



Concentrations of organohalogen compounds in the West-Nordic compared to the Baltic Region

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Preface

The project “A comparative assessment of persistent organic pollutants and their metabolites, with emphasis on non-traditional contaminants, in the West-Nordic and the Baltic Proper environments (CAPNE)” was funded by the Nordic Council of Ministers in the years 2004 to 2006. The aim was to analyse environmental pollution in guillemot (*Uria aalge*) eggs from the West-Nordic and compare to the Baltic Region to estimate the pollution burden in the biota.

This project included partners from Iceland, the Faroe Islands, Norway and Sweden with collaboration with a Canadian partner. During this project a strong co-operation between the different partners was successfully achieved, resulting in two manuscripts under preparation two posters on international conferences. Two PhD-students have been involved in and funded by the project. The project was in collaboration with the Sea and air quality group (Hav och luft gruppen) and the Environment monitoring and data group (Miljö och data gruppen).

Summary

The aim of the present project was to estimate the burden of organohalogen pollutants in biota from the West-Nordic and compare it to the Baltic Region. Guillemot (*Uria aalge*) egg was used as a biomarker due to the good experience of using this matrix for environmental monitoring.

The chemical analytical method used for chlorinated and brominated compounds was based on a modified extraction method with well documented clean-up steps. The method was further developed resulting in high efficiency, highly purified samples and good recovery. Analytes were then analysed with either gas chromatography equipped with an electron capture detector (GC/ECD) or a gas chromatography with a mass spectrometry (GC/MS). Perfluorinated compounds were analysed with a new and simple extraction method only applying methanol. The compounds were then analysed by liquid chromatography linked to a triple quadrupole mass spectrometer (LC/MS/MS).

High levels of most chlorinated pollutants were found in the Baltic region where the major distribution pattern showed a 5–20 times higher concentrations of chlorinated compounds compared to locations in the West-Nordic, Norway, the Faroe Islands and Iceland. The exception was HCB, showing a more equal distribution between all sampling locations. Another exception is the bis(4-chlorophenyl)sulfone (BCPS) with high levels in samples from the Baltic Region compared to almost non-detectable levels found in samples from the West-Nordic region.

The polybrominated diphenylethers (PBDEs) showed only a slightly different distribution pattern between the Baltic and the West-Nordic guillemot eggs, whereas the hexabromocyclododecane (HBCDD) is similar to the chlorinated compounds with major differences between the Baltic proper and West-Nordic locations. Methoxylated PBDEs, which mainly are considered to be naturally produced, were only detected in samples from the Baltic Region.

Perfluorinated compounds (PFCs) have a distribution pattern completely different from both chlorinated and brominated compounds and without any obvious relations within the group of perfluorinated compounds. Different groups, carboxyl acids, sulfonates and sulfoneamides, have different distribution pattern making it difficult to explain sources and emission.

Two major questions need to be answered after this study; why is the HCB and PBDE distribution different from the other chlorinated or brominated compounds and which are the main sources and distribution routes of perfluorinated compounds. We would recommend further studies, addressing these questions in the West-Nordic.

1. Introduction

1.1 Background

Iceland is a volcanic island in the North Atlantic, located between Greenland and Norway. With approximately 300 000 inhabitants, the magnitude of industry is not large compared to other European countries but there are some heavy industrial activities, e.g. aluminium production and iron smelters. The Faroe Islands are located north of the UK, a cluster of 18 islands with a population of approximately 48 000 inhabitants and with no major industrial activity. Norway is a part of the European mainland. Still, in the outskirts of the main-land, the population density is quite low, with some heavy industry but compared to the Baltic Region and central Europe, Norway might be considered remote. The use of pesticides in these areas has been very limited. The origins of most organo-halogen compounds found in the biota are therefore most likely due to long-range air stream and wind or sea current transport (Law *et al.*, 2003; Olafsdottir *et al.*, 2005; Vorkamp *et al.*, 2004a; Vorkamp *et al.*, 2004b; Wania, 2003). Both Iceland and the Faroe Islands shore lines are considered remote locations for environmental contamination (AMAP, 2002). In the East-Nordic several countries have Baltic Sea costal lines, which therefore receive large quantities of river water from areas with heavy industrial activities. The concentration of persistent organic pollution is considerably high in biota from the Baltic and it is therefore amongst the most investigated areas in the world concerning environmental contaminants in general, in particular polychlorinated biphenyls (PCBs), 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (p,p'-DDT) and related compounds (Bignert *et al.*, 1995; Burreau *et al.*, 2004; Jörundsdottir *et al.*, 2006; Roots, 1995; Roots and Zitko, 2001).



Figure 1. Guillemot (*Uria aalge*)

1.7 Guillemot as a monitoring matrix

Guillemots nesting in Iceland seem to be located in Icelandic waters all year around (Garðarsson, 1999). There they feed mostly on herring (*Clupea harengus*) and capelin (*Mallotus villosus*). The Baltic guillemot feeds mostly on herring and sprat (*Sprattus sprattus*) and is one of the few fish-eating birds that stay in the Baltic region all year. They nest in a few remote colonies, which is advantageous because it makes the individual population very homogenous with regard to variation of contaminant concentrations. Baltic guillemot eggs have been used as a monitoring matrix in the Baltic Region for the last 30 years. They are considered well suited for contaminant monitoring (Bignert *et al.*, 1995; Olsson and Reutergårdh, 1986). Normally one egg is laid per nest (no within breed variation of contaminants) but a lost egg can be replaced about 15 days later (Hedgren, 1980) and the concentrations of contaminants are known to be significantly higher in the replacement egg (Bignert *et al.*, 1995).

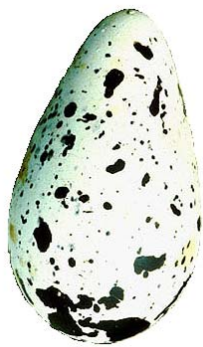


Figure 2. Guillemot egg

1.3 Organochlorine pesticides

Dichlorodiphenyltrichloethane (DDT) is an insecticide that has been used since the 1930s. When DDT is discussed it is in general the *p,p'*-DDT isomer that is discussed even though as much as 20% *o,p'*-DDT may be present as a by-product in technical DDT. DDT was banned in most western European countries during the seventies but worldwide, DDT is still used in areas where malaria is a health problem. DDT is transformed mainly to DDE but under reductive conditions also to DDD. Today DDE is the main environmental contaminant in biological samples. Due to the high biomagnification potential of DDE, it is now the most ubiquitous environmental contaminant known. DDE has shown a strong decreasing temporal trend over the last 30 years in the Baltic Region (Bignert *et al.*, 1995; Jörundsdóttir *et al.*, 2006). DDE has been linked to shell-density reduction with birds of prey, as white-tailed sea eagle (Helander, 1982) and has shown to have e.g. endocrine-related and neurodevelopmental effects (Eriksson, 1998). DDE can be further metabolised to both hydroxylated and methylsulfonyl substituted DDE (Jensen and Jansson, 1976; Metcalf, 1973).

Hexachlorbenzene (HCB) has been used as a fungicide and is the chemical that caused the tragic intoxication of approximately 5000 people and several deaths in Turkey in the 1950s (Morris and Cabral, 1986).

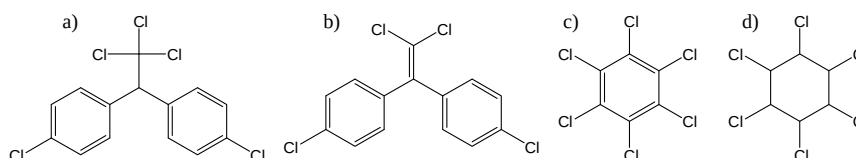


Figure 3. Chemical structure of a) *p,p'*-DDT, b) *p,p'*-DDE, c) HCB and d) HCH.

HCB is also a by-product in many chemical procedures such as in electrolytic production of magnesium (WHO, 1997) and in energy production from fossil fuel when performed at too low temperatures.

Hexachlorocyclohexane (HCH) exists in six isomeric forms, though only three of them are of environmental concern, α -, β - and γ -HCH. γ -HCH is the active isomer also known as the insecticide lindane. The technical products consists of about 55-70% of α -HCH, 5-14% of γ -HCH and 10-18% of other isomers (Barrie *et al.*, 1992). β -HCH has the highest biomagnification factor and is the isomer usually found in the highest concentration of the HCH isomers (Manuscript I, Jörundsdóttir *et al.*, 2006; Valters, 2001).

1.4 PCB and PCB metabolites

Concentrations, spatial and temporal trends of organohalogen compounds like PCBs have been documented worldwide and particularly well in the Nordic region (Bignert *et al.*, 1998; Jörundsdottir *et al.*, 2006). The PCBs were introduced on the market 1929 and soon thereafter technical PCB consisted of a large number of brands. Each of the PCB products was mixtures of some 50 to 100 homologous and isomers (congeners) among which several have proven to be very persistent and very bioaccumulative. PCB congeners are all highly hydrophobic but differently stable. Due to their lipophilicity, they need to be metabolised prior to excretion; metabolism leading to increased water solubility. Known metabolic products contain either a hydroxyl (OH-) or methylsulfonyl (MeSO₂-) group.

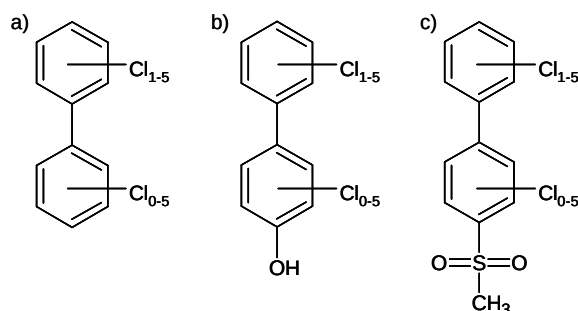


Figure 4. General chemical structures of a) PCBs, b) OH-PCBs and c) MeSO₂-PCBs

Methylsulfonyl-PCBs (MeSO₂-PCBs) and 2-(3-methyl-sulfonyl-4-chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloro ethene (3-MeSO₂-DDE) were first identified in Baltic grey seal (*Halichoerus grypus*) blubber (Jensen and Jansson, 1976). Since then, high levels of MeSO₂-PCBs have been found in e.g. marine mammals from the Baltic (Bergman *et al.*, 1994b; Haraguchi *et al.*, 1992; Larsson *et al.*, 2004) and even in humans but then at rather low concentrations (Hovander *et al.*, 2006; Meironyté Guvenius *et al.*, 2002). MeSO₂-PCBs and -DDE are only slightly less lipophilic than their parent compounds. They are distributed to lipid rich tissues, but show an affinity to liver and lung tissue due to specific protein binding properties (Larsen *et al.*, 1991; Lund *et al.*, 1985). The *meta*- and *para*-MeSO₂-PCB metabolites are formed from about 15 different PCB congeners (Letcher *et al.*, 2000). MeSO₂-PCBs and are amongst the most abundant anthropogenic compounds found in biota.

OH-PCBs were identified in experimental animals in the early 1970's (Sundström and Wachtmeister, 1975; Sundström and Jansson, 1975) and later in excreta from Baltic Sea grey seal and guillemot (Jansson *et al.*, 1975). Due to the hydroxyl group, they are both ionisable and more hydrophilic and in general conjugated in biota to promote excretion. The OH-PCBs are mostly found in blood or blood rich tissues (Bergman *et al.*, 1994a) where they can bind to transport proteins (Brouwer *et al.*,

1998). Several reports are published concerning levels and trends of MeSO₂-PCBs, -DDE and OH-PCBs both in wildlife (Jörundsdóttir *et al.*, 2006; Norström *et al.*, 2006) and humans (Hovander, 2006).

1.5 Bis(4-chlorophenyl)sulfone (BCPS)

Bis(4-chlorophenyl) sulfone (BCPS) is a compound first identified in perch (*Perca fluviatilis*) from the Gulf of Riga in 1995 (Olsson and Bergman, 1995). Since then it has been reported in several other species, both birds and fish (Norström *et al.*, 2004) and recently a temporal trend of BCPS over the last 30 years has been determined in guillemot egg from the Baltic proper island, Stora Karlsö (Jörundsdóttir *et al.*, 2006).

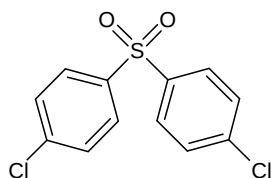


Figure 5. Chemical structure of bis (4-chlorophenyl)sulfone (BCPS)

Particularly high levels of BCPS were found in muscle tissue from guillemot sampled at Stora Karlsö where the concentrations were in the low ppm range (Norström *et al.*, 2004), but up till now the occurrence of BCPS in Atlantic guillemot is unknown.

BCPS is a commercial chemical used as a monomer in the production of thermostable polymers, such as Polysulfones and Polyether sulfones (Kwiatkowski *et al.*, 1974; Mark *et al.*, 1988). In the U.S., it is classified as a high production volume chemical with an annual production of up to 10.000 tons (Chhabra *et al.*, 2001). BCPS has a specific and high accumulation in grey seal liver tissue (Larsson *et al.*, 2004).

1.6 Polybrominated compounds

Polybrominated diphenyl ethers (PBDEs) are used as additive flame retardants in products like electrics, plastics and paint. They have been produced since the 1970's and are still used in increasingly larger quantities. Commercially there are three different products of PBDEs known as PentaBDE, OctaBDE and DecaBDE among which the first two were banned with in the European Union 2004 (Cox and Efthymiou, 2003). PBDEs were first detected in biota in 1981, in pike from Sweden (Andersson and Blomkvist, 1981) and they have thereafter proved to be

ubiquitous environmental contaminants (Birnbaum and Staskal, 2004; Hites, 2004; McDonald, 2002). Particularly high concentrations have been reported from human blood, milk and adipose tissue from North America (Mazdai *et al.*, 2003; Schechter *et al.*, 2003; Sjödin *et al.*, 2004). The dominating congener in the environment and in humans have been the 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) but also other congeners may be abundant nowadays.

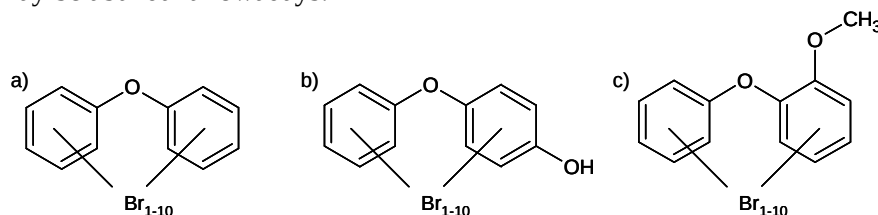


Figure 6. General chemical structure of a) PBDEs, b) OH-PBDEs and c) MeO-PBDEs

PBDEs are metabolised after entering an organism leading to the formation of hydroxylated PBDEs (OH-PBDE) as observed in experimental animals dosed with PBDEs (Malmberg *et al.*, 2005). As for the OH-PCBs, some OH-PBDEs are retained in the blood due to the structure of the OH-PBDEs. Hydroxylated and methoxylated PBDEs (MeO-PBDEs) have also been found as natural products in sponges and algae (Marsh, 2003) but there is no known natural source of PBDEs. PBDEs found in biota are therefore all anthropogenic. Concentrations of PBDEs in biota from the Baltic region are fairly well documented (Asplund *et al.*, 1999; Asplund *et al.*, 2004; Burreau *et al.*, 2004; Haglund *et al.*, 1997) where the knowledge of PBDE concentrations from the Faroe Islands and Iceland is limited (Fängström *et al.*, 2005a).

Hexabromocyclododecane (HBCDD) is another brominated flame retardant also used as an additive. The commercial product of HBCDD is a mixture of sixteen stereoisomers where the α -, β - and γ -HBCDD are the major isomers but with γ -HBCDD as the most abundant (>70%) (Tomy *et al.*, 2004a). Even if the HBCDDs are a mixture of isomers, these compounds will be referred to as HBCDD (single) and the concentration presented here is the sum concentration of all isomers.

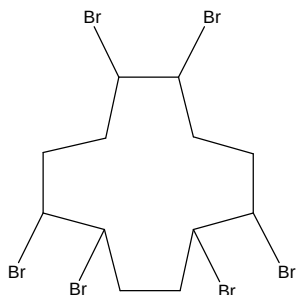


Figure 7. Chemical structure of hexabromocyclododecane (HBCDD)

HBCDD is mainly used in polystyrene foam and textiles for thermal insulation in buildings, packing materials and furniture upholstery (BSEF, 2003). HBCDD has been reported in different biological samples like fish, birds and mammals (Tomy *et al.*, 2004b; Janak *et al.*, 2005; Zegers *et al.*, 2005; Muir *et al.*, 2006) but also in sediment, sewage sludge and air samples (Eljarrat and Barcelo, 2004; Davis *et al.*, 2005). The uses of flame retardants have increased over time and temporal trend studies have showed an increasing trend of HBCDD in the Baltic Sea (Sellström *et al.*, 2003). Toxicological data are still sparse regarding HBCDD, but researches have indicated it as an endocrine disruptor. It is influencing the thyroid homeostasis and might amongst other be a peroxisome proliferator in rainbow trout (Ronisz *et al.*, 2004).

1.7 Polyfluorinated compounds

Polyfluorinated alkyl substances (PFAS) have been industrially produced for the last 50 years. Their unique anionic properties make them highly suitable for many commercial and industrial processes. PFAS are both lipophobic and hydrophobic and have strong surface-active properties and are therefore used as stain and water repellents for surface treatment of textiles, carpets, leather and paper products. PFAS are also used in fire-fighting foams and in chromium-plating industry (Key *et al.*, 1997).

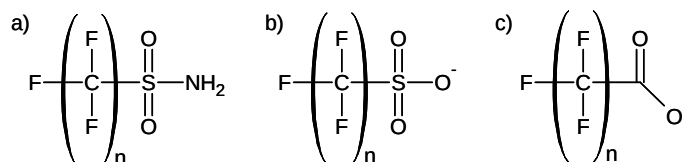


Figure 8. Chemical structures of a) perfluorinated sulfonamides, b) perfluorinated sulfonates and c) perfluorinated carboxylates.

PFAS consist of a variety of substances, most frequently studied is the perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). PFOS was first reported in wildlife in 2001 (Giesy and Kannan, 2001; Kannan *et al.*, 2001) and is one of the most commonly found PFAS in the environment even though it was withdrawn voluntarily by 3M from the US market in 2000. Still, telomer-based PFCs are marketed, which can degrade to PFOA (Dinglasan *et al.*, 2004). PFAS are globally distributed and PFOS and PFOA have been detected in both surface and ground water (Sinclair *et al.*, 2006), in wildlife (Bossi *et al.*, 2005; Giesy and Kannan, 2001; Holmström *et al.*, 2005; Kannan *et al.*, 2002) and in humans (Calafat *et al.*, 2006; Kannan *et al.*, 2003) worldwide. The levels of several PFCs are high in human blood. The more volatile perfluorooctane sulfonamide (PFOSA) has also been detected in air samples from Canada (Kubwabo *et al.*, 2005). Recently, a time trend for over 30 years of PFOS

in guillemot eggs from the Baltic Sea has been reported by Holmström *et al.* 2005 (Holmström *et al.*, 2005).

2. Aims and approach

The main objective of the project is to assess the environmental pollution situation in West-Nordic and Baltic Sea marine waters based on analysis of the biomarker bird species, guillemot (*Uria aalge*; lommevi, lomvi(e), sillgrissla, langvía), to apply the results in assessing the environmental quality in a geographical area where such data are limited, around Iceland and the Faeroe Islands. The data generated are aimed to serve as part of the hazard identification for persistent organic pollutants and their metabolites in the West-Nordic and South Baltic regions.

The more specific project aims were:

- to assess the load of organohalogen pollutants and/or their metabolites in guillemot, biomarker species for monitoring of POPs,
- to compare the levels of organohalogen contaminants in guillemot eggs in Iceland, the Faeroe Island and Stora Karlsö (the Baltic Sea), with Norwegian sampling sites added during the progress of CAPNE,
- to particularly improve the knowledge of non-traditional organohalogen pollutants and to relate their concentrations to selected, traditional contaminants,
- to provide data for further modelling transport of POPs to the remote West-Nordic areas,
- to improve understanding of the pathways of POPs into humans living in sub-arctic areas, and,
- to improve the Nordic competence in environmental science and to support mobility.

The project has a strong link to the Nordic Environmental Action plan, i.e. the Action area of the Ocean. There it is aimed at reducing xenobiotic substances to levels close to zero within one generation (25 years). This study reveals the present situation of many xenobiotics in the West Nordic and allows for a long term comparison. The project has also strong links with the Health action area. The project provides information on health risks due to feeding on eggs, which may have high levels of contaminants. The project links also to chapter 6.4 in the preliminary version of the Nordic Strategy for Sustainable Development (Mål och insatser 2005 – 2008), where it is seen as especially important issue to map new problems concerned with pollutants (kartläggning av nya föroreningsproblem). The project deals specifically with poorly known pollutants.

3. Results

All results acquired in this study are presented in this section. More detailed presentation and discussion are given in the manuscripts in preparation (Manuscripts I and II). For the analysis of chlorinated and brominated compounds, samples from Iceland, The Faroe Islands, three locations in Norway and one location in Sweden were analysed. Perfluorinated compounds were also analysed in these samples except for one location in Norway.

3.1 Analytical method for chlorinated and brominated compounds

The overall method applied in this project was both efficient and gave good recoveries. The extraction method used is described by Jensen *et al.*

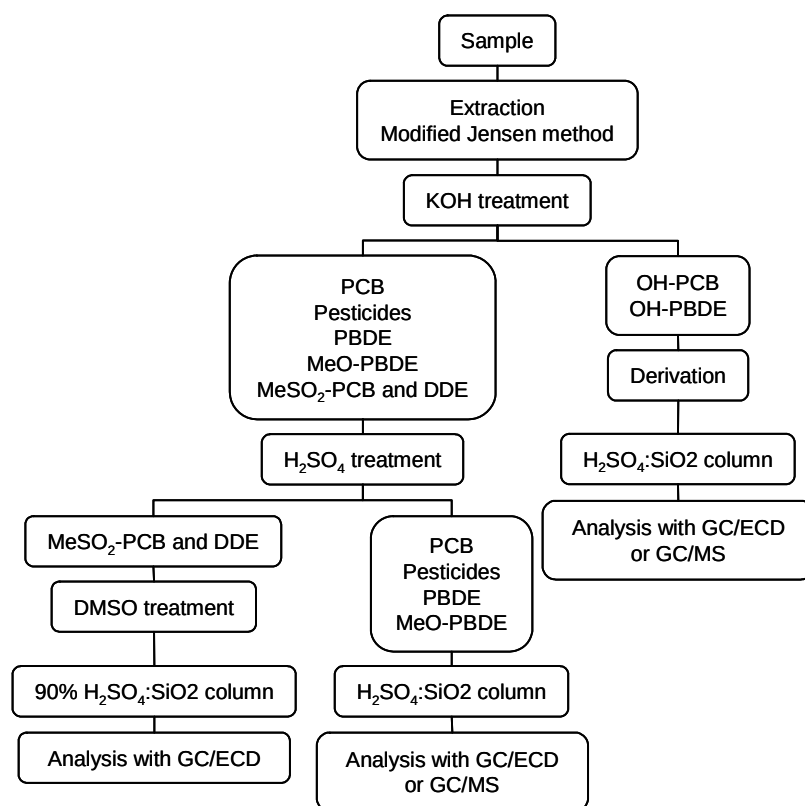


Figure 9. Analytical scheme for chlorinated and brominated compounds in guillemot eggs.

2003 (Jensen *et al.*, 2003) but due to the small sample sizes the solvent volumes were scaled down to 1/10 of the original method and the extractions were performed in test tubes. The lipids were determined gravimetrically. The samples extracted, cleaned up and analysed according to the general scheme shown in Figure 9.

Analysis and quantification of PCBs, DDTs, OH-PCBs, MeSO₂-PCBs, MeSO₂-DDEs and BCPS were performed by gas chromatography with electron capture detection (GC/ECD). Detailed description of the quantification is given elsewhere (Manuscript I).

Analysis and quantifications of PBDEs, OH-PBDEs and MeO-PBDEs were performed by GC linked to a massspectrometer. The details of the procedure are given by Jörundsdóttir *et al.* in a separate paper (Manuscript I). The PBDE and MeO-PBDE congeners were analysed with selected ion monitoring (SIM) by scanning for the negative bromide ions, m/z 79 and 81 (Buser, 1986).

3.2 Analytical method for polyfluorinated compounds (PFCs)

The extractions were performed according to Tomy *et al.* (Tomy *et al.*, 2006) of 0.1 g of a sample homogenate placed in a polypropylene tube and a ¹³C-labelled surrogate standard mixture was added. Extraction was carried out with methanol. The test tube was vortexed and centrifuged for 5 minutes. The extraction was repeated twice and all methanol supernatants were combined. The extract was reduced to 0.5 ml, transferred to a microcentrifuge vial and ultracentrifuged at 13.500 rpm for 15 minutes. The methanol extract was transferred to a HPLC injection vial and the instrument performance standard was added. Before LC-injection the samples were spiked with a mass labelled instrument performance standard mixture.

Analysis and quantification of PFCs were performed by liquid chromatography on line with a triple quadrupol mass spectrometer (LC/MS/MS). The detail of the procedure is given elsewhere (Manuscript II).

3.3 Samples and locations

Guillemot egg samples were collected from six locations, one in Iceland, the Faroe Islands and Sweden and three locations in Norway. The locations in Iceland, the Faroe Islands and Sweden were selected to give an east-west gradient while the locations in Norway were selected to give a north-south gradient. Eggs from Iceland were collected from the island Vestmannaeyjar, located out side of the southern coast. Eggs from the

Faroe Islands were collected from the island Sandøy, which is one of the southern islands in the island group which the Faroe Islands consist of. In Norway, eggs were collected from Bjørnøya which forms the most southern part of Svalbard, Hjelmsøya, in the northern parts of Norway and from Sklinna, a small island outside of the central Norweigan coast. The Swedish eggs were collected in the island Stora Karlsö, located outside the Swedis east coast in the Baltic Sea.

All the eggs were blown out, the content homogenised and then frozen. This was done at the Swedish Museum of Natural History, Stockholm.

3.4 Quality control

A pilot study was performed to estimate the concentration of organohalogen contaminants to determine which surrogate standard would be most suitable and so that the concentration of the surrogate standard would be similar to the analytes. A pilot study was also carried out with LC/MS/MS to make sure the isomeric pattern of HBCDD did not change in the GC/MS analysis applied.

Blank solvent samples were extracted and analysed simultaneously to the guillemot samples to verify that no external contamination was present. Also a homogenate sample was analysed simultaneously several times to determine the variation of the procedure. Volumetric standard was added just prior to analysis to calculate the recovery of the surrogate standards.

3.5 Recovery experiment

To ensure the method quality for assessment of the polychlorinated and polybrominated analytes, a recovery study was carried out. The method variability was also checked. Five groups, containing five samples from a homogenate were prepared from hen eggs (*Gallus domesticus*), one group analysed to visualize the blank pattern and concentrations. One group was spiked with contaminants prior to extraction, to calculate yields, and the other group was spiked just prior to GC-analysis and therefore assumed to be 100%. Both these groups were fortified at high concentrations of the analytes while another two groups were fortified at low concentrations. The latter two groups were prepared as described for the former two groups.

The results of the study including analytes, added amount to each sample and yields with coefficient of variation (C.V.) are shown in Table 1. CB-189 was used as a volumetric standard to quantify PCBs and pesticides and CB-207 was used as a volumetric standard to quantify hydroxy-

lated compounds and sulfone containing compounds. The method used in this study divides the analytes into three fractions, the first fraction containing the pesticides, PCBs, DDE, HBCDDs, PBDEs and MeO-PBDEs, the second fraction containing hydroxylated metabolites of PCBs and PBDEs, and the third fraction containing sulfone containing compounds, i.e. methyl sulfonyl metabolites of PCBs and p,p'-DDE, and BCPS. The recovery of the analytes are presented in Table 1. In summary, all compounds tested showed a recovery of 70% or higher, except for α -HCH and HBCDD with a recovery of 46% and 58%, respectively, for low dose and 51% for α -HCH high dose. The lower dose gave over all lower recoveries, 46-97%, than the high dose, 51-104%, and in general, compounds containing a sulfonyl group show the lowest recovery.

Table 1. Substances, amount of each of them and their yields introduced in recovery study, n = 5 in all groups. C.V. is the coefficient of variation.

	High concentration:			Low concentration:		
	Dose ng/sample	Recovery %	C.V. %	Dose ng/sample	Recovery %	C.V. %
PCBs and pesticides:						
α -HCH	200	51	6.1	3	46	7.2
CB-53	200	82	3.3	3	74	5.0
3,3'-DDE	600	93	1.9	30	86	4.5
CB-153	200	95	4.0	3	79	3.7
CB-200	200	98	4.7	3	79	4.0
Sulfones:						
BCPS	10	80	5.9	0.5	69	7.4
Trifon	10	85	2.4	0.5	74	6.7
4-MeSO ₂ -CB101	10	87	7.6	0.5	76	7.7
3-MeSO ₂ -DDE	10	89	10	0.5	73	8.6
MSF-IS	10	89	6.9	0.5	85	6.0
Hydroxy-PCBs:						
4-OH-CB146	10	97	9.3	0.1	79	9.4
4-OH-CB187	10	95	9.9	0.1	96	8.2
4-OH-CB193	10	104	20	0.1	97	9.1
Brominated compounds:						
BDE-77				3	75	4.4
HBCD				3	58	6.9

3.6 Chlorinated compounds

Concentrations of polychlorinated compounds in guillemot egg from the sampling locations in the Faroe Islands, Iceland and the Baltic proper are presented in Table 2.

Concentrations of PCBs and DDTs are consistent to what is presented in previous studies from the North-Atlantic and the Baltic regions (Bignert *et al.*, 1998; Jörundsdottir *et al.*, 2006; Riget *et al.*, 2003; Vorkamp *et al.*, 2004a). This can be used to verify the results presented in the present study. Concentrations of CB-153 and CB-101 are presented in Table 2 where CB-153 is used as a marker for total PCB concentration.

CB-101 is also presented being a less persistent PCB congener. p,p'-DDE is then used to present the total DDT concentration. The concentrations of these pollutants are an order of magnitude higher in samples from the Baltic region compared to the North-Atlantic. The use of DDT and PCB has been very limited in Iceland and the Faroe Islands (Olafsdottir *et al.*, 2005). Accordingly, long range transport is a likely explanation for the contamination found in these locations.

Table 2. Mean concentrations (ng/g l.w.) with ranges in the parenthesis of chlorinated substances analysed in the guillemot (*Uria aalge*) eggs from Iceland, the Faroe Islands, Norway and Sweden are presented. Statistical difference between locations is indicated.

	Vestmanna- eyjar	Sandøy	Bjørnøya	Hjelmsøya	Skinna	Stora Karlsö
	Iceland	Faroe Islands	Norway	Norway	Norway	Sweden
n	10	10	10	10	10	10
Sampling year	2002	2003	2005	2005	2005	2003
Lipids (%)	13	12	12	13	15	14
HCB	310 (250 - 360)	270 (160 - 330)	260 (210 - 320)	340 (260 - 400)	330 (250 - 440)	390 (310 - 520)
β-HCH ¹	12 (n.d. - 24)	8.3 (n.d. - 18)	11 (n.d. - 18)	13 (n.d. - 25)	12 (n.d. - 22)	270 (190 - 410)
p,p'-DDE	1800 (1400 - 2230)	1100 (710 - 1800)	1200 (830 - 1700)	1100 (870 - 1600)	1200 (650 - 1900)	17 000 (13 800 - 21 900)
CB-153	400 (180 - 750)	260 (180 - 340)	300 (200 - 430)	380 (210 - 680)	310 (180 - 490)	2500 (1900 - 3800)
3-OH-CB153	9.0 (4.60 - 16)	8.2 (3.5 - 16)	7.5 (4.0 - 14)	7.4 (3.2 - 13)	11 (5.7 - 18)	90 (53 - 170)
3'-OH-CB138	2.3 (1.1 - 4.0)	2.4 (1.0 - 4.8)	2.1 (1.3 - 3.2)	2.1 (0.8 - 3.8)	3.1 (1.8 - 4.9)	26 (17 - 43)
3'-OH-CB180	1.2 (0.85 - 1.7)	1.2 (0.69 - 2.1)	0.89 (0.64 - 1.4)	0.96 (0.45 - 1.5)	1.4 (0.73 - 2.4)	19 (7.7 - 38)
3-MeSO ₂ -DDE ²	1.6 (1.0 - 2.0)	1.5 (n.d. - 2.2)	n.d.	n.d.	n.d.	4.8 (4.1 - 6.3)
4-MeSO ₂ -CB149	1.52 (0.93 - 2.6)	1.2 (0.69 - 1.8)	2.0 (0.98 - 3.5)	3.8 (2.9 - 5.9)	3.1 (n.d. - 5.7)	16 (13 - 20)
BCPS	6.6 (5.1 - 8.8)	7.2 (4.5 - 16)	6.5 (3.3 - 10)	11 (6.3 - 17)	12 (n.d. - 18)	1100 (850 - 1300)

n.d. = below limit of quantification (LOQ). n.a. = data not yet analysed. 1 LOQ = 9.5 ng/g l.w.. 2 LOQ = 0.88 ng/g l.w.

Mean concentrations of β-HCH show the same pattern as PCBs, the concentrations in samples from the North-Atlantic is similar and an order of magnitude lower than in samples from Sweden. The concentrations found in the Swedish samples are similar to what has been presented in earlier studies (Bignert *et al.*, 1998; Jörundsdottir *et al.*, 2006).

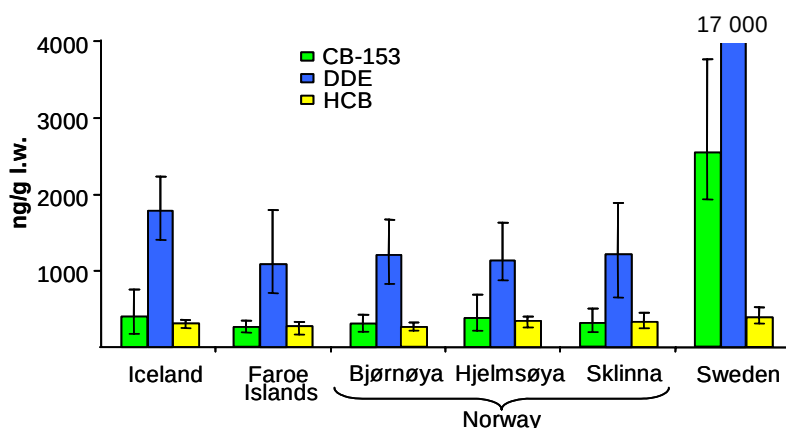


Figure 10. Mean concentrations and range of CB-153, *p,p'*-DDE and HCB in samples from Iceland, the Faroe Islands, Norway and Sweden. Please note that the concentration of DDE is out of scale for the Swedish samples.

Interestingly, there is no larger difference in PCB and DDE concentration between samples from the North-Atlantic. As seen in Table 2 and Figure 10, the concentration of HCB in all samples is more uniform between the sites than the concentrations of the other chlorinated compounds. This has been observed in other studies (AMAP, 2002) and then suggested to be due to the HCB volatility which is higher than that of PCBs and DDTs. It is hypothesized to be more easily transferred to remote areas. This explanation is questionable since β -HCH is a similarly volatile compound as HCB and β -HCH shows a similar concentration pattern as the PCBs. We are not yet able to suggest a likely reason for this remarkable behaviour of HCB.

The concentration pattern of PCB metabolites, OH-PCBs and MeSO₂-PCBs, is similar to the parent compounds. Their observed concentrations are an order of magnitude higher in samples from the Baltic Region compared to the samples from the North-Atlantic (Table 2). For 3-MeSO₂-DDE the difference in concentrations between the locations is not as large. The concentration is about three times higher in the samples from the Baltic Region compared to the samples from the North-Atlantic. This could be due to the fact that birds seem to have problems metabolising *para*-halogenated aryl compounds (Jörundsdóttir *et al.*, 2006). Due to analytical difficulties, 3-MeSO₂-DDE was not detected in the Norwegian samples.

The OH-PCB pattern found in the guillemot eggs in the present study is different compared to what has been published for other bird species, fulmars (Fängström *et al.*, 2005b), albatrosses (Klasson Wehler *et al.*, 1998) and white tailed sea eagles (Olsson *et al.*, 2000), where the major congeners were 4-OH-CB146 and 4-OH-CB187 for the albatrosses and the white tailed sea eagles both these accompanied by 3-OH-CB153 in the fulmars. In the present study, only OH-PCB congeners were found substituted with the OH-group in the *meta*-position. The parent compounds suggested for 4-OH-CB146 and 4-OH-CB187 are CB-138/CB-

153 and CB-183/CB-187, respectively (Klasson Wehler *et al.*, 1998). This could indicate that guillemots do have a different metabolism compared with the birds previously investigated, being less able to perform 1,2-shift of a chlorine atom, which is necessary for the formation e.g. 4-OH-CB-146.

BCPS was not analysed in the Norwegian samples. Concentration of BCPS in samples from the Baltic is 200 times higher compared to samples from Iceland and the Faroe Islands. BCPS has not been analysed in many samples outside of the Baltic Region, but according to these results, BCPS seems to be a more isolated problem for the Baltic Sea. There are indications that BCPS is transported more with water currents than air currents compared to i.e. PCB. There are probably no local sources of BCPS contamination in the West-Nordic locations as there is for the Baltic Sea. These results are in accordance with that theory.

3.7 Polybrominated compounds

Concentrations of polybrominated compounds in guillemot egg from the sampling locations in the Faroe Islands, Iceland, Norway and the Baltic proper are presented in Table 3.

Table 3. Mean concentrations (ng/g l.w.) with ranges in the parenthesis of polybrominated substances analysed in the guillemot (*Uria aalge*) eggs from the Faroe Islands, Iceland, Norway and the Baltic proper (Sweden) are given in the table.

	Vestmanna- eyjar	Sandøy	Bjørnøya	Hjelmsøya	Skinna	Stora Karlsö
	Iceland	Faroe Islands	Norway	Norway	Norway	Sweden
BDE-47	44 (13 - 96)	26 (7.1 - 58)	13 (3.2 - 27)	13 (6.2 - 28)	8 (2.3 - 29)	127 (65 - 190)
BDE-99	12 (5.0 - 24)	9.1 (3.2 - 20)	1.9 (0.69 - 3.4)	2.0 (0.64 - 4.7)	2.4 (0.83 - 6.5)	24 (17 - 42)
BDE-153	3.0 (1.3 - 7.0)	2.3 (0.68 - 6.6)	0.30 (0.17 - 0.41)	0.44 (0.33 - 0.69)	0.64 (0.06 - 1.2)	4.2 (2.2 - 7.7)
BDE-209 ^{1,2}	3.2 (n.d. - 19)	2.4 (n.d. - 15)	n.d.	n.d.	n.d.	n.d.
HBCD	22 (7 - 47)	28 (11 - 47)	28 (11 - 52)	42 (10 - 81)	33 (3.8 - 55)	340 (170 - 630)
2'-OH-BDE68 ³	0.39 (0.23 - 0.53)	0.23 (0.077 - 0.50)	0.22 (n.d. - 0.49)	0.25 (n.d. - 0.51)	0.21 (n.d. - 0.42)	11 (9.7 - 14)
6-OH-BDE47	4.5 (2.7 - 8.1)	2.0 (1.0 - 4.5)	10 (4.7 - 17)	5.13 (0.44 - 16)	2.7 (0.83 - 5.1)	130 (79 - 210)
2'-MeO-BDE68	n.d.	n.d.	n.d.	n.d.	n.d.	10 (6.1 - 13)
6-MeO-BDE47	n.d.	n.d.	n.d.	n.d.	n.d.	5.3 (3.6 - 8.1)
6-MeO-BDE90	n.d.	n.d.	n.d.	n.d.	n.d.	3.0 (1.7 - 4.1)

1 LOQ = 0.74 ng/g l.w.

2 BDE-209 was only quantified in 3 Faroic samples and 4 Icelandic samples

3 LOQ = 0.39 ng/g l.w. for Norwegian samples

n.d. below limit of detection

PBDE levels are rather well documented from the Baltic region (Sellström *et al.*, 2003) but the situation in the North-Atlantic is not as well known. The pattern of the PBDEs concentrations between the Baltic guillemot eggs and the West Nordic are very different from the PCB concentration pattern as can be seen in Table 3. The difference in concentrations of PBDEs in the samples from the different locations is small. The samples from Iceland and the Faroe Islands do not show a significant difference in concentration, compared to lower concentrations in Norwegian samples and the samples from the Baltic Region have slightly higher concentrations.

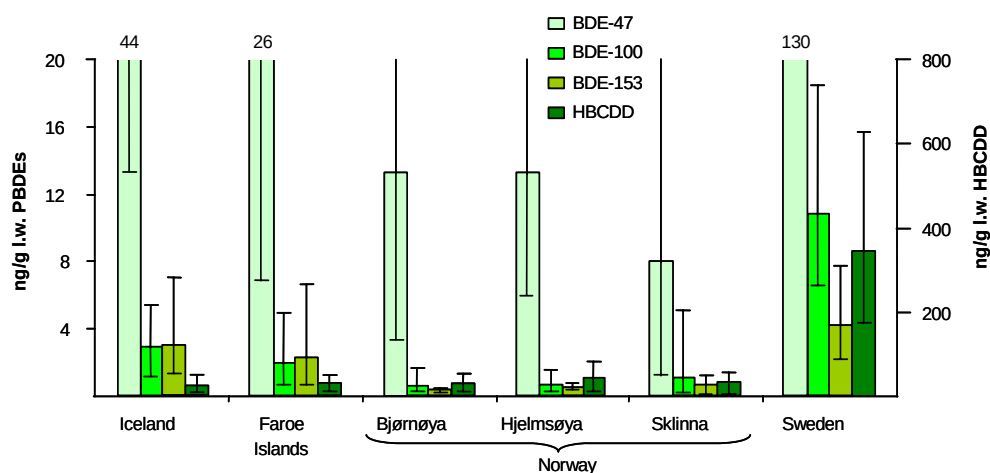


Figure 11. Concentrations of PBDEs and HBCDDs in guillemot egg samples from the Faroe Islands, Iceland and Sweden. Please note that there are two y-axes, one for the PBDEs and one for HBCDDs and that the concentration of BDE-47 is out of scale.

The lowest ratio between Baltic Sea guillemot eggs and West Nordic is only three as shown for BDE-47. There is almost no difference in the concentrations of BDE-153 between locations and interestingly, BDE-209 is only detected in the West Nordic area. The distribution of the PBDEs, some of the PBDE congeners more than others, is similar to HCB discussed above. For BDE-209 it is even a reversed ratio but too few data points are yet available to elaborate any further on this finding. The latter compound is one of the least volatile contaminant one can imagine. Our study clearly shows that the West Nordic can be as polluted as the Baltic proper.

The small difference in PBDE concentrations between the Baltic proper guillemot eggs and the West-Nordic egg is indeed intriguing. The distribution pathways of PCBs and DDE are different than for PBDEs. It is difficult to explain this with differences of the physico-chemical characteristics of the chemicals. Is it then possible that the ongoing use of PBDEs should be a reason for the different distribution. It is questionable since HBCDD is distributed similarly as PCBs and DDE between the areas. PBDEs and HCB have different properties. This reasoning leaves us with the possibility of local sources both in case of the PBDEs and of HCB, but it can not be proven. Consumer products containing the PBDEs, e.g. electronics, plastics, household appliances, cars etc. are equally used in these areas as in the Baltic region. Still, there seems to be a west-east gradient in PBDE concentration if only the West-Nordic samples are considered. This is most obvious for BDE-47. One reason could be that the main flame retardant used in USA are PBDEs, while the usage in Europe is limited. The main brominated flame retardant used in Europe is HBCDD. The different spatial pattern of PBDEs could be a long range transport mainly from USA. Fängström and coworkers have presented results of PBDEs in fulmar eggs from the Faroe Islands showing similar concentrations as determined in the present study (Fängström

et al., 2005a). Notable is that the fulmar eggs from the Faroe Islands have PCB concentrations that are an order of magnitude higher than the guillemot eggs from the Faroe Islands (Fängström *et al.*, 2005a). This may be explained with different feeding habits of the bird species. Fulmars usually follow fishing boats out at sea whereas guillemots mainly feed closer to land and are therefore closer to the exposure of PBDEs emitted from households and industry.

In contrast to the PCB metabolites, the OH-PBDEs do not show a similar picture. This is quite obvious since the OH-PBDEs are not only PBDE metabolites but also natural products. Interestingly 6-OH-BDE47 is as high as BDE-47, a very strong indication of not being a BDE-47 metabolite. The samples from Sweden have higher concentrations than the samples from the North-Atlantic, but the difference between the two areas is much greater than for the parent compounds. The difference in concentration is two orders of magnitude (Table 3). A difference, that could therefore be due to PBDE metabolism.

MeO-PBDEs seem to be only produced naturally and not formed metabolically from PBDEs. The MeO-PBDEs analyzed in the present study could not be detected in samples from the North-Atlantic, but only in samples from the Baltic Sea. Algal blooming is a problem in the Baltic Sea due to over fertilization and the environmental conditions are quite poor in general due to heavy emission of number of pollutants over the last decades. If the natural production of MeO-PBDEs is a cause of poor environmental conditions is a question that is not easy to answer.

HBCDD has not been reported from Iceland or the Faroe Islands before. Reports show low concentrations in polar cod (*Boreogadus saida*) from Bear Island in the North-East Atlantic (Bytingsvik *et al.*, 2004). In the present study, HBCDD is one of the most abundant flame retardant analyzed, equal to BDE-47 (Table 3, Figure 11). No statistical difference was found in concentrations of HBCDD in samples from Iceland and the Faroe Islands. The concentration of HBCDD in samples from Sweden was an order of magnitude higher compared to the North-Atlantic. This difference is much larger than for the PBDEs, making the distribution of HBCDD different from HCB and PBDEs. As said before, the reason is likely due to that HBCDD is the main brominated flame retardant used in Europe while PBDEs are mainly used in the USA.

3.8 Polyfluorinated compounds

Concentration of polyfluorinated compounds in guillemot eggs from Iceland, the Faroe Islands, Norway and Sweden are presented in Table 3. Egg samples from Bjørnøya were not analysed. Please note that the concentrations are presented on a fresh weight basis.

Table 4. Geometric mean concentrations are presented in ng/g f.w. (ppb), with ranges in the parenthesis of the polyfluorinated substances analysed in the guillemot (*Uria aalge*) eggs from the Faroe Islands, Iceland, Norway and Sweden.

	Vestmannaeyjar	Sandoy	Skinna	Hjelmsöya	Stora Karlsö
	Iceland	Faroe Islands	Norway	Norway	Sweden
PFOA	n.d.	n.d.	n.d.	n.d.	n.d.
PFNA ¹	n.d.	n.d.	n.d.	n.d.	48 (n.d. - 120)
PFDA ²	38 (n.d. - 74)	n.d.	42 (n.d. - 110)	n.d.	n.d.
PFUA	30 (9.0 - 110)	57 (27 - 110)	26 (14 - 72)	18 (10 - 28)	82 (18 - 140)
PFDoA ³	28 (2.2 - 81)	19 (n.d. - 26)	4.6 (n.d. - 17)	2.7 (n.d. - 5.5)	18 (n.d. - 48)
Acids total	96	76	73	21	150
PFOS	16 (5.2 - 22)	15 (6.0 - 34)	85 (3.2 - 210)	85 (54 - 110)	400 (200 - 760)
PFOSA ⁴	1.0 (n.d. - 2.1)	0.69 (n.d. - 1.5)	9.9 (n.d. - 57)	n.d.	3.7 (n.d. - 9.8)
N-Et-PFOSA ⁵	0.77 (n.d. - 1.7)	n.d.	0.98 (n.d. - 3.8)	2.0 (n.d. - 9.9)	1.1 (n.d. - 3.1)

n.d. = below limit of quantification (LOQ). 1 LOQ = 32 ng/g f.w.. 2 LOQ = 67 ng/g f.w.

3 LOQ = 1.6 ng/g f.w.. 4 LOQ = 1.1 ng/g f.w.. 5 LOQ = 1.1 ng/g f.w.

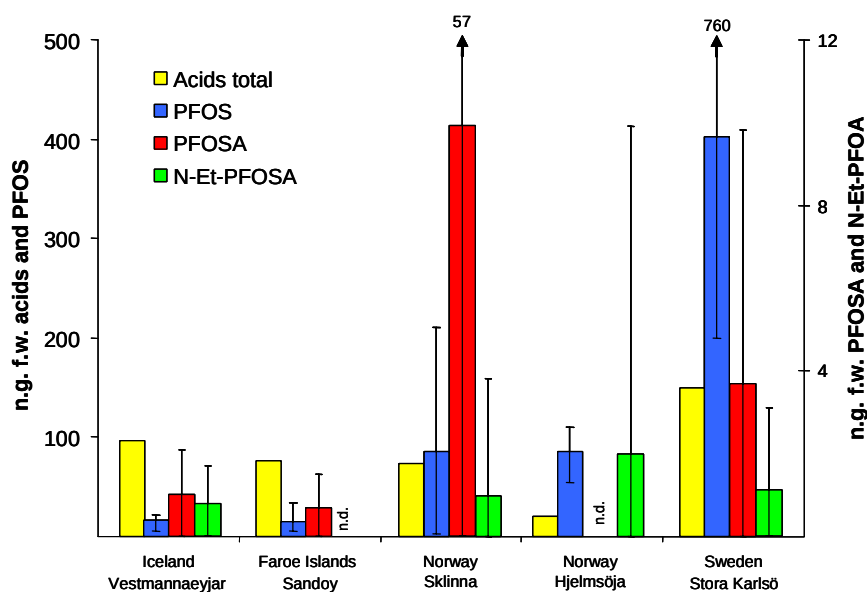


Figure 12. Concentrations of some polyfluorinated compounds in guillemot eggs from the West-Nordic presented on fresh weight basis. Please note that there are two y-axes, one for the acids and PFOS (left side of the graph) and one for PFOSA and N-Et-PFOA (right side of the graph).

As can be seen in Table 4 and Figure 12, the polyfluorinated compounds do not all show the same pattern as the chlorinated traditional compounds (e.g. PCBs) where it is assumed that Sweden is closest to the contamination source, Norway further away and Iceland and the Faroe Islands are considered remote locations. PFOS is the only compound showing this traditional pattern. For the sum concentrations of acids, samples from the Faroe Islands have almost the highest concentrations, where only Swedish samples have higher concentrations. The same is true for PFOSA where samples from Sklinna have by far the highest concentrations. For N-Et-PFOA, samples from Hjelmsöya contained the highest concentration. There seems to be no connection between the different perfluorinated compounds where all of them show a different distribution pattern. Not much is known about perfluorinated compounds.

4. Recommendations

Even if the problem of halogenated environmental contaminants has been known for over 40 years, the problem has not yet been solved. On the contrary, new compounds are being discovered and the need of studies concerning distribution, toxicity and fate grows. Our data clearly show that also the West Nordic region is significantly contaminated by persistent organic chemicals. For some of the present contaminants, there is no difference in levels between the Baltic and West Nordic regions. We therefore recommend intensified studies of organohalogen compounds in the West Nordic area. It is particularly obvious that the least understanding is related to some of the brominated flame retardants and to all the polyfluorinated surfactants. In the present study, the problem of environmental distribution is addressed. New questions emerge and based on this study at least two major issues need to be further investigated:

- First, the different distribution of HCB and PBDEs compared to most of the traditional contaminants need to be clarified. The distribution of HCB and PBDEs is influenced by matters not yet known to us.
- Second, the polyfluorinated compounds are indeed present in the study areas but further investigations are required to understand the sources of these compounds and how they are distributed in the environment and within the organism.

We like recommend further studies to better understand the reasons for the fate of HCB and PBDE congeners in the West-Nordic environment

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Manuscripts (produced within the project)

I Jörundsdóttir H, Svavarsson J, Weihe P, Bignert A, Bergman Å. Guillemot egg exposure load of some traditional and emerging halogenated contaminants in the West-Nordic and Baltic proper regions. Manuscript in preparation

II Mattiasson K, Jörundsdóttir H, Tomy G, Svavarsson J, Weihe P, Nygård T, Bergman Å. Spatial trends of perfluorinated alkylated substances in

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Optional summaries¹

Målet med projektet var att bedöma betydelsen av halogenerade miljöföroreningar i biota i Väst-Norden jämfört med Östersjön. Sillgrissleägg (*Uria aalge*) användes som biomarker på grund av lång erfarenhet med denna matris vad gäller miljöövervakning.

Metoden för kemisk analys av klorerade och bromerade substanser byggdes på en modifierad extraktionsmetod med väl dokumenterade uppreningssteg. Metoden utvecklades vidare för att uppnå hög effektivitet, rena prov och bra återvinning. Analyserna utfördes antingen med gas kromatograf kopplad till en "electron capture" detektor (GC/ECD) eller med gas kromatograf/mass spektrometri (GC/MS). Perfluorerade substanser isolerades med en ny och enkel extraktionsmetod i vilken endast metanol används. Substanserna analyserades med en vätskekromatografi/mass spektrometer (LC/MS/MS).

Höga halter av klorerade miljöföroreningar påvisades i Östersjön, ca 5–20 ggr högre än av samma substanser i prover från Väst-Norden; Norge, Färöarna och Island. Undantaget var HCB, som visade liknande halter i prover från samtliga lokaler. Ett annat undantag var bis(4-chlorophenyl)sulfone (BCPS) med höga halter i Östersjön och halter enbart nära detektionsgränsen i prover från Väst-Norden.

Polybromerade difenyletrar (PBDEs) visade endast en liten skillnad mellan sillgrissleprover från Östersjön och Väst-Norden. Hexabromocyclododecan (HBCDD) visar istället liknande monster som klorerade substanser med stor skillnad mellan Östersjön och Väst-Norden. Metoxyletrade PBDEs, som anses vara naturprodukter, åtfanns endast i prover från Östersjön.

Perfluorerade substanser (PFCs) visar en annorlunda spridning jämfört med både klorerade och bromerade substanser och utan någon riktigt relation inom den flurerade gruppen. Olika grupper; karboxylsyror, sulfonater och sulfonamider, har olika spridningsmönster som gör det svårt att förklara källor och spridning.

Två huvudfrågor måste besvaras efter denna studie; varför är spridningsmönstret för HCB och PBDE annorlunda från andra klorerade och bromerade substanser, och vilka är de huvudsakliga källorna och spridningsvägarna för flurerade substanser. Vi anser att fler studier behövs.

¹ If the main language of the report is English (or any other non-Scandinavian language), the summary must be translated into one Scandinavian language (Danish, Norwegian or Swedish). Summaries in Finnish or Icelandic should be included if considered relevant.