but due to the considerable year-to-year and within-year variation, more data points will be needed to verify these indications.

As described above, the concentrations of the NFRs were clearly lower than those of the main PBDE congeners, BB-153 or HBCDD. No time trend could be established for DBDPE, the potential replacement product of BDE-209, or EH-TBB and BEH-TEBP, the two components of the Firemaster 550® product, because of their low detection frequencies. Based on lipid-normalised concentrations, the two dechlorane plus isomers showed increasing trends, but they were not statistically significant at the 5% level. For DPTE, a significant decreasing trend was found, with an annual decrease of -2.8% (p=0.04).

Little information is available in the literature on time trends of these NFRs. Eggs of black kite *(Milvus migrans)*, white stork *(Ciconia ciconia)* and greater flamingo *(Phoenicopterus roseus)* from Spain were collected in two different years and analysed for dechlorane plus (Barón et al., 2015). No significant

change was found from around the year 2000 to around 2012, but the authors discussed that potential changes could be masked by the high intra-species variability. Dechlorane plus as well as EH-TBB and BEH-TEBP were found to increase in the atmosphere of the Great Lakes with doubling times of 3-9 years (Liu et al., 2016). Considering the migration routes of the peregrine falcons of our study, this could be significant for their exposure.

7.4.3 Discussion of the results in relation to the Stockholm Convention

Penta- and OctaBDE were added to the Stockholm Convention in 2009. The concentrations of PBDEs in peregrine falcon eggs from Greenland increased over the time period 1986-2014, but this increase was not statistically significant, except for BDE-209. Compared with the previous project, the increase had thus changed from significant to non-significant. While it cannot be ruled out that method differences contributed to this change, it is also possible that the increase has slowed down following the global regulations of PBDEs. A shift to decreasing trends has been documented in some time series (Braune et al., 2015; Rigét et al., 2016). It is remarkable that BDE-209 was detected in the peregrine falcon eggs at significantly increasing concentrations, as DecaBDE only recently was added to the Stockholm Convention.

BB-153 was included in the Stockholm Convention at the same time as Penta- and OctaBDE. It showed a significantly decreasing trend in the peregrine falcon eggs, as it also did in the previous project. Considering the peregrines' migratory route via North America, the production and use stop of PBBs following the Michigan incident in the 1970s might be the key factor for the decreasing concentrations. HBCDD has been included in the Stockholm Convention since 2013, and recently updated time series showed decreasing concentrations (Braune et al., 2015; Rigét et al., 2016). The concentrations in the peregrine falcon eggs still increased, but the trend was not statistically significant. Likewise, dechlorane plus showed non-significant increasing trends. Despite the abscense of statistical significance, this might be worth noting for future research and risk assessment of these currently unregulated compounds. DPTE on the other hand, of which very little information and environmental data are available, decreased significantly over the study period 1986-2014.

7.4.4 Toxicological considerations

Little is known about the effects of brominated flame retardants on peregrine falcons, although they add to a cocktail of many chemicals present at what have to be considered high concentrations in a bioaccumulation context. The American kestrel *(Falco sparverius)* is well-studied with regard to exposure to brominated flame retardants, and these studies have shown a wide spectrum of effects at environmentally relevant concentrations. PBDEs were found to affect the immunosystem and to alter hormone levels and behaviour, with consequences for reproduction (Fernie et al., 2005; 2008; Marteinson et al., 2011). Similar effects were also observed for HBCDD (Fernie et al., 2011; Marteinson et al., 2012). The authors also found that the kestrels' exposure to PBDEs and HBCDD led to thinner eggshells and discussed that these effects might contribute to the decrease that they observed in the American kestrel population (Fernie et al., 2009). The knowledge available of effects in kestrels and the comparable or higher concentrations in peregrine falcons could indicate a risk of adverse effects caused by brominated flame retardants accumulating in peregrine falcons.

7.5 Conclusions

A wide range of chemically diverse brominated flame retardants, including PBDEs, BB-153, HBCDD and various “novel” flame retardants, possibly replacing banned flame retardants, could be detected in the peregrine falcon eggs from South Greenland. The structurally similar BDE-153 and BB-153 had the highest concentrations, although BDE-99 had gained importance in comparison with the previous project. ΣPBDE and ΣHBCDD concentrations appeared lower than those from US studies, but higher than the concentrations found in some European studies. However, the comparability with other studies is limited by different study periods and the large variability between eggs. PBDEs and ΣHBCDD increased from 1986-2014, whereas BB-153 decreased. Among the novel flame retardants, DPTE, EH-TBB, BTBPE and dechlorane plus were detectable in the majority of eggs, but their concentrations were roughly 100 times below those of the PBDEs. No direct toxicological evidence is available of BFR effects, but analogies to the better-studied American kestrels indicate that PBDEs and HBCDD can cause effects at the levels observed in peregrine falcon eggs.

8 Polychlorinated naphthalenes

8.1 Introduction

Polychlorinated naphthalenes (PCNs) were used in industrial applications similar to those of polychlorinated biphenyls (PCBs), i.e. in capacitor dielectrics, cutting oils, wood and paper preservatives, cable insulation, dye carriers etc. (Yamashita et al., 2000). Their production and use began prior to that of PCBs, but also generally declined or stopped in the 1970s / 1980s. The total production volume was estimated at about 150 000 tons, which is nearly ten times lower than that of PCBs (Falandysz, 1998; Breivik et al., 2002).

Besides their emissions from industrial use, PCNs can also enter the environment via combustion sources although the formation pathways are not yet fully understood (Schneider et al., 1998; Ryu et al., 2013). Along with the identification of individual congeners in commercial PCN mixtures (Falandysz et al., 2006; 2008), typical combustion indicators have been suggested, for example CN-54 (Helm et al., 2004). As the industrial use of PCNs decreased, combustion processes might have gained importance as a PCN source (Meijer et al., 2001). A third source of PCNs in the environment is their occurrence as impurities in PCB formulations (Yamashita et al., 2000).

The hydrogen atoms at the naphthalene ring can be substituted by one to eight chlorine atoms, leading to a theoretical number of 75 PCN congeners (Figure 15). Because of their planar structure, PCNs can exhibit dioxin-like toxicity via the activation of the aryl hydrocarbon (Ah) receptor, which can lead to modulations of gene transcription and numerous toxic effects, including carcinogenesis and teratogenesis (Blankenship et al., 2000). Similarly to the toxic equivalent factors for dioxins, furans and dioxin-like PCBs, relative potency factors (RPFs) have been derived for PCNs, which express the toxicity of PCNs relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) (Falandysz et al., 2014). The highest RPFs were suggested for the hepta- and hexachlorinated congeners, ranging up to 10^{-3} compared to 2,3,7,8-TCDD (Falandysz et al., 2014).

PCNs were included in the Stockholm Convention on Persistent Organic Pollutants in 2015, under both Annex A (elimination) and Annex C (unintentional production) (UNEP, 2015a). PCNs are also on OSPAR's List of Chemicals for Priority Action, Group C (no current production or use interest in the OSPAR region).

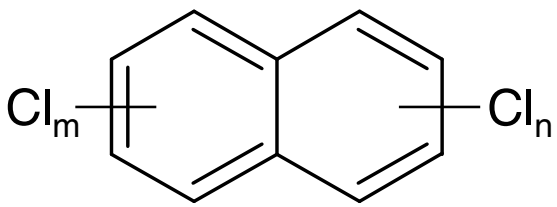


Figure 15. Chemical structure of polychlorinated naphthalenes (PCNs).

Given the long time-span of PCN use and their potential toxicity, PCN measurements in the Arctic are surprisingly sparse, as reviewed by Bidleman et al. (2010). They are not included in the AMAP Core Programme, but a previous screening of PCNs in marine samples from Greenland and the Faroe Islands

showed relatively low concentration, the highest being 4 ng / g lw in pilot whale *(Globicephala melas)* blubber (Vorkamp et al., 2004b). However, a widespread occurrence of PCNs in Arctic air has been shown, and PCNs have been detected in Arctic seabirds and marine mammals (Bidleman et al., 2010).

8.2 Analytical methods

PCNs were analysed in the 41 eggs representing the new time series from 1986 to 2014. The extraction and clean-up was combined for PCNs and the "novel" flame retardants (except BEH-TEBP). As described for the NFRs, the extracts were cleaned up on a column consisting of aluminium oxide and silica with and without sulphuric acid, from which the compounds were eluted with hexane:dichloromethane (1:1). Because of the low concentrations expected on the basis of the previous analyses of marine mammals (Vorkamp et al., 2004b), the extracts were concentrated to 200 µl and analysed by GC-MS-ECNI. Several PCN congeners could not be separated in the gas chromatographic analysis, which is in agreement with other studies (e.g. Rotander et al., 2012).

The congeners selected for this study are summarised in Table 13, together with their detection limits. Unlike for PCBs, there is no defined set of "indicator PCNs" which most laboratories analyse, with the consequence of limited comparability between studies. As described for the NFRs, the samples were analysed together with one blank, two spiked control samples as well as spiked and non-spiked samples of the laboratory reference material. Two peregrine falcon egg samples were analysed in duplicate, with good agreement.

Table 13. Summary of the polychlorinated naphthalenes (PCNs) analysed in this study.

Compound	Acronym	CAS number	Limit of detection* (ng/g wet weight)
1,3,5,7-tetrachlorinated naphthalene	CN-42	53555-64-9	0.016
1,2,3,5,7-/1,2,4,6,7-pentachlorinated naphthalene	CN-52/60	53555-65-0/ 150224-21-8	0.0062
1,2,3,5,8-pentachlorinated naphthalene	CN-53	150224-24-1	0.031
1,2,3,6,7-pentachlorinated naphthalene	CN-54	150224-16-1	0.0031
1,2,3,4,5,6-hexachlorinated naphthalene	CN-63	58877-88-6	0.0031
1,2,3,4,6,7-/1,2,3,5,6,7-hexachlorinated naphthalene	CN-66/67	103426-96-6/ 103426-97-7	0.0062
1,2,3,5,6,8-/1,2,3,4,5,7-hexachlorinated naphthalene	CN-68/64	103426-95-5/ 67922-27-4	0.0062
1,2,3,5,7,8-hexachlorinated naphthalene	CN-69	103426-94-4	0.0031
1,2,3,6,7,8-hexachlorinated naphthalene	CN-70	17062-87-2	0.0031
1,2,4,5,6,8-hexachlorinated naphthalene	CN-71	90948-28-0	0.0031
1,2,3,4,5,6,7-heptachlorinated naphthalene	CN-73	58863-14-2	0.0031
1,2,3,4,5,6,8-heptachlorinated naphthalene	CN-74	58863-15-3	0.0031

* for 2.5 g sample. The sample intake varied between 0.028 and 2.90 g.

8.3 Results and discussion

8.3.1 Concentrations of polychlorinated naphthalenes

The ΣPCN concentration ranged between 6.6 and 493 ng / g lw, with a median concentration of 21.4 ng / g lw. Less literature data are available for PCNs than for other compound groups analysed in this study, and no other data are

available on PCNs in peregrine falcon eggs. PCNs have been analysed in seabird eggs from the Arctic, including several gull species from the Norwegian Arctic and the Faroe Islands as well as thick-billed murre and northern fulmar from Canada (Verreault et al., 2005; Bidleman et al., 2010). The ΣPCN mean concentrations were generally between 0.5 and 5 ng / g lw (Bidleman et al., 2010), with higher mean concentrations of 49 ng / g lw (range 1.8-162 ng / g lw) in glaucous gull *(Larus hyperboreus)* eggs from Bear Island near Svalbard (Verreault et al., 2005). These mean concentrations are similar to that in peregrine falcon eggs (40 ng / g lw). However, the differences in the PCN suite analysed in the different studies limits comparability.

Studies in the Great Lake region included eggs of double-crested cormorants *(Phalacrocorax auritus)* and herring gulls *(Larus argentatus)* (Kannan et al., 2001). The concentrations were within the range also reported for the Arctic, i.e. mean concentrations of about 18-26 ng / g lw and 4-6 ng / g lw for the double-crested cormorant and the herring gull eggs, respectively. No significant difference was found between concentrations at three sampling stations although they differed in their pollution impact from urban and industrial sources (Kannan et al., 2001), suggesting relatively uniform background levels. Concentrations exceeding the median or mean values in the peregrine falcon eggs were found in eggs of white-tailed sea eagle *(Haliaeetus albicella)* from the Baltic Sea collected in 1985 and 1989 (Järnberg et al., 1997). Those concentrations were 120 and 130 ng / g lw. Considering this time period, the peregrine falcon eggs had a ΣPCN mean concentration of 40 ng / g lw, i.e. similar to the overall mean.

PCNs are not included in the AMAP Core Programme, but were analysed in a screening study of marine animals from Greenland and the Faroe Islands (Vorkamp et al., 2004b). Pilot whales from the Faroe Islands had the highest ΣPCN concentration of about 4 ng / g lipid weight (lw). No bird eggs were included in the study.

The main congeners detected in the peregrine falcon eggs were CN-52 / 60, followed by CN-66 / 67 and CN-42. These are penta-, hexa- and tetrachlorinated naphthalanes, respectively (Table 13). The predominance of CN-52 / 60 and CN-66 / 67 was also found for glaucous gull eggs from the Norwegian Arctic (Verreault et al., 2005) and is in line with the bioaccumulation properties of different PCN congeners as described by Falandysz (1998), mainly determined by the position of the Cl atoms on the naphthalene structure. In the commercial mixture Halowax 1041, the congeners CN-52 / 60 and CN-66 / 67 account for < 5% (Falandysz et al., 1998) and are clearly enriched in the peregrine falcon eggs. CN-54 is an indicator of combustion sources and only present in traces in Halowax mixtures (Helm et al., 2004). It accounted for 2.4% on average in the peregrine falcon eggs, indicating that combustion sources contribute to the PCN accumulation in the peregrine falcon eggs.

8.3.2 Time trends of polychlorinated naphthalenes

Based on lipid-normalised concentrations, all PCN congeners showed decreasing trends in the peregrine falcon eggs. ΣPCN was close to being significant ($p=0.06$) (Figure 16). Statistically significant decreases of about 4-6% per year were found for the congeners CN-53, CN-54 and CN-63 ($p<0.05$). For CN-63, the non-linear trend component was also significant ($p<0.01$), showing a maximum in 1988.

PCN time trends were recently studied for ringed seals *(Phoca hispida)* from four locations in the Canadian Arctic, comprising the time period since 2008 (one location) or 2011 (three locations) (Houde et al., 2016). The time series only showed a continuous decrease for the location where measurements began in 2008. However, in all cases, the lowest value was found for the most recent measurements. The same tendency of the most recent data point being the lowest one was also found for pilot whales, ringed seals and other marine mammals from the European Arctic (Rotander et al., 2012). As mentioned above, time trend monitoring of PCNs is not included in the AMAP Core Programme in Greenland.

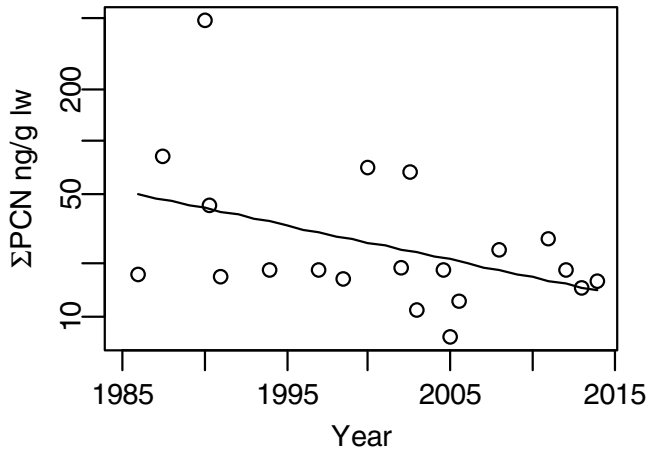


Figure 16. Concentrations (in ng/g lipid weight) of ΣPCN in peregrine falcon eggs from South Greenland (1986-2014).

The time trend of ΣPCNs in guillemot *(Uria aalge)* eggs from the Baltic Sea showed a peak at 220 ng / g lw in 1976 and a subsequent decrease to 84 ng / g lw in 1987, for which the last data point is available (Järnberg et al., 1997). Further time trend studies are available from the abiotic environment: Covering the time period from 1944-1986 soil analyses in the UK showed a local maximum of ΣPCN in 1956 and the absolute maximum in 1980 when the concentration was approximately 15 ng / g dry weight (Meijer et al., 2001). It then decreased sharply to < 1 ng / g dry weight in 1986. In a dated lake sediment core from the UK, however, PCNs peaked around the 1960s (Gevao et al., 2000). This peak clearly preceded that of PCBs, which occurred around 1980.

8.3.3 Discussion of the results in relation to the Stockholm Convention

Our results of PCNs in peregrine falcon eggs are in line with other studies reporting decreasing concentrations of PCNs in the environment. As described above, PCNs were included in the Stockholm Convention in 2015. The studies pre-dating the inclusion into the Stockholm Convention showed that the environmental concentrations in industrial countries had decreased prior to the global regulation. More recent studies indicate that this decrease continues, however, no results have been reported from systematic effectiveness monitoring.

PCNs are included in Annex A and Annex C of the Stockholm Convention, regulating elimination and unintentional production, respectively. Here it is remarkable that the peregrine falcon eggs also show a significant decrease of CN-54, a marker of combustion-related sources. These results might indicate that the Annex C regulation has the desired effect of reducing the unintentional production, however, no causal relationship can be established from these data.

8.3.4 Toxicological considerations

PCNs have dioxin-like toxicity and contribute to the total toxicity equivalents of a given sample along with dioxins, furans and dioxin-like PCBs (Falandysz et al., 2014). The hexachlorinated congeners CN-63, CN-66/67 and CN-69 are the most potent ones. Due to the relatively high concentrations of CN-66/67 in the peregrine falcon eggs, these congeners contribute most to the overall toxicity. Although CN-52/60 have the highest concentrations, they contribute less because of their lower RPFs.

Using the RPFs published by Falandysz et al. (2014), the mean concentration of PCNs in the peregrine falcon eggs expressed in toxicity equivalent (TEQ) units was between 0.004 and 0.04 ng TEQ/g lw. The range reflects the RPF range in the literature, but uses the upper limit in case of RPFs given as "less than" values. These estimated TEQ concentrations are similar to those of the herring gull and double-crescent cormorant eggs studied from the Great Lakes region (range 0.008-0.024 ng TEQ/g lw) as well as glaucous gull eggs (mean 0.03 ng TEQ/g lw) from Bear Island in the Norwegian Arctic (Kannan et al., 2001; Verreault et al., 2005). However, the PCN congener list included in these studies is not identical, and differences in the calculation exist as well.

It should be noted that individual birds had much higher concentrations than reflected by the mean concentration discussed here. For the sample with the highest PCN concentration in this study (from 1990), the TEQ concentration was about ten times higher than that of the mean.

In other studies, the contribution of PCNs to the overall dioxin-related toxicity was small, i.e. 2-3% (herring gulls and double-cresent cormorant eggs) and <1% (glaucous gulls) (Kannan et al., 2001; Verreault et al., 2005). As data on other dioxin-like compounds are not available, the same assessment is not possible for the peregrine falcon eggs. Kannan et al. (2001) discussed that the higher TEQ contributions in some studies might be related to a more localized toxic impact of PCNs compared with PCBs or dioxins/furans.

8.4 Conclusions

PCNs are present in peregrine falcon eggs in addition to the other halogenated compounds analysed in this study and partly detected in high concentrations. The PCN concentrations also appear relatively high compared with literature data, but were similar to those of glaucous gulls in the Norwegian Arctic and surpassed by PCN concentrations in eagle eggs from the Baltic Sea studied in the 1980s. In contrast to PCB analysis, no standardized set of indicator PCNs exists, which limits comparability between studies.

The PCN pattern in the peregrine falcon eggs is dominated by the congeners previously identified as the most bioaccumulating ones. The time trend analysis shows decreasing concentrations, which agree with other time trends available in the literature. However, PCNs are monitored in the environment to a lesser degree than other organochlorine compounds of the Stockholm Convention. PCNs can exhibit dioxin-like toxicity although their potency is lower than that of most dioxins and furans. As discussed for other compounds, individual birds have concentrations far above mean values and are particularly at risk to experience adverse effects.

9 Per- and polyfluorinated alkylated substances (PFASs)

9.1 Introduction

Per- and polyfluorinated alkylated substances (PFASs) consist of fully (per-) or partly (poly-) fluorinated carbon chains and a functional group (Buck et al., 2011). The main sub-groups are fluorinated sulfonic acids (PFSAs) and carboxylic acids (PFCAs) which include the best studied compounds perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (Figure 17). Other relevant subgroups are fluorotelomer alcohols (FTOH), perfluoroalkyl sulfonamides (FOSAs) and perfluoroalkyl sulfonamidoethanols (FOSEs), some of which are precursors to PFOS and PFOA (Ellis et al., 2004).

PFASs have been produced since the 1950s (Buck et al., 2011). Their unique properties of being both water and oil repellent have created a wide range of industrial and commercial applications. For example, PFASs have been used as surfactants, stain repellents and dispersants in many products including kitchenware, food packaging, textiles, fire extinguishers and paints (Vorkamp et al., 2014b). Some PFASs have also been used as processing aids in the manufacture of fluoropolymers. Between 1970 and 2002, perfluorooctane sulfonyl fluoride (PFOSF), a starting material in the production of PFOS, was produced in a quantity of 96 000 t in total (Paul et al., 2009).

The stability of the C-F bond increases the persistence of PFASs beyond those of many organochlorine compounds recognized as POPs. About 15 years ago, some PFASs were discovered to be global pollutants (Giesy and Kannan, 2001), and PFOS in particular was found to bioaccumulate and biomagnify in food chains. In 2002, the largest producer of PFOSF, the US 3M company, had phased out its PFOSF-based chemicals including PFOS (Paul et al., 2009). However, the PFOSF production in China increased rapidly in the following years and was still in operation in 2011 (Lim et al., 2011). A general shift of industrial production sites has been observed, from Japan, Western Europe and the USA to China, India, Russia and Poland (Wang et al., 2014). The EU banned PFOS in 2008.

In 2009, PFOS, its salts and PFOSF were included in Annex B (restriction) of the Stockholm Convention, still allowing their use for eight “acceptable purposes” (e.g. fire-fighting foams, aviation hydraulic fluids, certain medical devices) as well as twelve “specific exemptions” (e.g. chemically driven oil production, textiles and photo masks in the semiconductor and liquid crystal display industries) (UNEP, 2009d). In 2015, the European Union proposed PFOA, its salts and PFOA-related compounds for inclusion in the Stockholm Convention (UNEP, 2015b). Recently, PFHxS was proposed for inclusion in the Stockholm Convention as well. With these regulations in place or under consideration, the production of PFASs has shifted to short-chain PFASs, amongst these perfluorobutane sulfonate (PFBS), which are expected to be less bioaccumulative and toxic (Wang et al., 2013). However, degradation was still found to be slow, due to the stable C-F bond (Quinete et al., 2010) and several scientists have expressed their concern about potential impacts on human health and the environment (Scheringer et al., 2014).

Many studies have shown the presence of PFASs in the Arctic (Bossi et al., 2005; Butt et al., 2010). The monitoring of PFASs under the AMAP Core Programme showed a significant increase of PFOS until 2006, followed by a rapid decrease (Rigét et al., 2013). Likewise, increases were observed for perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnA) until 2006, but the subsequent development was less clear. The peregrine falcons from South Greenland had not previously been studied for PFASs, but results are available for PFASs in peregrine falcon eggs collected in Sweden between 1974 and 2002 (Holmström et al., 2010). Furthermore, eggs of several birds of prey, including peregrine falcons, have been analysed in Norway and PFAS levels were considered "alarming" (Gjershaug et al., 2008).

PFASs have been associated with a number of adverse effects on mammals, such as hepatoxicity, developmental toxicity, immunotoxicity and endocrine disruption (Lau et al., 2007). In human populations, PFASs have also been associated with cancer (Bonefeld-Jørgensen et al., 2011). Avian toxicity has mainly been studied for PFOS and shown indications of hepatoxic, reproductive and developmental effects (Peden-Adams et al., 2009; Custer et al., 2012; 2013).

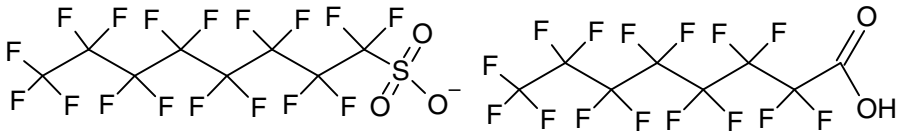


Figure 17. Chemical structures of PFOS (left) and PFOA (right).

9.2 Analytical methods

For the majority of samples, 1 g sample material was used, but less than 1 g was available of some samples. Based on the method by Ahrens et al. (2009), the compounds were extracted with acetonitrile. Acetic acid was added to the extracts and they were cleaned on ENVI-Carb columns. After evaporation to dryness, the compounds were re-dissolved in methanol-ammonium acetate buffer and analysed by high performance liquid chromatography (HPLC) with tandem mass-spectrometry (LC-MS-MS). The compounds included in this study and their detection limits are given in Table 14.

Table 14. List of PFAS compounds included in this study and their detection limits.

PFAS acronym	Full name	Carbon chain length	CAS number	Limit of detection (ng/g ww)*
PFBS	Perfluorobutane sulfonate	C_4	375-73-5/ 59933-66-3/ 45187-15-3	0.006
PFHxS	Perfluorohexane sulfonate	C_6	355-46-4/108427-53-8	0.006
PFHpS	Perfluoroheptane sulfonate	C_7	375-92-8	0.020
PFOS	Perfluorooctane sulfonate	C_8	1763-23-1/45298-90-6	0.078
PFDS	Perfluorodecane sulfonate	C_{10}	335-77-3/126105-34-8	0.161
PFOSA	Perfluorooctane sulfonamide	C_8	754-91-6	0.024
PFPeA	Perfluoropentanoic acid	C_5	2706-90-3	0.018
PFHxA	Perfluorohexanoic acid	C_6	307-24-4	0.291
PFHpA	Perfluoroheptanoic acid	C_7	375-85-9	0.025
PFOA	Perfluorooctanoic acid	C_8	335-67-1	0.103
PFNA	Perfluorononanoic acid	C_9	375-95-1	0.006
PFDA	Perfluorodecanoic acid	C_{10}	335-76-2	0.090
PFUnA	Perfluoroundecanoic acid	C_{11}	2058-94-8	0.004
PFDoA	Perfluorododecanoic acid	C_{12}	307-55-1	0.044
PFTrA	Perfluorotridecanoic acid	C_{13}	72629-94-8	0.013
PFTeA	Perfluorotetradecanoic acid	C_{14}	376-06-7	0.019

* based on 1 g sample, adjusted in case of lower sample intake.

9.3 Results and discussion

9.3.1 Concentrations of perfluorinated alkylated substances

As described in chapter 4, some of the samples had increased in dry matter content during the storage over several decades. Therefore, Table 15 summarizes the PFAS results on a fresh weight and a dry weight basis. As expected, PFOS had by far the highest concentrations of the individual compounds, accounting for, on average, 73% of ΣPFAS in this study and 94% of the sulfonic acids (PFBS, PFHxS, PFHpS, PFOS, PFDS). Although increasingly used as a PFOS replacement, PFBS was not detectable in any of the samples. PFBS has been detected in abiotic environmental media (Codling et al., 2014) and in low trophic level biota (Naile et al., 2013), but concentrations in high trophic level animals such as mink *(Neovison vison)*, black-footed albatross *(Phoebastria nigripes)* and herring gulls *(Larus argentatus)* were either very low or undetectable (Persson et al., 2013; Chu et al., 2015; Letcher et al., 2015).

The predominance of PFOS is in line with most studies on PFASs in biota, including the results by Holmström et al. (2010) for peregrine falcon eggs from Sweden, which also agree with our results in terms of absolute concentrations of PFOS and PFHxS (Table 15). Peregrine falcon eggs from Norway sampled from 1991-2005 contained approximately 100 ng / g ww for ΣPFAS (Gjershaug et al., 2008). While the individual PFAS compounds were not specified, the predominance of PFOS in our samples and the results from Sweden suggest that an average concentration of ΣPFAS would only be slightly above that of PFOS. This agreement seems surprising considering the different migratory routes of the birds: As described in the previous chapters, the Greenland peregrine falcons migrate to Central and South America along the east coast of the American continent, while the peregrine falcons from Sweden and Norway have winter habitats in Europe (Ratcliffe, 2000; Holmström et al., 2010).

Table 15. Examples of results for PFASs in peregrine falcon eggs from South Greenland and comparisons with results of Holmström et al. (2010). n.a.: not available.

Compound	Concentration (ng/g ww)			Concentration (ng/g dw)			Holmström et al. (2010) [a]
	Mean	Median	Range	Mean	Median	Range	Mean (ng/g ww)
PFBS	< 0.065	< 0.065	< 0.065	< 0.11	< 0.11	< 0.11	n.a.
PFHxS	0.97	0.46	0.14-5.0	3.7	2.1	0.37-18	0.8
PFOS	108	65	22-714	448	290	107-3886	83
PFDS	4.9	1.5	0.32-88 [b]	16	7.0	< 0.76-152	0.66
PFOSA	< 0.24	< 0.24	< 0.24	< 0.42	< 0.42	< 0.42	n.a.
PFOA	0.13	< 0.10	< 0.10-2.2	0.53	< 0.56	< 0.35-8.5	n.a.
PFNA	12	3.0	0.60-106	41	16	2.8-222	1.6
PFDA	4.2	2.9	0.90-19	17	13	3.6-58	3.1
PFUnA	11	8.7	2.9-31	43	39	11-93	4.2
PFDoA	4.8	4.2	1.5-14	19	16	6.8-40	3.2
PFTrA	3.9	1.9	0.61-25	15	7.4	2.6-128	7.3
PFTeA	0.67	0.18	0.053-13	2.9	0.86	0.25-68	2.7

[a] Samples from 2006, N=10, [b] Sample 01-1617 (1989): < 1.6 ng/g ww; < 1.9 ng/g dw

Considering only the most recent samples (2011-2014), for comparisons with other recently published data, the average PFOS concentrations in the peregrine falcon eggs is 158 ng / g ww, i.e. above the overall average given in Table 15. However, this value is strongly influenced by the maximum concentration of 714 ng / g ww in a sample from 2012. These concentrations are at the higher end of PFOS values published for eggs of other bird species, as summarised in Table 16.

Yordy et al. (2013) concluded for other birds of prey that PFASs were similar in magnitude to organochlorine contaminants. Although the PFAS concentrations in our study are high, they are clearly exceeded by those of the main groups of organochlorines. PCBs, for example, have mean and median concentrations of 4020 and 2783 ng / g ww, respectively, for the entire time series. For p,p'-DDE, the mean and median values are 2791 and 2062 ng / g ww, respectively.

Table 16. Examples of the last five years of PFOS concentrations in bird eggs. Concentrations are arithmetic means in ng/g wet weight unless specified otherwise.

Species	Location	Year	PFOS	Reference
Peregrine falcon	South Greenland	2011-2014	158	This study
Herring gull *(Larus argentatus)*	Great Lakes, USA and Canada	2012-2013	43-723 [a)]	Letcher et al. (2015)
Rhinoceros auklets *(Cerorhinca monocerata)*	Pacific coast, Canada	2010	97; 43 [b)]	Miller et al. (2015)
Leach's storm-petrels *(Oceanodroma leucorhoa)*	Pacific coast, Canada	2011	47; 45 [b)]	Miller et al. (2015)
Great blue herons *(Ardea herodias)*	Pacific coast, Canada	2012	83	Miller et al. (2015)
Double-crested cormorants *(Phalacrocorax auritus)*	Pacific coast, Canada	2011	20	Miller et al. (2015)
Ancient murrelet *(Synthliboramphus antiquus)*	Pacific coast, Canada	2009	17	Miller et al. (2015)
Great blue heron *(Ardea herodias)*	St. Paul, USA	2010-2011	62-396 [a), c)]	Custer et al. (2013)
European starling *(Stumus vulgaris)*	Brantford, ON, Canada	2009	703 [d)]	Gewurtz et al. (2013)
Great cormorant *(Phalacrocorax carbo sinensis)*	Lake Vänern, Sweden	2007-2009	552 [e)]	Nordén et al. (2013)
Herring gulls *(Larus argentatus)*	Lake Vänern, Sweden	2007-2009	292 [e)]	Nordén et al. (2013)
Herring gull *(Larus argentatus)*	Great Lakes, Canada	2010	100-500 [a), f)]	Gebbink et al. (2011)
Feral pigeon *(Columba livia f. domestica)*	Germany	2008	0.8-1.5 [a)]	Rüdel et al. (2011)
Rook *(Corvus frugilegus)*	Germany	2009	6.2	Rüdel et al. (2011)
Herring gull *(Larus argentatus)*	North Sea	2008	50; 119 [b)]	Rüdel et al. (2011)
Herring gull *(Larus argentatus)*	Baltic Sea	2008	159	Rüdel et al. (2011)
Cormorant *(Phalacrocorax carbo)*	Baltic Sea	2009	90	Rüdel et al. (2011)
Cormorant *(Phalacrocorax carbo)*	Elbe estuary, Germany	2009	540	Rüdel et al. (2011)
White ibis *(Threskiornis molucca)*	Sydney harbour, Australia	2008	34 [c)]	Thompson et al. (2011)
Silver gull *(Saccostrea commercialis)*	Sydney harbour, Australia	2008	33 [c)]	Thompson et al. (2011)

[a)] Multiple locations. [b)] Two locations. [c)] Geometric mean. [d)] Near landfill, maximum concentration of the data set. [e)] Median concentration. [f)] Approximate value, taken from figure.

9.3.2 Time trends of perfluorinated alkylated substances

The time trends are discussed on a dry weight basis, to ensure comparability between samples. No significant trend was observed for PFOS, the main PFAS in the peregrine falcon eggs (Figure 18). This result is different from the trend of PFOS in the marine species of the AMAP Core Programme, which showed a peak in the concentration of PFOS in 2006, for both ringed seals *(Phoca hispida)* (from West and East Greenland) and polar bears *(Ursus maritimus)* (from East Greenland) (Rigét et al., 2013). The variation between the samples is

much larger in the case of the peregrine falcon eggs and might mask potential trends. As discussed for Table 16, the sample from 2012 had the highest results of the data set and might also influence the overall time trend.

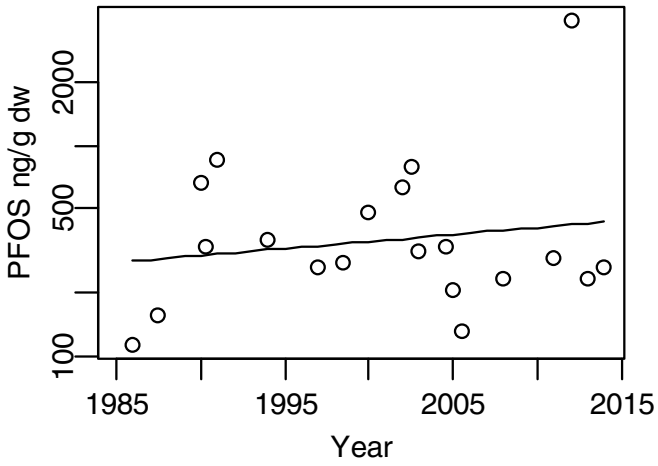


Figure 18. Concentrations (in ng/g dry weight) of PFOS in peregrine falcon eggs from South Greenland (1986-2014).

Holmström et al. (2010) observed an increase in PFOS concentrations in peregrine falcon eggs from Sweden until about 1984 after which the concentrations were levelling off. Other time trend studies involving bird eggs are not conclusive in their trends: The Swedish monitoring programme in the Baltic Sea observed a sharp peak for PFOS in guillemot eggs in 1997 (Holmström et al., 2005). In the Great Lakes region, PFOS decreased in herring gull eggs over the study period 1990-2010, but not for the location with the highest concentrations (Gebbink et al., 2011; Gewurtz et al., 2013). PFOS decreased in eggs of tawny owl *(Strix aluco)* from Norway (1986-2009) and in eggs of blue herons *(Ardea herodias)* from the USA from 1993 to 2010/2011 (Ahrens et al., 2011; Custer et al., 2013). However, besides differences in feeding behaviour, the migratory nature of the peregrine falcon will result in an exposure situation of limited comparability to monitoring programmes relying on non-migratory species.

Our results show significant decreases for most other sulfonic acids except PFOS (i.e. PFHxS, PFHpS and PFDS) and significant increases for PFNA, PFDoA and PFTeA. The Greenland monitoring of ringed seals and polar bears did not include PFHpS, but PFHxS showed a similar trend to that observed in the peregrine falcon eggs, i.e. non-linearity, but overall decreasing tendencies. The long-chain PFCAs showed inconclusive results as some, but not all time series decreased in the last few years, however, some of these decreases might be temporary (Rigét et al., 2013).

Our results also agree with other studies on bird eggs with regard to trends of long-chain PFCAs being different from trends of PFOS. In the peregrine falcon eggs from Sweden the concentrations of long-chain PFCAs increased over the whole study period until 2007, but levelled off in the last few years of the study (Holmström et al., 2010). Increasing concentrations of long-chain PFCAs were also found in eggs of herring gulls from the Great Lakes, tawny owls from Norway and blue herons from the USA (Ahrens et al., 2011; Gebbink et al., 2011; Custer et al., 2013; Gewurtz et al., 2013).

9.3.3 Discussion of the results in relation to the Stockholm Convention

As the first compound of the PFAS group, PFOS was globally regulated through the Stockholm Convention in 2009. While other monitoring studies have documented decreasing concentrations in the environment (e.g. Rigét et al., 2013), no time trend was observed for PFOS in the peregrine falcon eggs from Greenland. Despite the regulation, PFOS has remained the predominant compound in peregrine falcon eggs, accounting for 73% on average of ΣPFAS in this study.

PFOA and PFHxS are under consideration for inclusion in the Stockholm Convention. PFOA was only detected in 15% of the peregrine falcon egg samples, and the mean concentration was low (0.13 ng / g ww). PFHxS on the other hand was detected in all samples. Its mean value (0.97 ng / g ww) was higher than that of PFOA, but still much lower than the PFOS mean concentration of 108 ng / g ww. Compared with other halogenated compounds of this study, the concentrations of PFOA and PFHxS are in the lower end of the scale. Due to the low detection frequency of PFOA, it was not possible to analyse a time trend for this compound. PFHxS was found to decrease in a non-linear way ($p<0.01$; annual change <1.2%). It is worth noting that some of the currently unregulated PFAS compounds show significantly increasing concentrations, i.e. PFDoA and PFTeA.

9.3.4 Toxicological considerations

PFOS toxicity reference values have been developed for bobwhite quail *(Colinus virginianus)* and mallard *(Anas platyrhynchos)* (Newsted et al., 2005). Based on reproductive toxicity, the no observable adverse effect level (NOAEL) of PFOS in mallard egg yolks was 53 µg / ml. For bobwhite quail, a lowest observable effect level (LOAEL) of 62 µg / ml was determined in egg yolk. Following EU technical guidance documents, Newsted et al. (2005) used an assessment factor of 60 to derive predicted no effect concentrations (PNEC) for a generic avian predator from the quail results. Nordén et al. (2013) showed for blue heron eggs that the concentrations in yolk were about 10% higher than concentrations in whole eggs, per gram sample. This would lead to approximate PNEC values in whole eggs of 900 ng / ml. Assuming an egg yolk density of 1 g / ml (Custer et al., 2013), the approximate PNEC in whole eggs would be 900 ng / g, which is not much higher than the maximum value of 714 ng / g in the peregrine falcon eggs (Table 15).

Several studies have addressed effects of PFOS in eggs of leghorn chicken *(Gallus domesticus)*, with the following results: An LOAEL for PFOS in eggs of only 100 ng / g was found above which reduced hatchability was observed (Molina et al., 2006). This PFOS concentration has been exceeded in our study and other studies (Table 16). O'Brien et al. (2009) found an LD_{50} of 93 000 ng / g for the same species. Although not directly comparable to the LOAEL, it suggests lower acute toxicity of PFOS in eggs. No effect on hatching was found at a dose of 5000 ng / g, but developmental effects were observed (Peden-Adams et al., 2009). Indications of developmental effects have also been found for PFUnA (O'Brien et al., 2013).

9.4 Conclusions

PFASs were widely detected in peregrine falcon eggs from South Greenland, with PFOS being the predominant compound. A transition to short-chain compounds and concurrent decrease of PFOS could not be observed in our

study. Long-chain PFCAs increased, while PFSAs other than PFOS showed indications of non-linear decreases. The PFOS concentrations were high in an international context, but comparable to levels found in eggs of blue herons and herring gulls. Toxicological evidence does not exist for PFOS in peregrine falcon eggs and appears inconclusive in other species. However, developmental and reproduction effects have been observed in some species at the levels found in our study. The fact that PFASs add to very high concentrations of organochlorines and other persistent organic pollutants in peregrine falcon eggs, has not yet been addressed from a toxicological point of view.

10 Eggshell thickness

10.1 Introduction

Ever since it was first shown that DDT caused eggshell thinning and breeding failure in wild peregrine falcon populations (Ratcliffe, 1967) the effects of POPs on the eggshell thickness and breeding success in high-trophic level birds have been widely documented. Especially DDT and its degradation products have been identified as a key group of POPs responsible for the widespread reduction in breeding success and subsequent population decline in the peregrine falcon (Hickey, 1969; Newton, 1979; Cade et al., 1988).

The Greenland peregrine falcon population has been the subject of long-term studies as described in chapter 3. Autumn migration counts in the eastern US, where peregrines from Greenland and the eastern Canada mix during the migration, suggest an increase in Arctic populations (Titus and Fuller, 1990). It is thus to be expected that a population of Arctic peregrines possibly recovering from the effects of POP-exposure will show an increase in eggshell thickness over time.

Eggshell thickness analyses have often relied on measurements of whole dead eggs, which, however, i) are relatively rare occurrences, ii) are not present in the most successful nests (all eggs hatch), and iii) may potentially be biased since very thin-shelled eggs might break (Odsjö and Sondell, 1982). By using eggshell fragments from all nests, a more representative and comprehensive survey of the wild population can be obtained. Based on the intra- and inter-clutch variation in shell thickness, Falk and Møller (1990) recommended that studies of eggshell thinning should include fragments from as many nests as possible.

Studies of Arctic peregrine falcon populations have shown that thinning in recent eggs is less severe than in older samples (Ambrose et al., 2000; Johnstone et al., 1996). In a previous study we found a significant increase over time in thickness of eggshell fragments from peregrines in West and South Greenland (1972-2003, 13.9% thinning decreasing to 7.8% thinning, compared to the mean value prior to introduction of DDT in the environment) (Falk and Møller, 1990). A similar significant increase in thickness could not be detected in whole eggs from the same population (Falk et al., 2006). Outside the Arctic only one study has shown similar results in peregrine falcons: Eggshells from Germany (both former East and West) reached normal pre-DDT thickness around 2002 after a reduction of up to 28% in 1970-71 with extreme cases of eggs completely lacking shell (Wegner et al., 2005). In addition, long term trends in Swedish ospreys (*Pandion haliaetus*) showed that it took 30 years after the DDT ban until eggshell thickness was completely recovered (Odsjö and Sondell, 2014).

10.2 Samples

The study combines samples from two study areas: South Greenland (samples from 1981-2014), and West Greenland (samples from 1972-1988). Eggshell thickness measurements for 1972-2003 have previously been analysed (Falk et al., 2006) but here the time series is extended to 2014 and all data re-analysed based on the statistical procedures applied in the AMAP Core Programme (chapter 4).

In both survey areas, active nests were visited at least once post-hatching and, when conditions allowed, the nest scrape carefully searched for eggshell fragments deriving from the hatched eggs. In addition, the whole dead eggs analysed for contaminants were included in this analysis of eggshell thickness. Finally, egg clutches collected from Greenland peregrines between 1881 and 1930 are stored at the Zoological Museum, University of Copenhagen, and provide the reference material for comparison with the recent samples (Falk and Møller, 1990), so the total samples available covers a 133 year time span.

10.3 Measurements and statistical analyses

The eggshell thickness was determined for samples from fragments from hatched eggs as well as the sample of whole, addled eggs as follows:

The shell fragments were measured with a computer-connected Mitutoyo Digital Micrometer (type 293-521-30) with a small stainless steel ball glued to the rotating jaw in order to fit the inner curved surface of the eggshell fragments. Each fragment was scrutinised to determine whether any membrane was still adhering to the inner surface. Measurements were performed only on (parts of) fragments without any membrane because on fragments it is difficult to be certain if both membranes (shell and egg membrane) are present. Since eggshell thickness varies within the egg there is a risk that too few samples may bias results. Hence, we included only clutches that provided 20 or more measurable fragments – the same threshold selected by Odsjö and Sondell (1982) in a study of Swedish ospreys – and assumed they represented the thickness of the entire clutch.

Whole, addled eggs were opened in the laboratory and the content removed for the contaminant analyses; the eggs were cut along the equator and the empty half shells washed with water before left to dry for 3 months at room temperature. The half shells were measured along the equator with a modified (adding a small arm to access the holes in the whole eggs) Mitutoyo Micrometer (type 147-301) – the same device used to measure the reference collection of 16 pre-DDT clutches from Greenland stored in the collection at the Zoological Museum, Copenhagen (Falk and Møller, 1990).

There was no significant difference in measurements taken with the two different micrometer tools. Mean shell thickness for fragments from South Greenland and West Greenland did not differ when comparing data from the period during which both types of samples were collected (1981-1989; t-test; df=20,22, p=0.123). Hence, further analyses are based on pooled data samples from the two survey areas. In this analysis, mean shell thickness was estimated for 184 clutches based on at least 20 fragments measured and for 56 whole addled eggs from 44 clutches. From 19 clutches samples of fragments as well as whole eggs were available. Paired t-tests showed no significant difference (t=0.38, p=0.71) between mean shell thickness based on fragments and whole eggs. Therefore, data from fragments and whole eggs were combined. When comparing measurements with and without membranes, a membrane factor of 0.071 mm was applied, based on measurements of neighbouring shell areas with and without membranes.

For the analyses of the temporal trend the mean annual shell thickness was analysed by log-linear regression analysis using the same method as described for the contaminant time trends (Chapter 4).

10.4 Results and discussion

During the period 1972-2014 there was a significant increasing trend in the average eggshell thickness (Figure 19). The slope of the linear regression shows an average increase of 0.25% per year. This would correspond to a change in eggshell thinning from 13.9% in 1972 to 3.4% thinning in 2014 (7.8% in 2003) when compared to pre-DDT eggs collected in Greenland (Falk and Møller, 1990). Shell thickness may continue to increase and level out when "normal", pre-DDT average is reached which, based on the current rate of increase, is predicted to be by 2034 (Figure 19). However, the 95 % confidence limit on the predicted value (red dashed lines) indicates that the year for the eggshell to obtain unaffected thickness can also be later. A few clutches are still below the critical limit today, as indicated by the black line in Figure 19.

The embryo may extract minerals from the eggshell, but studies of the potential effect on the shell thickness have been inconclusive: Some studies showed that while shell density measured as shell index (Ratcliffe, 1967) was affected, the shell thickness *per se* did not change significantly during incubation (Bunck et al., 1985; Bennett, 1995). Other studies of captive peregrine falcons showed a 0.91% to 4.79% – depending on peregrine subspecies – decrease in shell thickness between eggs with undeveloped vs. fully developed embryos (Castilla et al., 2010). Our study included samples from eggs with fully developed embryos, i.e. all the shell fragments from hatched eggs, as well as shells from eggs with no or little embryo development, i.e. the dead / addled whole eggs. We found no difference in mean thickness of whole eggs and fragments from nests where both sample types were available.

In addition, shell thickness varies across different parts of the shell which may bias studies based on small samples or if only certain parts of the eggs, e.g. the butted ends, are measured (Odsjö and Sondell, 1982; Orłowski and Hałupka, 2015). In this study we only took measurements from the equator of whole eggs (= the reference standard from museum collections, and with "average" thickness). The potential bias introduced by those factors might slightly influence the reported *value* of the shell thickness in Greenlandic peregrine falcons - and hence the predicted timing of full recovery in about 20 years from now. But since the same methods have been applied over the entire 42-year time span, the *trend* remains unaffected.

We have found a highly significant long-term gradual increase in the shell thickness over the 42-year survey period. With the average rate of change the eggshell thickness in peregrine falcons from Greenland can be expected to reach pre-DDT-levels by 2034, as described above. In Germany, peregrine shell thinning was back to normal 30 years after the legal ban of DDT in 1972 (Wegner et al., 2005). In Denmark, eggshell samples from the re-established and increasing peregrine population revealed that the pre-DDT level was already reached in 2011 (Falk and Møller, 2010). A long term study of shell thinning in Swedish ospreys showed that it took 30 years to reach full thickness again after the lowest level in 1973 (Odsjö and Sondell, 2014). From the beginning of the decrease it took more than 50 years to reach unaffected conditions (Odsjö and Sondell, 2014). Hence, the much slower recovery of the shell thickness in the Greenland population in this study might be indicative of the slower phasing out of DDT in the Americas (Vorkamp et al., 2009).

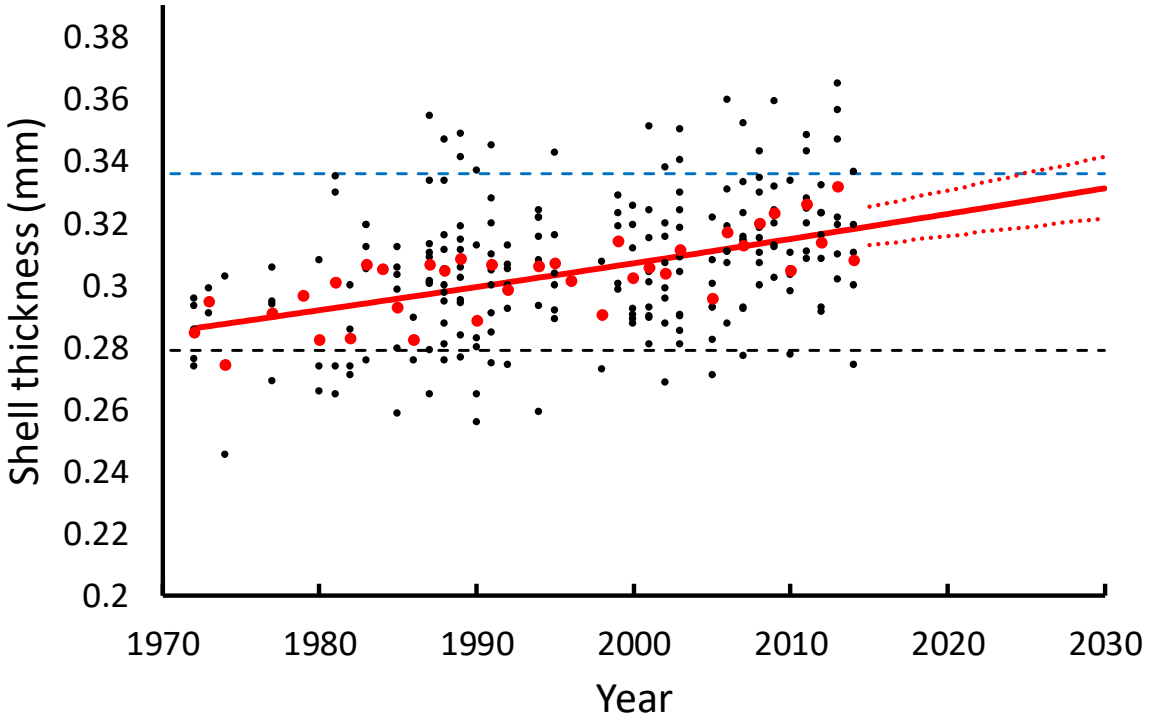


Figure 19. Shell thickness of peregrine falcons eggs from Greenland shown as clutch means (black symbols), annual means (red symbols) and projected trend line (red) with confidence limits (red dashed lines) for projections according to which the mean shell thickness may reach pre-DDT normal thickness by 2034 (0.336 mm, blue line, Falk and Møller 1990; Falk et al. 2006). The black dashed line indicates the empirical "17% threshold" (0.279 mm) associated with population declines across the world (Peakall and Kiff, 1988).

As discussed by Falk et al. (2006) the shell thinning in the Greenlandic population was probably near or below the empirical limit of 17% considered the critical threshold for negative population effects only for a very short time span, if ever (Peakall and Kiff, 1988) - contrary to the breeding populations of the same subspecies in Arctic Canada and Alaska. The large sampling coverage of eggshell fragments - and a long time series - have allowed us to verify that the peregrine falcon population in Greenland is responding to the expected gradually reduced exposure to shell-thinning POPs such as DDT and metabolites. But it also revealed, along with the chemical analyses, that the DDT metabolites were still widespread. The effect of the DDT metabolite exposure in the areas the peregrines "sample" can be monitored by continued low-cost collection of eggshell material in Greenland.

11 Conclusions

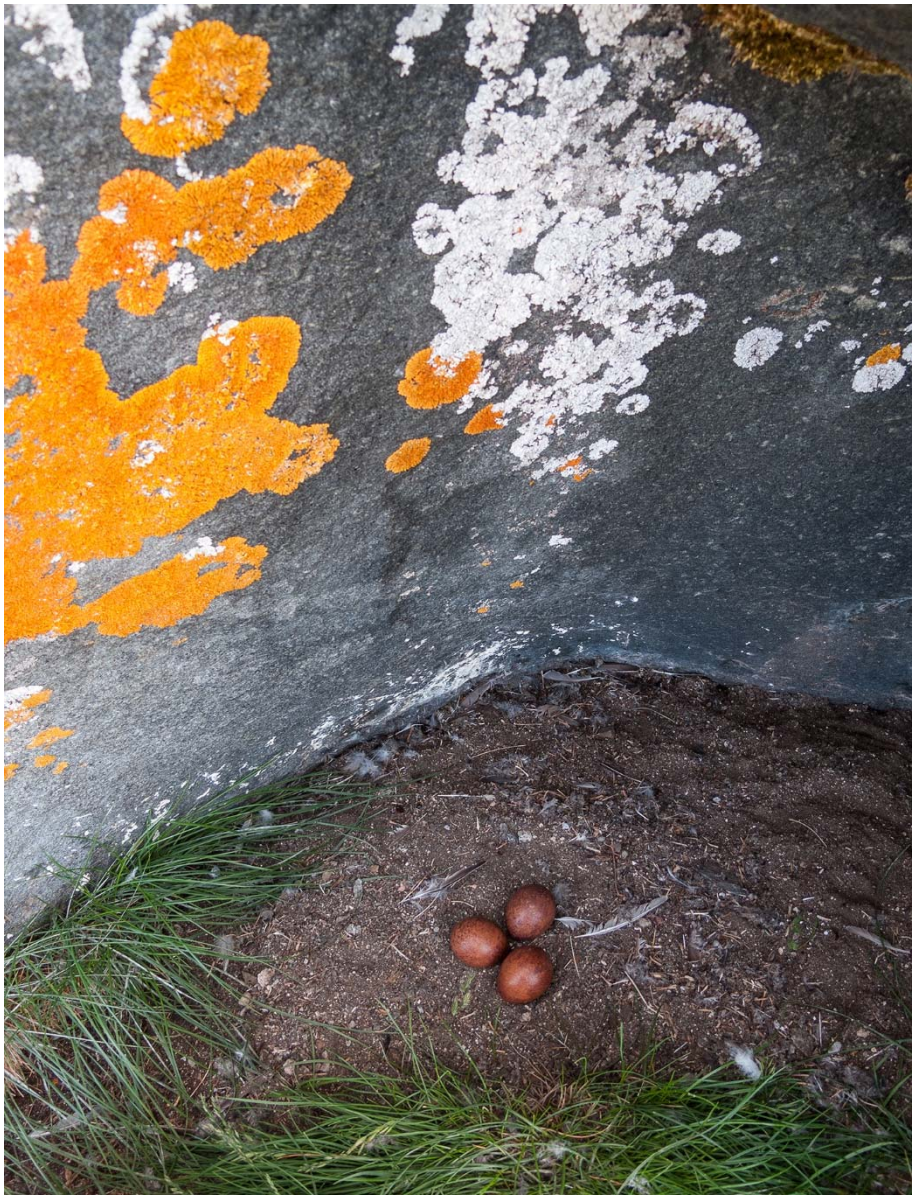
The legacy POPs PCBs and DDT (and its degradation products) still accounted for the highest concentrations measured in peregrine falcon eggs from South Greenland. However, the concentrations were decreasing. They were generally below critical threshold values, but individual eggs stood out with higher concentrations and a potentially smaller (or closed) margin to effect levels. Likewise, other organochlorine pesticides (HCH, HCB, chlordane-related pesticides and toxaphene) had high concentrations in peregrine falcon eggs compared with other wildlife samples from Arctic regions. The trends were generally decreasing as well, with the exception of α-HCH and toxaphene. Both are globally regulated alongside other legacy POPs, and the use history of toxaphene is similar to that of chlordane-related pesticides. For α-HCH, climate effects might favour the volatilization from seawater.

In general, the peregrine falcon eggs showed a larger variation between samples and years than observed in the marine species of the AMAP Core monitoring programme. Most of this variation can likely be attributed to the migration to winter grounds in Central and South America. Although initial tracking data indicate the possibility of one bird returning to the same winter grounds, the population is likely spread over most of the continent, with consequences for their contaminant exposure.

The brominated flame retardants showed a striking contrast of decreasing and increasing time trends for BB-153 and PBDEs, respectively. However, of the PBDE congeners, only BDE-209 increased significantly. This congener was phased out in the USA and Europe later than the lower brominated PBDEs and was only recently included in the Stockholm Convention. HBCDD was mainly present as α-HBCDD, also showing an increasing trend, while other monitoring studies have lately shown stagnation or decreases. Several non-regulated flame retardants could be detected in the peregrine falcon eggs as well, i.e. EH-TBB, BTBPE, DPTE and syn- and anti-dechlorane plus, while DBDPE and BEH-TEBP were undetectable in the majority of the eggs. However, the concentrations were considerably lower than those of PBDEs. The trend of dechlorane plus suggested an increase over time, however, it was not statistically significant. DPTE on the other hand decreased significantly.

For the first time, polychlorinated naphthalenes were determined in peregrine falcon eggs. Their concentrations appeared relatively high compared to literature data. However, similarly to other legacy POPs, most congeners decreased over the study period. In the PFAS group, PFOS is still the dominating compound and did not show any time trend over the study period, although it has generally been found to decrease in monitoring studies. Long-chain perfluorinated carboxylic acids (PFCAs) increased, while perfluorohexane sulfonate (PFHxS) and perfluoroheptane sulfonate (PFHpS) decreased. The potential replacement product PFBS was generally below detection limits. With these exceptions, nearly all compounds newly analysed in the peregrine falcon eggs from South Greenland were present at relatively high concentrations compared with other wildlife studies. They all add to the total contaminant burden in the peregrines, with the potential implication of mixture effects. As mentioned above, individual birds also appear to be exposed to a much higher degree than average, for one or few compounds.

Measurements of the eggshell thickness showed increases towards the pre-DDT level. Based on extrapolations, this will be reached in 2034. While some European populations already have pre-DDT eggshell thicknesses, the Greenland population recovers more slowly, possibly reflecting a slower phase-out of DDT in the winter grounds of the peregrine falcons. In the last few years, breeding success of the peregrine falcon in Greenland has been low. Climate factors might play a role, but the reasons are still largely unknown.



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NEW AND UPDATED TIME TRENDS OF PERSISTENT ORGANIC POLLUTANTS AND THEIR EFFECTS ON EGGS OF PEREGRINE FALCONS *(FALCO PEREGRINUS)* FROM SOUTH GREENLAND

Peregrine falcons *(Falco peregrinus)* accumulate persistent organic pollutants (POPs) to high concentrations. DDT and its metabolites caused severe effects on reproduction and population survival in the past. In this study, we addressed the following organic pollutants in eggs of peregrine falcons from South Greenland: Polychlorinated biphenyls (PCBs), DDT and its metabolites, hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), chlordane-related pesticides, toxaphene, polychlorinated naphthalenes (PCNs), several groups of brominated flame retardants (polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), hexabromobiphenyl (BB) 153, "novel" flame retardants), dechlorane plus and perfluorinated alkylated substances (PFASs). The concentrations were generally high in a bioaccumulation context, i.e. in the µg/g range for the organochlorine POPs. Some eggs reached critical levels for DDE, but those were generally eggs from the 1980s. Time trend analyses covering the period 1986-2014 showed decreasing concentrations for the organochlorine POPs, including PCNs, with the exception of α- HCH and toxaphene. BB-153 and some perfluoroalkyl sulfonates (PFSAs) decreased as well, while significant increases were found for BDE-209 and some of the longchain perfluoroalkyl carboxylic acids (PFCAs). The "novel" flame retardants were detectable in the peregrine falcon eggs, but concentrations were comparably low (i.e. < 5 ng/g lipid weight) and only seemed to increase for dechlorane plus. The eggshell thickness increased significantly over the study period and was predicted to reach the pre-DDT level by 2034. However, breeding success of the South Greenland peregrine population has lately been low, possibly related to climate factors.

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