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# Organohalogenated Contaminants in Eggs of Snow Buntings (*Plectrophenax nivalis*) from Human Settlements in Svalbard

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## Abstract

Contaminants in the Arctic environment are mainly transported from lower latitude areas by atmospheric transport. However, the Russian settlements (Barentsburg and Pyramiden) in Svalbard have shown to be heavily influenced by local pollution of polychlorinated biphenyls (PCB), as high concentrations have been found in vegetation, soil and sediments. The Norwegian settlements (Longyearbyen and Ny-Ålesund) are to a lesser extent influenced by local pollution of PCB. Birds have been utilized as sentinels for environmental pollution in several studies, as the use of bird-eggs is considered as a non-invasive method. The aim of this study was to investigate whether the snow bunting (*Plectrophenax nivalis*) is influenced by local pollution of PCB in the Russian settlements.

During the 2010 field season and the 2011 field season, 32 eggs of snow buntings were collected in Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7). The analysis was conducted at the Norwegian Institute of Air Research (NILU) in Tromsø. The eggs were analyzed for PCBs, organochlorinated pesticides (OCPs), brominated diphenyl ethers (PBDE) and perfluoroalkylated compounds (PFASs).

The results showed that PCBs were the most abundant contaminant group in the Russian settlements, while PFASs was the most abundant contaminant group in the Norwegian settlements. Significant higher concentrations (ng/g wet weight) of  $\sum_7$ PCB (sum of the seven most common PCBs) were found in the eggs from the Russian settlements (Barentsburg and Pyramiden) than in the eggs from the Norwegian (Longyearbyen and Ny-Ålesund). Further on, the PCB congener composition in the eggs was comparable with the technical PCB-mixtures previous used in the Russian settlements. The results thus indicate influence of local pollution of PCB in eggs of snow buntings in the Russian settlements. Further on, local influence of dichlorodiphenyldichloroethylene (*p,p'*-DDE) and PFASs cannot be excluded. However, the contaminant burden of hexachlorobenzene (HCB), *trans*-nonachlor, *p,p'*-DDE and PFASs in the eggs of snow buntings in Svalbard are mainly explained by; I: atmospheric transport of contaminants to the Arctic environment, II: transport of contaminants by sea birds, III: exposure during migration, IV: exposure in overwintering areas.

The concentration of organohalogenated compounds (OHCs) in eggs of snow buntings in this study is considerable lower than concentrations in previously studies that have reported to cause adverse effect in other bird species. Further are the concentrations of OHCs in this study in general lower when compared with other studies on Svalbard seabirds. However, it should be noted that the concentration of  $\Sigma$ PCB in eggs of snow buntings is comparable with previous studies on Svalbard seabirds. The results in this study indicate that the snow bunting may be utilized as a sentinel of local pollution in Svalbard in the future.

## Sammendrag

Selv om atmosfærisk langtransport er hovedkilden til antropogen forurensning i Arktis, er det også lokale kilder til forurensning på Svalbard. Tidligere studier av vegetasjon, jord og sedimenter har vist at de russiske bosetningene (Barentsburg og Pyramiden) er påvirket av lokal forurensning av polyklorerte bifenyler (PCB). De norske bosetningene (Longyearbyen og Ny-Ålesund) er ikke påvirket i like stor grad, selv om små mengder lokale kilder til PCB er funnet i Longyearbyen. Flere fuglearter fra både det marine og det terrestriske miljø har tidligere blitt brukt som miljøovervåkende arter. Spesielt har fugleegg vist seg å være en skånsom måte å overvåke miljøgiftnivået i miljøet. Hensikten med denne studien var å kartlegge hvorvidt egg fra snøspurv (*Plectrophenax nivalis*) fra de russiske bosetningene på Svalbard inneholder mer PCB enn egg fra de norske bosetningene.

I løpet av feltsesongene i 2010 og 2011, ble til sammen 32 snøspurv egg samlet in i Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) og Pyramiden (n=7). Miljøgiftanalysene ble utført ved Norsk Institutt for Luftforskning (NILU) i Tromsø. Eggene ble analysert for PCBer, organoklorerte pesticider, bromerte flammehemmere og perfluorerte stoffer (PFAS).

Resultantene viste at PCB utgjorde den største gruppen av miljøgifter i de Russiske bosetningene, mens PFAS utgjorde den største gruppen av miljøgifter i de norske bosetningene. Konsentrasjonen (ng/g våt vekt) av  $\Sigma_7$ PCB (sum av de syv mest vanlige PCB-kongenere) var signifikant høyere i snøspurv egg i de russiske bosetningene (Barentsburg og Pyramiden) enn i de norske bosetningene (Longyearbyen og Ny-Ålesund). Videre var PCB-kongener sammensetningen i eggene sammenlignbar med tekniske PCB-blandinger tidligere brukt i de russiske bosetningene. Dette indikerer dermed påvirkning av lokal forurensning av PCB. Heller ikke lokal forurensning av diklorodifenyldikloroetylen (*p,p'*-DDE) og PFAS kan utelukkes. Til tross for dette kan hovedvekten av heksaklorobensen (HCB), *trans*-nonachlor, *p,p'*-DDE og PFASs i snøspurvegg forklares med; I: atmosfærisk langtransport av miljøgiftene, II: transport av miljøgiftene via sjøfugler, III: eksponering under migrasjon, IV: eksponering på overvintringsområdet.

Konsentrasjonen av miljøgifter i snøspurvegg på Svalbard viste seg å være lavere enn tidligere studier, der uønskede effekter er påvist. Videre er konsentrasjonene av miljøgifter i denne studien generelt lavere sammenlignet med andre studier på sjøfugl på Svalbard. Til tross for dette var konsentrasjonen av  $\Sigma$ PCB i snøspurvegg sammenlignbar med tidligere studier på sjøfugl fra Svalbard. Resultatene utledet i denne studien viser at snøspurv kan brukes som miljøovervåkningsart på Svalbard i framtiden.



## List of abbreviations

$\Sigma$ PCB	Sum of individual PCB congeners
$\Sigma$ PFAS	Sum of individual perfluoroalkylated compounds
ANOVA	Analysis of variance
BFR	Brominated flame retardants
CHL	Chlordanes
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EI	Electron ionization
EOM	Extracted organic material
GC	Gas chromatography
GPC	Gel permeation chromatography
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
id	Inner diameter
ID	Identification number
$K_{oa}$	Partitioning coefficient between octanol and air
$K_{ow}$	Partitioning coefficient between octanol and water
LC	Liquid chromatography
LOD	Limit of detection
MS	Mass-spectrometry
n	Number of observations
NIST	National Institute of Standards and Technology
OC	Organochlorinated compounds
OCP	Organochlorinated pesticides
OHC	Organohalogenated compounds
PBDE	Polybrominated diphenyl ether
PC	Principal component
PCA	Principal component analysis
PCB	Polychlorinated biphenyls
PFAS	Perfluoroalkylated substances

PFCA	Perfluoroalkyl carboxylic acid
PFDCa	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFNA	Perfluorononaic acid
PFOS	Perfluorooctanesulfonic acid
PFOSA	Perfluorooctane sulfonamide
PFSA	Perfluoroalkane sulfonic acid
PFTriA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid
POP	Persistent organic pollutants
PPAR	Peroxisome proliferator receptor
Q <sup>2</sup> X	Goodness of prediction
qstd	Quantification standard
r <sub>s</sub>	Spearman's correlation coefficient
R <sup>2</sup> X	Goodness of fit
RiS	Research in Svalbard
RRF	Relative response factor
rpm	Rounds per minute
SD	Standard deviation
SE	Standard error
SPE	Solid phase extraction
spl	Sample
SRM	Standard reference material
UV	Unit variance
w.w.	Wet weight

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## **1. Introduction**

The Arctic is a vulnerable area and is characterized by low temperature, large seasonal fluctuations and short growing seasons (AMAP, 1998; Burkow and Kallenborn, 2000). These areas are regarded among the least polluted areas in the world, even though it receives anthropogenic contaminants from more temperate areas. Because of few local sources in the Arctic environment, contaminants are transported to the Arctic by four main routes; the atmosphere, ocean currents, large arctic rivers and transpolar ice pack (AMAP, 1998). However, long range atmospheric transport is regarded as the most important source of contaminants to the Arctic environment (Oehme et al., 1996). Semi-volatile compounds are transported to remote high latitude regions by global distillation and fractionation, also known as “the grasshopper effect”, that is a repeated vaporization and condensation of the compounds from lower latitude to higher latitude areas (Mackay and Wania, 1995). Oceans, lakes and the terrestrial environment, which are in constant exchange with the atmosphere, are important storages for the contaminants. This results in only a small fraction present in the atmosphere (Burkow and Kallenborn, 2000). Furthermore, organisms such as crustaceans, fish and marine mammals are contributing to the transport of contaminants to the Arctic environment by their seasonal migration (AMAP, 2002). In addition, seabirds may transport organochlorinated compounds (OCs) from the ocean to the terrestrial environment in their guano (Evenset et al., 2007; Choy et al., 2010). Wania, (1998) estimated that seabird transport of persistent organic pollutants (POPs) in and out of the northwest Atlantic water in Canada to be in range of grams to kilograms per year due to the high number of migrating birds. This may have consequences for both the terrestrial and freshwater environment.

### **1.1 Persistent organic pollutants in the Arctic environment**

Persistent organic pollutants are released into the environment as pesticides, industrial produced compounds and industrial byproducts such as polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB). Further more, pesticides such as dichlorodiphenyltrichloroethane (DDT), mirex, endosulfan, dieldrin, chlordanes and hexachlorocyclohexane (HCH) are manufactured to be toxic and not easily biodegradable. This results in compounds that are not only toxic against its targets such as fungi and insects, but also towards humans and animals. Many of the mentioned

compounds are either banned or restricted in use (AMAP, 1998). These compounds are well known contaminants in the Arctic environment, and were listed in 2001 under the Stockholm Convention. Initially, 12 persistent compounds were listed, and additionally 9 were listed in 2009 (Stockholm Convention, 2001). By using a precautionary approach, new chemicals could potentially be listed here in the future (Godduhn and Duffy, 2003). Restriction and banning of many industrially produced chemicals have contributed to the decline in the Arctic regions (AMAP, 2002; Riget et al., 2010). Research has shown an increase in the emerging “new chemicals”, such as brominated flame retardants (BFR) (Knudsen et al., 2005; Sagerup et al., 2010; de Wit et al., 2010) and poly- and perfluoroalkylated substances (PFASs) (reviewed by Butt et al., (2010)). Because of their special physical and chemical properties such as high thermal stability and low surface energy, PFASs have been useful in several applications, such as lubricants, textiles, leathers and fire-fighting foams (Hekster and Voogt, 2002). As a result of their low volatility, they are not expected to be found in the Arctic environment. However, their presence implies an occurrence of long range transportation (Verreault et al., 2005; Butt et al., 2010). Perfluorooctanesulfonic acid (PFOS), tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) are all very persistent compounds that potentially may bioaccumulate and biomagnify. Further on, they are transported to the Arctic environment. In 2009, these chemicals were proposed to be listed as “new POPs” in the Stockholm Convention (Stockholm Convention, 2009).

## **1.2 Local pollution**

Even though atmospheric transport is the main route to contaminants in the Arctic, there is also contribution from local settlements which could pose a risk to both the terrestrial and the marine environment. The locations investigated in this study were the Norwegian settlements, Longyearbyen and Ny-Ålesund, and the Russian settlements, Barentsburg and Pyramiden.

In 2008, the governor of Svalbard, in cooperation with several institutions, conducted a survey on PCB contamination on Svalbard (Lundkvist, 2008). It was concluded that active sources of PCB were present in the settlements, all though PCB was banned during the 1980s. Sources to PCB were capacitors, paint, hydraulic oil and building materials that could possibly leak into the environment. Even though the main sources

of PCB are phased out materials and equipment, PCB could possibly be produced through combustion processes (Lee et al., 2005; Ishikawa et al., 2007; Lundkvist, 2008). The amount PCB found in surface soil in Barentsburg and Pyramiden was elevated compared to Longyearbyen. The amount PCB found in Barentsburg was elevated when compared to locations on the mainland, such as Bergen. These findings were also supported by surveys done by NGU (Jartun et al., 2007; Jartun et al., 2009a; Jartun et al., 2010), where soil, paint, concrete and oils were sampled and analyzed for PCBs. Further on, Typhoon investigated the vegetation (vascular plants and mosses) in and around Barentsburg. The authors reported that PCB-52, PCB-99, PCB-101, PCB-105, PCB-118, PCB-138 and PCB-153 were found in every vegetation sample (Typhoon, 2010). Ny-Ålesund contains secondary sources for PCB, but the concentrations were low. As a result of this, the settlement is considered as “PCB clean” (Eggen et al., 2008).

Monitoring of sediments outside the settlements has revealed a steadily increase in levels of PCB from 1998-2009 in Billefjorden (Pyramiden) (Evenset, 2010). The highest levels of PCB in the sediments were found close to the settlement. This is probably related to PCB leaking from the settlement during rainfall and snowmelt (Evenset et al., 2006). However, in 2006 there was a flood in the settlement, probably contributing to a high amount of PCB leaking into Billefjorden. The same pattern was indicated in Grønfjorden (Barentsburg), but the levels in the sediments have declined after 2005. On the other hand, a high proportion of dichlorodiphenyldichloroethane (DDD) and DDT were found in Grønfjorden, indicating a fresh source of DDT. The source of DDT in Barentsburg is not known. However, it is suggested that DDT was used for combating lice. This means that it may still be containers containing DDT in the settlement (Evenset, 2010). There are also indications that “new pollutants”, such as polybrominated diphenyl ethers (PBDEs) and PFASs, are present in Adventfjorden (Longyearbyen), Billefjorden and Grønfjorden. However, it is not known whether this is caused by long range transport or local sources (Evenset et al., 2006). An additional potential pollution caused by local activity is tourism that contributes with both cruise ships and airplane activity (Evenset et al., 2009b).

PCB is now mainly found as a secondary source, which is temporary dissolved in soil, snow, sediments, air, vegetation and animals (Lundkvist et al., In press). Thus, it is a

possibility that climate change could contribute to redistribution of PCB bound to glaciers and freshwater. This could lead to an increased amount of PCB deposited in both marine and terrestrial environment (Macdonald et al., 2005; Lamon et al., 2009). Jartun et al., (2009c) reported a large amount of electrical installations, building materials and scrap metal in close nearby to Barentsburg and Pyramiden. Weathering processes may contribute to disperse pollutants such as PCB to soil, and eventually to the marine environment (Jartun et al., 2008; Jartun et al., 2009b; Jartun et al., 2010). It is calculated that as much as 430 kg/km<sup>2</sup> PCB is in the surface soil in Pyramiden, 300 kg/km<sup>2</sup> PCB in surface soil in Barentsburg, and 3,3 kg/km<sup>2</sup> PCB in surface soil in Longyearbyen (Jartun et al., 2009a; Jartun et al., 2010). The PCB load in surface soil in pristine areas on Svalbard are calculated to be 0.4 to 1.0 kg/km<sup>2</sup> (Jartun et al., 2010; Lundkvist et al., In press). Even though these settlements only constitute a minor part of Svalbard, there is a possibility of dispersion of these pollutants to other areas and fiords (Evenset et al., 2006; Jartun et al., 2009c). Since 2008, initiative to remove PCB sources has been taken on Svalbard. Local sources of PCB in all the settlements have been either mapped and marked as containing PCB, or removed (Lundkvist et al., In press). Despite this, the secondary sources will continue to pose a risk to the Arctic environment in the future.

### **1.3 Potential effects of environmental pollution**

Different organohalogenated compounds (OHCs) have different structures and properties. Common are the physical chemical properties such as low water solubility, high lipophilicity (hydrophobicity) and resistance to biological and chemical biodegradation (Oehme et al., 1996; AMAP, 1998; Borga et al., 2004). However, as PFASs have different properties than traditional POPs (Houde et al., 2006), they bind to blood proteins and accumulate in the liver, kidneys and bile secretions (Jones et al., 2003). The carbon-fluorine bonds are extremely strong, and as a result these compounds are very persistent and difficult to biodegrade. Potential adverse effects as a consequence of exposure of PFASs, is activation of peroxisome proliferator receptor (PPAR) and tumor promoting pathways (reviewed by Lau et al., (2007)).

A number of factors may affect the accumulation of pollutants, such as age, gender, seasonality, body size, lifecycle, biotransformation, migration, habitat use and feeding



ecology (Borga et al., 2004). The marine ecosystem have been extensively studied, and lipids are an important part of the marine food web (AMAP, 1998; Borga et al., 2004). The contaminants biomagnify to high levels in top predators, such as the glaucous gull (*Larus hyperboreus*) and the polar bear (*Ursus maritimus*) (Letcher et al., 2010). Once accumulated, the contaminants acts as stressors and effect the endocrine system, and pose adverse long term effects (Skaare et al., 2000; Gabrielsen, 2007; Bustnes et al., 2008; Letcher et al., 2010). Potential effects in seabird that are correlating with contaminants are reduced egg size, reduced nesting success, wing feather asymmetry, reduced reproductive success, immune system suppression and effect on the thyroid hormones (Bustnes et al., 2002; Verreault et al., 2004b; Letcher et al., 2010; Verreault et al., 2010).

The terrestrial environment, on the other hand, has not been as extensively studied. The level of OCs have shown to be lower in the Arctic terrestrial ecosystem compared to the marine ecosystem (AMAP, 2002). The terrestrial food webs are often short and consisting of plants and lichens as primary producers, herbivores and main predators (AMAP, 1998). A thoroughly investigated terrestrial food chain is the lichen-caribou-wolf chain, which indicates biomagnifications of both organochlorines and perfluorinated compounds in the terrestrial food webs (Kelly and Gobas, 2001; Mueller et al., 2011). The peregrine falcons (*Falco peregrinus tundrius*) have been an important long term indicator of exposure of anthropogenic pollutants in the terrestrial environment, with eggshell thinning and reduced breeding success as a result (Johnstone et al., 1996). Further on, previous studies on passerine birds have shown accumulation and trophic transfer of OCs by aquatic and terrestrial insects (Dauwe et al., 2006; Maul et al., 2006), demonstrating the accumulation potential of OCs in terrestrial insectivorous food web.

Accumulation of OCs in the terrestrial environment is not only related to the chemicals  $K_{ow}$ , but additionally the  $K_{oa}$ . This is explained by chemicals that have a high  $K_{oa}$  ( $K_{oa} \geq 6$ ) have a low rate of elimination through respiration. This means that chemicals that are not expected to bioaccumulate as a result of low  $K_{ow}$  ( $K_{ow} < 5$ ) could potentially accumulate in the terrestrial environment (Kelly et al., 2007). Effect studies on birds in

both marine and terrestrial environment are important for gaining more knowledge about possibly consequences and action that needs to be made.

#### **1.4 The snow bunting**

The snow bunting (*Plectrophenax nivalis*) is a well studied bird regarding its ecology in Svalbard. However, there is no information regarding contaminants in snow buntings in Svalbard. The snow bunting reaches a length of approximately 16-17 cm, and is easy recognizable by its white patterns on its wings (Jonsson, 1994). It has a circumpolar distribution north of the tree boarder in Alaska, Northern Canada, Greenland and the arctic parts of Russia. In Norway, the snow bunting breeds in high mountains and in the northern part of Norway. On Jan-Mayen and on Svalbard it also breeds close to the coast. This is the sole passerine bird that breeds on Svalbard, and it is distributed over the whole island. The breeding locations varies between bird cliffs, tundra, crevices, cracks in house walls, nesting boxes and other human made constructions (Gjershaug et al., 1994; Hoset et al., 2009). The snow bunting is a migratory bird, and is assumed to migrate trough the northern part of Russia to the North side of the Caspian Sea, Russia and Kazakhstan. This is based on the fact that birds from the North-East parts of Greenland have been relocated in these areas (Gjershaug et al., 1994). However, the exact migratory route for Svalbard snow buntings remains unknown.

The male arrives at Svalbard from the end of March, to the beginning of April, while the female arrives two-three weeks later. It leaves the breeding grounds on Svalbard during September-October. The female lays 5-7 eggs that are incubated in approximately 12-13 days. If good conditions, some snow buntings breed twice during one season. The snow bunting is predated upon by the Arctic fox (*Vulpes lagopus*), glaucous gulls and skuas. Unlike the seabirds who feed on lipid rich food from the marine environment, the snow buntings diet consists mainly of seeds. However, it also feeds and feed the chick on insects, such as dipterans and spiders (Jonsson, 1994; Skjøstad, 2008). It can build fat reserves, but it most likely need to consume nourishment every day. It is assumed to be 10 000-50 000 pairs of breeding snow buntings in Svalbard (Svorkmo-Lundberg et al., 2006).

### **1.5 Birds as sentinels of environmental pollution**

Birds have been used as bioindicators and monitoring species regarding OCs, brominated flame retardants (BFR) and PFASs in several studies. These studies have been conducted both in the terrestrial (Dauwe et al., 2007; Van den Steen et al., 2009b; Van den Steen et al., 2010), as well as the marine environment (Verreault et al., 2010; Helgason et al., 2011). Using eggs for biomonitoring purposes is regarded as a non-invasive method, and is well suited for long-term monitoring. Since egg tissue is directly indicative of the levels in the tissue of the mother bird (Drouillard and Norstrom, 2001), it is a useful tool for monitoring levels of pollution in various bird species. Passerine birds are useful for monitoring local pollution, in contrast to predatory species, because of their small home ranges, territories and foraging areas (Dauwe et al., 2003). The snow bunting, on the other hand, is a migratory bird. Thus the eggs may reflect levels of pollutants both from its overwintering areas, as well as its breeding locations.

### **1.6 Aim of the study**

The main objective of this study was to investigate OHCs in eggs of snow buntings in Svalbard. Further, elevated levels of environmental contaminants, especially PCB, have been reported in soil, vegetation and paint in the two Russian settlements, Barentsburg and Pyramiden (Jartun et al., 2010; Typhoon, 2010). Therefore, the aim was to assess whether there was a difference in contaminant concentrations in eggs of snow buntings breeding in the Russian settlements compared with snow buntings breeding in the Norwegian settlements.

Based on the fact that more PCB is found in and around Barentsburg and Pyramiden, it is hypothesized that eggs from Barentsburg and Pyramiden will have a higher concentration of PCBs, compared with eggs from Longyearbyen and Ny-Ålesund.

## 2. Method and materials

### 2.1 Study area and sampling

The fieldwork was conducted during June 2010 and June 2011 at four different locations on Spitsbergen, Svalbard (74-81° N, 10-35° E). The four different sample locations were Longyearbyen, Ny-Ålesund (Kongsfjorden), Barentsburg and Pyramiden (Figure 1).



Figure 1. Sampling locations in Spitsbergen, Svalbard. The eggs of snow bunting (*Plectrophenax nivalis*) were collected in Longyearbyen, Ny-Ålesund, Barentsburg and Pyramiden. Map: Oddveig Øien Ørvoll (NPI).

The nests were located by observation, and 1-2 eggs from each clutch were collected. The results include only one egg from each clutch. The eggs were measured (length and width), wrapped in aluminum foil, and placed in ziplock plastic bags marked with its respectively egg number, nest location in addition to GPS-position, clutch size and date. The egg volume was calculated by using Hoyt's equation:  $(width^2 * length * 0.51)$  (Hoyt, 1979). Where possible in the field, the eggs were stored in a refrigerator, before they were frozen at -20°C. The transport of the eggs to NILU in Tromsø from Longyearbyen was conducted in a frozen condition, and stored at -20 until analysis. In this study, 32 eggs are included in the results. From the 2011 field season, 29 eggs are included, and from the 2010 field season, 3 eggs are included. The sample size from each location is 8

eggs from Longyearbyen, 9 eggs from Barentsburg, 7 eggs from Pyramiden and 8 eggs from Ny-Ålesund. The sample locations in the different settlements are illustrated in Figure 2.

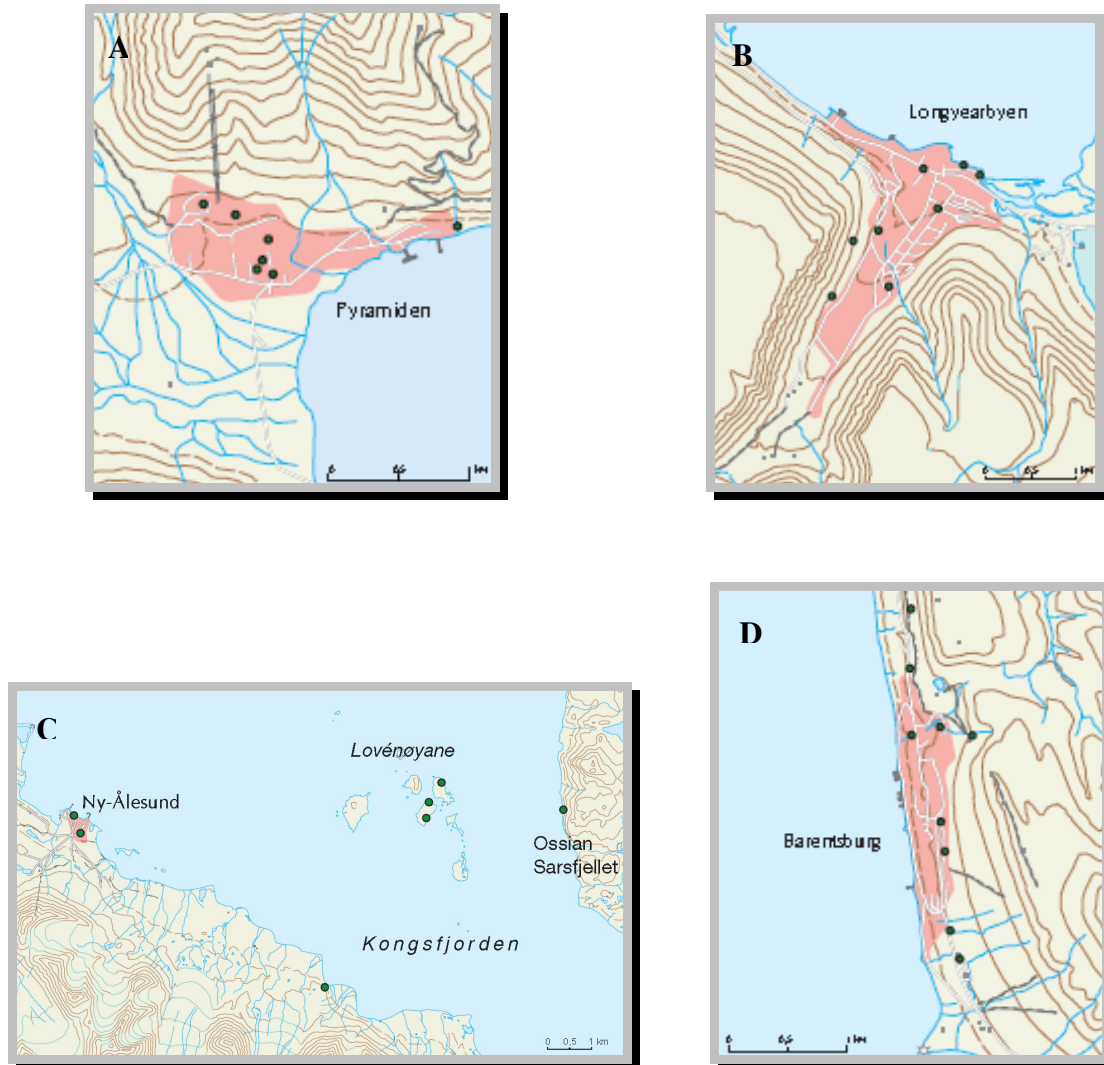


Figure 2. The different settlements where the eggs of snow bunting (*Plectrophenax nivalis*) were collected. A-Pyramiden n=7, B-Longyearbyen n=8, C-Ny-Ålesund and Kongsfjorden n=8, D-Barentsburg n=9). Each egg collected in the respective location is marked. Map: Oddveig Øien Ørvoll (NPI)

Approval for conducting the fieldwork was given by the Governor on Svalbard (reference number: 2011/00488-14). In addition, the project is registered in the Research in Svalbard (RiS) database, with RiS-ID: 3755.

## **2.2 Chemical analysis of contaminants in eggs of snow bunting**

The analyses were conducted at the Norwegian Institute of Air Research (NILU), section Tromsø. The egg samples were analyzed for several different environmental contaminants; PCBs, organochlorinated pesticides (OCPs), PBDEs and PFASs. In addition, the extracted organic matter (%) in the eggs was determined. The extracted organic matter will hereafter be referred to as lipid content (%).

## **2.3 Preparation**

The eggs were thaw in room temperature prior preparation. The eggshell was removed, and the egg content was homogenized. Approximately 0.5 grams of the sample was prepared for analysis of the PFASs. The remaining sample was weighed and added Na<sub>2</sub>SO<sub>4</sub> (burned at 600 °C for 8 hours) in relation 1:20. The sample was thoroughly mixed with the Na<sub>2</sub>SO<sub>4</sub>, and left in the freezing compartment (-18°C) over night.

## **2.4 Chemical analysis of PCBs, chlorinated pesticides and brominated compounds**

Table 1 describes the different groups and individual compounds of chlorinated industrial products and by-products, chlorinated pesticides and brominated compounds that were analyzed.

### **Cold column extraction**

For the extraction of the samples, cold column extraction was used. Each sample was spiked with 20 µl internal standard solution containing mass labeled OHC (Appendix A, Table A.1). The samples were extracted three times with 50 ml cyclohexane:acetone (3:1) with an extraction time of 1 hour used for each extraction step. The columns were at any time covered with aluminum foil to prevent any potential contamination that may occur from the laboratory environment. After sample extraction was complete, extracts were concentrated to 0.5 ml using a Turbovap (Turbovap 500, Zymark) evaporator, and quantitatively transferred to a 4 ml vial using approximately 1 ml portions of dichloromethane (DCM) and hexane and stored for further sample matrix clean-up.

Table 1. Different chlorinated industrial and by-products, chlorinated pesticides and brominated compounds analyzed in eggs of snow bunting (*Plectrophenax nivalis*).

<b>Organochlorinated and brominated compounds</b>		
<b>Group</b>	<b>Acronym</b>	<b>Chlorinated industrial products and by-products</b>
PCBs	PCB-28/31	2,4,4'-Trichlorobiphenyl/ 2,4',5-Trichlorobiphenyl
	PCB-52	2,2',5,5'-Tetrachlorobiphenyl
	PCB-101	2,2',4,5,5'-Pentachlorobiphenyl
	PCB-118	2,3',4,4',5-Pentachlorobiphenyl
	PCB-138	2,2'3,4,4',5'-Hexachlorobiphenyl
	PCB-152	2,2',3,5,6,6'-Hexachlorobiphenyl
	PCB-180	2,2',3',4,4',5,5'-Heptachlorobiphenyl
HCB	HCB	Hexachlorobenzene
<b>Chlorinated pesticides</b>		
CHLs	<i>trans</i> -Chlordane	<i>trans</i> -Chlordane
	<i>cis</i> -Chlordane	<i>cis</i> -Chlordane
	<i>oxy</i> -Chlordane	<i>oxy</i> -Chlordane
	<i>trans</i> -Nonachlor	<i>trans</i> -Nonachlor
	<i>cis</i> -Nonachlor	<i>cis</i> -Nonachlor
Mirex	Mirex	1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta(cd)pentalene
HCHs	$\alpha$ -HCH	1 $\alpha$ ,2 $\alpha$ ,3 $\beta$ ,4 $\alpha$ ,5 $\beta$ ,6 $\beta$ -Hexachlorocyclohexane
	$\beta$ -HCH	1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\alpha$ ,6 $\beta$ -Hexachlorocyclohexane
	$\gamma$ -HCH	1 $\alpha$ ,2 $\alpha$ ,3 $\beta$ ,4 $\alpha$ ,5 $\alpha$ ,6 $\beta$ -Hexachlorocyclohexane
DDTs	<i>p,p'</i> -DDT	4,4'-Dichlorodiphenyltrichloroethane
	<i>o,p'</i> -DDT	2,4'-Dichlorodiphenyltrichloroethane
	<i>p,p'</i> -DDE	4,4'-Dichlorodiphenyldichloroethylene
	<i>o,p'</i> -DDE	2,4'-Dichlorodiphenyldichloroethylene
	<i>p,p'</i> -DDD	4,4'-Dichlorodiphenyldichloroethane
	<i>o,p'</i> -DDD	2,4'-Dichlorodiphenyldichloroethane
<b>Brominated compounds</b>		
PBDEs	PBDE-47	2,2',4,4'-Tetrabromodiphenyl ether
	PBDE-99	2,2',4,4',5-Pentabromodiphenyl ether
	PBDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether

### Lipid-removal using GPC- Gel Permeation Chromatography

Lipid removal from the sample extracts was performed using gel permeation chromatography (GPC). The sample extract (~1.5 ml) was injected onto a Waters 515 HPLC pump equipped with Waters Envirogel GPC columns. Using DCM as a mobile phase at a flow rate of 5 ml/min, lipid material was separated from the analytes of interest and discharged to the waste. The lipid-free analyte fraction was collected and concentrated down to 0.5 ml, followed by quantitative transfer to a 2 ml vial using hexane.

### **Clean-up using florisil**

To remove remaining matrix interferences, sample extracts were further cleaned up by solid phase extraction (SPE). Florisil (magnesium silica) was activated (burned 450°C for 8 hours) and packed in solid phase extraction (SPE) cartridges (0.15 – 0.25 mm, Merck, Darmstadt, Germany). Each cartridge was individually packed with florisil (1g (+/- 0.02 g)) between two glass fiber frits (rinsed with DCM) in each end of the column. Sample extracts were concentrated to 0.5 mL on a RapidVap (Vacuum Evaporation System Model 7900001, Kansas city, MO, US) evaporator. Sample extract was then added to the pre-made Florisil columns using the RapidTrace SPE Work Station (Caliper Life Science, Hopkinton, USA). Analytes of interest were eluted using a mobile phase of 10 % DCM in n-hexane. Collected analyte fraction was then evaporated down to 0.2 mL and quantitatively transferred to a gas chromatography sample vial. Sample extract was further concentrated to approximately 200 µl using nitrogen gas (N<sub>2</sub>, 99 % purity, AGA, Oslo, Norway). Prior to quantification, 20 µl recovery standard (octachloronaphthalene, OCN, 200 pg/µl) was added to each sample.

### **Instrument analysis**

Gas chromatography mass spectrometry was used for separation and detection of the investigated analytes. Separation of analytes is based on differences in boiling points and chemical interactions with the column stationary phase between the various analytes. The mass spectrometer ionizes the gaseous analyte which are separated through an electric field according to their mass to charge ratio,  $m/z$ . The ratio is detected and visualized in a mass spectrum (Harris, 2010).

### **Instrumental setting**

#### **Pesticide analysis**

Analysis of  $\alpha$ -,  $\beta$ -,  $\gamma$ - hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), heptachlor and heptachlor epoxide, oxy-chlordane, *trans*- and *cis*- chlordane, *trans*- and *cis*- nonachlor, and Mirex was carried out using an Agilent 7890A gas chromatograph equipped with a 5975c mass spectrometer (Agilent Technologies, Böblingen, Germany). A 30 m DB5-MS column (0.25 mm id and 0.25 µm film thickness; J&W, Folsom, USA) was used for separation with helium (6.0 quality, Hydrogas, Porsgrunn, Norway) as carrier gas at a flow rate of 1 mL/min. A sample volume of 1 µL was injected in a split/splitless



injector held at a temperature of 250°C. The GC temperature program incorporated an initial temperature of 70°C with a hold time of 2 min, increased by 15°C/min to 180°C, followed by a ramp of 5°C/min to 280°C and held for 10 min. Electron capture negative ionization mode using methane as a reagent gas was used for analyte detection. Source temperature was held at 160°C.

### PCB analysis

Polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDTs) and respective metabolites were analyzed using an Agilent 7890A gas chromatograph (Agilent Technologies, Böblingen, Germany) equipped with a 5975c mass spectrometer (Agilent Technologies, Böblingen, Germany). PCBs and DDT group were analyzed separately with two separate injections. Separation was performed on a 30 m DB5-MS column (0.25 mm id and 0.25 µm film thickness; J&W, Folsom, USA) with a split/splitless injector heated at 250 °C (220°C for DDT analysis). An injection volume of 1 µL was injected using splitless mode with He as a carrier gas at 1 ml/min under constant flow conditions. Oven temperature program for separation was as follows: initial oven temperature was held at 70°C (3 min hold), ramped at 15°C/min to 180°C, followed by a second temperature ramp of 5°C/min until a final temperature of 280°C (6 min hold). Source temperature was set at 250°C in EI mode with ionization energy of 70 eV.

### Quantification

Quantification of the samples was done by running a quantification standard (qstd) with a known concentration of <sup>13</sup>C and <sup>12</sup>C together with the samples. A relative response factor (RRF) was calculated from the ratio between <sup>13</sup>C and <sup>12</sup>C in the quantification standard.

$$RRF = \frac{Amount_{13c - qstd}}{Area_{13c - qstd}} = \frac{Amount_{12c - qstd}}{Area_{12c - qstd}} \quad \text{Equation 1}$$

The RRF was used to calculate the amount of <sup>12</sup>C in the samples (spl), based on the amount of <sup>13</sup>C added.

$$Amount_{12c - spl} = \frac{Area_{c12 - spl} \times Amount_{c13 - spl}}{RRF \times Area_{c13 - spl}} \quad \text{Equation 2}$$

The recovery was calculated by the difference in the calculated amount of <sup>13</sup>C (cal) and the added amount of <sup>13</sup>C (added).

$$Recovery(\%) = \frac{Amount_{c13 - cal}}{Amount_{c13 - added}} \times 100\% \quad \text{Equation 3}$$

### Quality assurance of the method

Prior to the extraction and clean-up procedures, all the glassware was rinsed with acetone and cyclohexane, and burned at 450°C for 8 hours. For every tenth sample, one blank and one standard reference material (SRM 1945, Whale Blubber, National Institute of Standards and Technology, NIST, MD, USA) was extracted. Limit of detection (LOD) was defined as three times blank or background signal (Appendix B, Table B.1).

### 2.5 Chemical analysis of perfluorinated compounds

Table 2 describes the different groups and individual compounds of PFASs that were analyzed. The volume based method for the extraction and clean-up procedures is previously described by (Powley et al., 2005).

#### Extraction

The samples were weighed into a PP-centrifuge tube and spiked with 20 µl internal standard (<sup>13</sup>C labeled internal standard (allPFC) 0.5 ng/µl) (Appendix C, Table C.1). Exactly 8 ml acetonitrile was added and mixed by using vortex. The samples were put three times for 10 minutes into ultrasonic bath and vortexed in between. For sedimentation, the samples were centrifuged (2000 rpm, 5min).

Table 2. Different PFASs analyzed in eggs of snow bunting (*Plectrophenax nivalis*) that are members of three different groups.

Perfluoro- and polyfluoroalkyl substances (PFASs)			
Group	Acronym	Perfluoroalkyl carboxylic acids	Chemical formula
PFCA	PFBA	Perfluorobutanoic acid	C <sub>3</sub> F <sub>7</sub> COOH
	PFPA	Perfluoropentanoic acid	C <sub>4</sub> F <sub>9</sub> COOH
	PFHxA	Perfluorohexanoic acid	C <sub>5</sub> F <sub>11</sub> COOH
	PFHpA	Perfluoroheptanoic acid	C <sub>6</sub> F <sub>13</sub> COOH
	PFOA	Perfluorooctanoic acid	C <sub>7</sub> F <sub>15</sub> COOH
	PFNA	Perfluorononanoic acid	C <sub>8</sub> F <sub>17</sub> COOH
	PFDCa	Perfluorodecanoic acid	C <sub>9</sub> F <sub>19</sub> COOH
	PFUnA	Perfluoroundecanoic acid	C <sub>10</sub> F <sub>21</sub> COOH
	PFDoA	Perfluorododecanoic acid	C <sub>11</sub> F <sub>23</sub> COOH
	PFTriA	Perfluorotridecanoic acid	C <sub>12</sub> F <sub>25</sub> COOH
		Perfluorotetradecanoic acid	C <sub>13</sub> F <sub>27</sub> COOH
		<b>Perfluoroalkane sulfonic acid</b>	
PFSA	PFBS	Perfluorobutane sulfonic acid	C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> H
	PFHxS	Perfluorohexane sulfonic acid	C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> H
	PFOS	Perfluorooctane sulfonic acid	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H
	PFDCS	Perfluorodecane sulfonic acid	C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> H
		<b>Perfluoroalkane sulfonamide</b>	
PASF	PFOSA	Perfluorooctane sulfonamide	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> NH <sub>2</sub>

### Clean up

The supernatant was transferred to PP-centrifuge tubes and concentrated down to exactly 1 ml in RapidVap. The supernatant extract was transferred to Eppendorf centrifuge tubes (1.7 ml) with 25 mg ENVI-Carb (Superclean ENVI-Carb 120/400, Superlco 57210-U) and 50 µl glacial acetic acid, followed by vortexing. Next, the samples were centrifuged (10 000 rpm, 10 min), 500 µl of the supernatant solution was transferred to an auto injector vial, and 20 µl recovery standard (0.1 ng/µl, 3.7 brPFDCa, in methanol) was added. Prior the LC-MS analysis, 100 µl extract and 100 µl 2 mM NH<sub>4</sub>OAc in HLB-water were transferred to a LC-vial.

### Instrumental analysis

Liquid chromatography is preferred when the compounds is not sufficient volatile for gas chromatography. High performance liquid chromatography utilizes pressure to move solvents through closed columns, where they are separated based on their affinity to the stationary phase. The column contains fine particles, which contributes to a high-resolution separation (Harris, 2010).

### **Instrumental setting**

100 µl extract was transferred to an autosampler vial with insert and diluted with the 100 µl 2mM aqueous NH<sub>4</sub>OAc. The different PFASs were analysed by ultrahigh pressure liquid chromatography with triple-quadrupole mass spectrometry (UHPLCMS/MS). The analysis was performed on a Thermo Scientific quaternary Accela 1250 pump with a PAL Sample Manager coupled to a Thermo Scientific Vantage MS/MS (Vantage TSQ). An injection volume of 10 µl was used for sample separation on a Waters Acquity UPLC HSS 3T column (2.1 X 100 mm, 1.8 µm) equipped with a Waters Van guard HSS T3 guard column (2.1 X 5 mm, 1.8 µm). A Waters XBridge C18 column (2.1 X 50 mm, 5 µm) was installed after the pump and before the injector in order to separate PFCA contamination leaching out from the pump and the degasser. Separation was achieved using 2 mM NH<sub>4</sub>OAc in 90:10 water:metanol and 2 mM methanolic NH<sub>4</sub>OAc as the mobile phases.

### **Quantification**

Quantification on the PFASs was performed by the same internal standard procedure as for the organochlorinated and brominated compounds.

### **Quality assurance of the method**

Prior to the extraction and clean-up procedures, all the equipment was rinsed with methanol. For every tenth sample, one blank and one standard reference material (SRM 1957, Human Serum, National Institute of Standards and Technology, NIST, MD, USA) was extracted. Limit of detection (LOD) was defined as three times blank or background signal (Appendix D, Table D.1).

### **2.6 Statistical analysis**

The statistical analysis was performed using SPSS Statistical Software (Version 19.0 for Windows, IBM, SPSS Inc., Chicago, IL).

To test for normal distribution when  $n < 50$ , Shapiro-Wilk test were applied and Lavene's test was applied to test for homogeneity of variance in the dataset. The significant test for the different means of contaminants between the locations were performed with one way analysis of variance (ANOVA) on ranked values. Welch

correction were used for unequal variances and Games-Howell were performed for unequal sample size and unequal variance to investigate the difference between the groups. The significant tests were performed on ranked values because it was not possible to achieve normal distribution for all the variables (Conover and L.I., 1981).

To test the difference of the biological variables between the different locations, Kruskal-Wallis test and Mann-Whitney test (2-tailed) was performed on untransformed data. Mann-Whitney test was additionally used to investigate differences between the Russian settlements as one group, and the Norwegian settlements as one group. Correlation between the different variables was investigated by using Spearman's correlation coefficient test (2-tailed) on  $\log_{10}$  transformed data. The significant level was set to  $p < 0.05$  for all the tests.

Contaminants detected in less than 60 % of the samples were excluded from the results. This includes *p,p'*-DDT, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, *trans*-chlordane, *cis*-chlordane, *oxy*-chlordane, *cis*-nonachlor, mirex, PBDE-47, PBDE-153, PFOSA, PFBS, PFHxS, PFDcS, PFBA, PFPA, PFHxA, PFHpA, PFOA and PFTeA. As a result of instrumental errors, PBDE-99 was not included in the statistics. Concentrations below the limit of detection (LOD) in the samples included in the results were given a value of  $0.5 \cdot \text{LOD}$  to avoid missing values. The results include biometric parameters (lipid content (%), egg volume ( $\text{cm}^3$ ), clutch size) and contaminant concentrations (wet weight [w.w.]). Figures are based on mean concentration, and additionally standard deviation when error bars are presented.

## **2.7 Principal component analysis**

Multivariate analysis was conducted using Simca-P+ 12.0 (Umetrics, Umeå, Sweden). A principal component analysis (PCA) utilizes orthogonal transformation of possibly correlated variables into a dataset uncorrelated variables called principal components (Eriksson et al., 2006). These principle components (PCs) explain as much as possible of the variance in the dataset, and the first principal component explains the main load of the variance. Prior to PCA, the variables were mean centered (the mean of the variables are subtracted) and scaled by using unit variance (UV) to obtain equal unit variance of the variables, independent of their absolute value (Eriksson et al., 2006). In addition, all

the variables were  $\log_{10}$  transformed in order to improve the model. Further on, the model was interpreted with respect to the goodness of fit ( $R^2X$ ) and goodness of prediction ( $Q^2X$ ).

The PCA analysis was applied to visualize the relationship of the contaminants with concentrations given in wet weight, biological variables and the individual eggs between the respective locations. To avoid strong correlations,  $\sum_7\text{PCB}$  (i.e. the sum of the concentration of PCB-28/31, PCB-52, PCB-118, PCB-153, PCB-138, PCB-180) and  $\sum_6\text{PFAS}$  (i.e. the sum of the concentration of PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA) were excluded from the model. The number of principal components in this model were four, explaining 75.5 % of the variation.

### 3. Results

#### 3.1 Biological variables

Biological measurements in eggs of snow buntings (volume (cm<sup>3</sup>), lipid content (%) and clutch size) are presented in Table 3. The individual biological measurements are presented in Appendix E, Table E.1.

Table 3. Egg volume (cm<sup>3</sup>), clutch size and lipids (%) in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (LYB), Ny-Ålesund (NÅ), Barentsburg (BAR) and Pyramiden (PYR).

	Egg volume (cm <sup>3</sup> )				Clutch size				Lipids (%)			
	Mean	SD	Median	Range	Mean	SD	Median	Range	Mean	SD	Median	Range
LYB	3.11	0.05	3.06	2.34-4.15	5.67	1.05	5.67	4.00-7.00	7.08	1.99	6.40	4.13-9.75
NÅ	3.01	0.31	2.97	2.62-3.52	4.50 <sup>a</sup>	0.38	4.50	4.00-5.00	6.60	1.37	6.90	4.36-8.38
BAR	2.97	0.24	2.79	2.48-3.27	5.40	0.39	5.40	5.00-6.00	7.53	2.42	7.52	4.56-12.62
PYR	3.02	0.22	2.99	2.70-3.31	5.57	0.53	6.00	5.00-6.00	4,79 <sup>b</sup>	0.72	4.59	0.72-5.90

a: Significant lower clutch size compared to the other locations.

b: Significant lower lipid content compared to the other locations.

No significant difference was found between the locations regarding egg volume (Kruskal-Wallis,  $H = 3$ ,  $p > 0.199$ ). Significant differences were found between the locations regarding the lipid content in the eggs (Kruskal-Wallis,  $H = 3$ ,  $p < 0.026$ ) and the clutch size (Kruskal-Wallis,  $H = 3$ ,  $p < 0.004$ ). The clutch size in Ny-Ålesund was significant lower than in Longyearbyen (Mann-Whitney U test;  $U = 9$ ,  $p = 0.013$ ), Barentsburg (Mann-Whitney U test;  $U = 3$ ,  $p < 0,001$ ) and Pyramiden (Mann-Whitney U test;  $U = 3$ ,  $p < 0,002$ ). Some eggs were collected before the egg laying sequence of the clutch was finished. As a consequence, the clutch size mean from the respectively location was used as replacement for missing values. This means that the clutch size mean is an inaccurate variable, and must be interpreted with regard to this uncertainty. There was no difference in clutch size from Pyramiden, Barentsburg and Longyearbyen. Furthermore, lipid content in eggs from Pyramiden was significant lower than the lipid content in eggs from Longyearbyen (Mann-Whitney U test;  $U = 7$ ,  $p = 0.014$ ), from Barentsburg (Mann-Whitney U test;  $U = 7$ ,  $p = 0,008$ ) and from Ny-Ålesund (Mann-Whitney U test;  $U = 9$ ,  $p = 0,029$ ). No difference in the lipid content was found between Longyearbyen, Barentsburg and Ny-Ålesund.

### 3.2 Concentrations

The concentration of  $\Sigma_7$ PCB, *p,p'*-DDE, HCB, *trans*-nonachlor and  $\Sigma_6$ PFAS at the four locations are presented in Figure 3 and Appendix F, Table F.1 and F.2. The individual concentrations of OHCs are presented in Appendix I, Table I.1 and I.2.

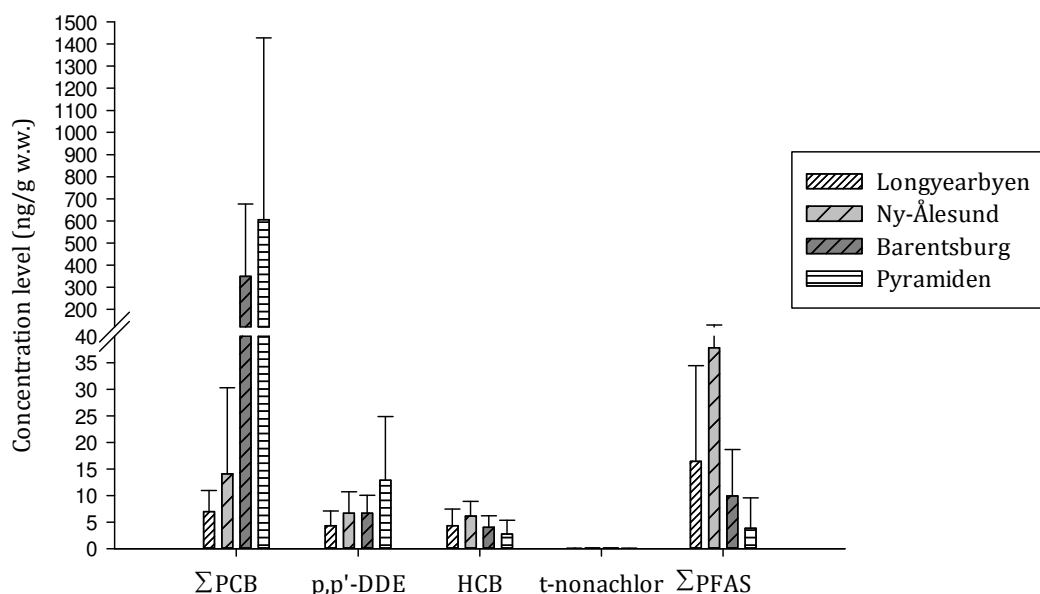


Figure 3. Concentration level (mean and standard deviation, ng/g w.w.) of  $\Sigma_7$ PCB, *p,p'*-DDE, HCB, *trans*-nonachlor and  $\Sigma_6$ PFAS in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7).  $\Sigma_7$ PCB includes PCB-28/31, PCB-53, PCB-118, PCB-153, PCB-138 and PCB-180.  $\Sigma_6$ PFASs includes PFOS, PFNA, PFDcA, PFUnA, PFDoA and PFTriA.

The concentration of  $\Sigma$ POP in eggs of snow buntings in Longyearbyen was  $32.06 \pm 27.98$  ng/g w.w. (mean  $\pm$  SD), Ny-Ålesund  $64.80 \pm 114.28$  ng/g w.w., Barentsburg  $370.27 \pm 341.06$  ng/g w.w. and Pyramiden  $624.33 \pm 843.12$  ng/g w.w. The concentration of  $\Sigma$ POP in eggs of snow buntings in the Russian settlements was 5-20 times higher than in the Norwegian settlements. In two samples from Pyramiden, PYR9 and PYR10, the concentrations for all the PCB congeners were below detection limit. Further on, sample PYR7 had twice the concentration of PCB compared with the sample with second highest concentration. This contributes to a great standard deviation for the Pyramiden samples regarding  $\Sigma_7$ PCB. The group of compounds that were most abundant in Longyearbyen and Ny-Ålesund were  $\Sigma_6$ PFAS, with  $16.43$  ng/g w.w. and  $37.80$  ng/g w.w., respectively. The concentration of sample NÅ15 was 100 times higher for PFOS compared with the sample with the second highest concentration. This contributes to a wide range and



elevated mean of  $\sum_6$ PFAS in the Ny-Ålesund samples. As a consequence, this may contribute to a misleading interpretation of the contaminant pattern. Thus, the mean concentration levels must be assessed with caution.

$\sum_7$ PCB, as well as the individual congeners PCB-28/31, PCB-52, PCB-118, PCB-153, PCB-138, PCB-180, HCB, *trans*-nonachlor and the individual PFAS compounds PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA differed significantly between the locations (Welch's F(3, [13.997-15.516], all  $p < 0.040$ ). Neither  $p,p'$ -DDE (Welch's F(3, 14.991) = 2,492,  $p = 0.100$ ) nor  $\sum_6$ PFAS (Welch's F(3, 15.349) = 2.391,  $p = 0.108$ ), differed between any of the locations.

When comparing the concentration in eggs of snow buntings from Longyearbyen with the two Russian settlements, Barentsburg depicted a significant higher concentration of all the different PCB congeners (Games-Howell, all  $p < 0.008$ ), including  $\sum_7$ PCB (Games-Howell,  $p < 0.001$ ). On the other hand, when comparing Longyearbyen with Pyramiden, significant higher concentration in Pyramiden was found only for PCB-28/31 (Games-Howell,  $p = 0.045$ ). No significant differences were found for any of the other PCB congeners, including  $\sum_7$ PCB (Games-Howell, all  $p > 0.152$ ). When comparing Ny-Ålesund with Barentsburg, significant higher concentration in Barentsburg was found for all the different PCB congeners (Games-Howell, all  $p < 0.044$ ), including  $\sum_7$ PCB (Games-Howell,  $p = 0.001$ ). When comparing Ny-Ålesund and Pyramiden, significant higher concentration of PCB-52 (Games-Howell,  $p = 0.049$ ) was found in Pyramiden, but no significant concentration was found for any of the other PCB congeners, including  $\sum_7$ PCB (Games-Howell, all  $p > 0.115$ ). There were no significant differences between the two Russian settlements or between the two Norwegian settlements for any of the PCB congeners, nor  $\sum_7$ PCB (Games-Howell, all  $p > 0.215$ ).

With respect to the PFASs in eggs of snow buntings, the results indicated a minor contribution of these compounds in Pyramiden compared with Longyearbyen, Ny-Ålesund and Barentsburg. Even though  $\sum_6$ PFAS did not differ between the locations, there were some differences in single compounds between the locations. The details in the statistics show that Pyramiden had significant lower concentration of PFNA, PFDoA, PFDcA and PFUnA (Games-Howell, all  $p < 0.034$ ), than Barentsburg. Further on,

Pyramiden had significant lower concentrations of PFNA, PFDoA, PFDcA and PFOS (Games-Howell, all  $p < 0.041$ ) than Longyearbyen. Finally, Pyramiden had significant lower concentration of PFNA, PFDoA and PFTriA (Games-Howell, all  $p < 0.039$ ) than Ny-Ålesund.

With respect to HCB and *trans*-nonachlor in eggs of snow buntings, Ny-Ålesund showed significant higher concentration when compared to Pyramiden (Games-Howell, all  $p < 0.028$ ), while none of the other locations were significant different regarding concentrations of these contaminants (Games-Howell, all  $p > 0.132$ ). The compound that contributed least in all the locations was *trans*-nonachlor, with a concentration mean range of 0.04-0.11 ng/g w.w.

### 3.3 Contaminant pattern

Figure 4 shows the relative distribution of the different contaminants in eggs of snow buntings among the four different locations. The contaminant pattern indicates a different distribution of the compounds between the Russian and the Norwegian settlements. The contaminants that were most abundant in eggs from Longyearbyen and Ny-Ålesund were  $\sum_6$ PFAS followed by  $\sum_7$ PCB, *p,p'*-DDE, HCB and *trans*-nonachlor. The contribution of  $\sum_6$ PFAS to Ny-Ålesund is influenced by an extreme outlier regarding PFOS, thus, the results must be interpreted with regards to the outlier. In Barentsburg and Pyramiden on the other hand, the contaminants that mainly contributed to the total contaminant load was  $\sum_7$ PCB.  $\sum_6$ PFAS, *p,p'*-DDE, HCB and *trans*-nonachlor are only minor contributors to the total contamination load in the Russian settlements, with *trans*-nonachlor contributing with less than 0.03 % in Barentsburg and Pyramiden.

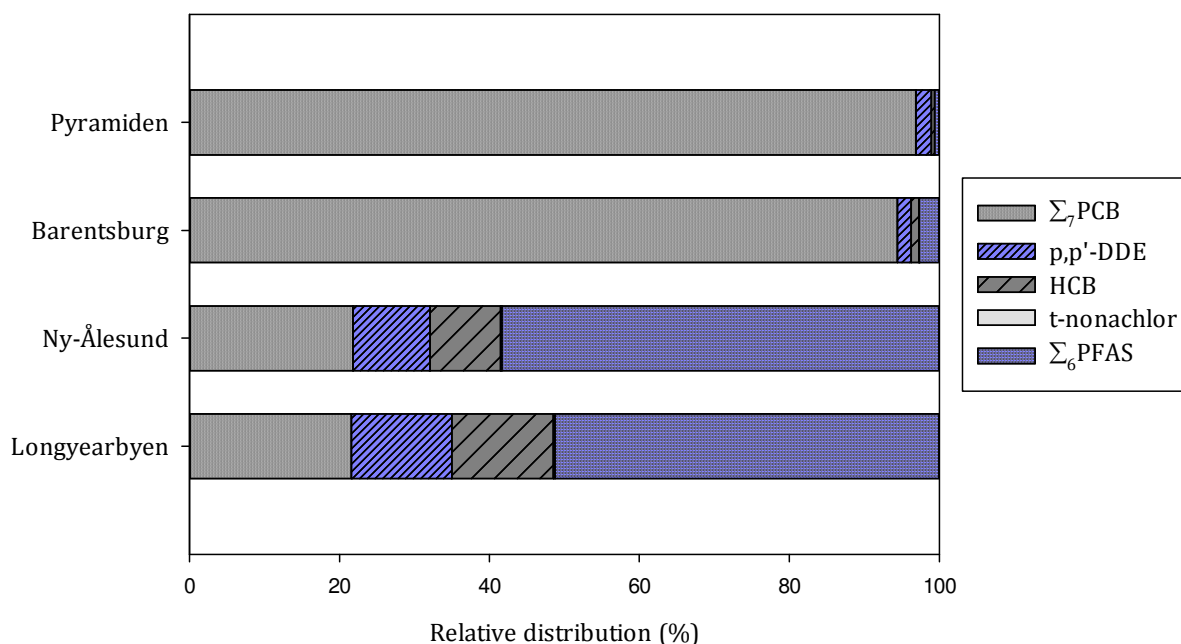


Figure 4. Relative distribution (%) of  $\Sigma_7$ PCB, p,p'-DDE, HCB, trans-nonachlor and  $\Sigma_6$ PFAS derived from wet weight mean concentration in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7).

Figure 5 shows the relative distribution of the different PFASs in eggs of snow buntings among the different locations.  $\Sigma_6$ PFASs includes both perfluorinated sulfonates (PFSA) and perfluorinated carboxylates (PFCA). The perfluorinated sulfonate, PFOS, constituted approximately 60 % of the PFASs, while the perfluorinated carboxylates, PFNA, PFDCa, PFUnA, PFDoA and PFTriA, made up the remaining amount of the contaminant burden in the eggs. The PFASs that were most abundant in eggs from Longyearbyen were PFNA, PFUnA and PFOS, which were all similar distributed. The PFASs that were most abundant in eggs from Ny-Ålesund were PFOS constituted 84 % of the PFAS burden. The high PFOS contribution in Ny-Ålesund is possibly caused by an outlier. Moreover, the total PFOS contribution to the PFAS burden in Ny-Ålesund is also influenced by this outlier. As a result of the outlier, PFNA, PFDCa, PFUnA, PFDoA and PFTriA constituted a minor part of the total PFAS burden in Ny-Ålesund. Finally, the PFASs that were most abundant in eggs from Barentsburg and Pyramiden were PFOS, PFUnA and PFTriA. PFCAs with a carbon chain shorter than 8C were only detected in less than 60 % of the samples.

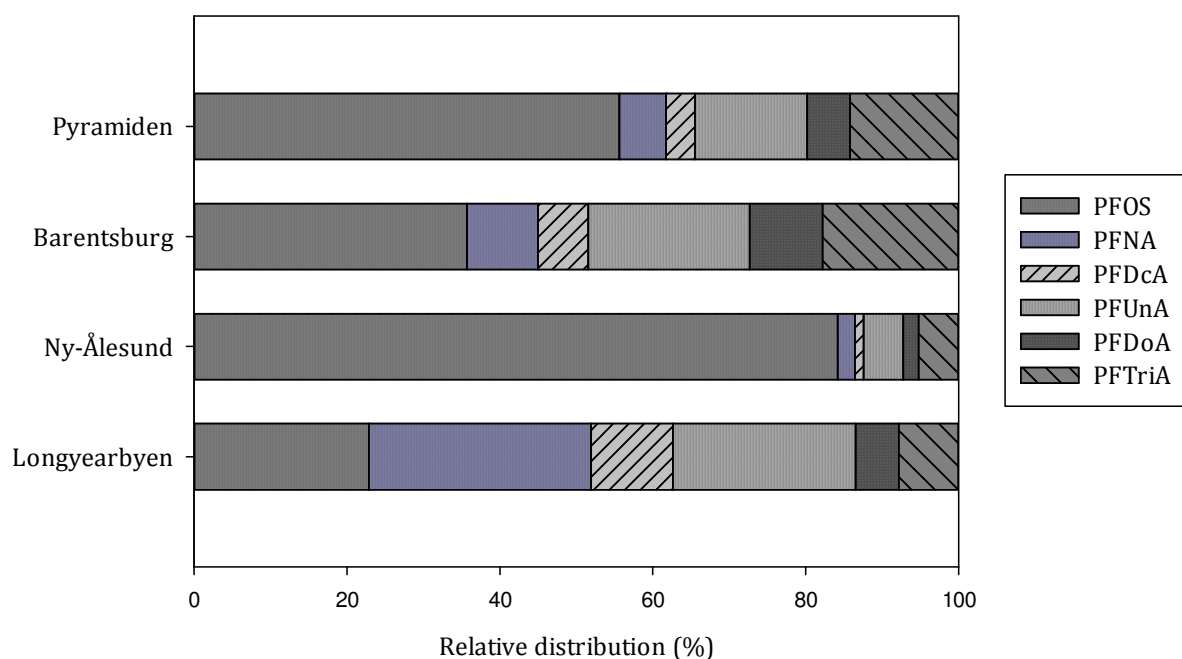


Figure 5. The relative distribution (%) of individual PFASs derived from wet weight mean concentrations in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7).

The PCB congener pattern in eggs of snow buntings indicates different distribution of the less and more chlorinated PCBs between the Russian and the Norwegian settlements. The PCB congeners that contributed mainly in eggs from Barentsburg and Pyramiden were PCB-118, PCB-138, and PCB-153 (Figure 6). In Longyearbyen and Ny-Ålesund on the other hand, the more heavy PCB congeners contribute more to the total PCB distribution in the eggs; PCB -138, PCB-153 and PCB-180.

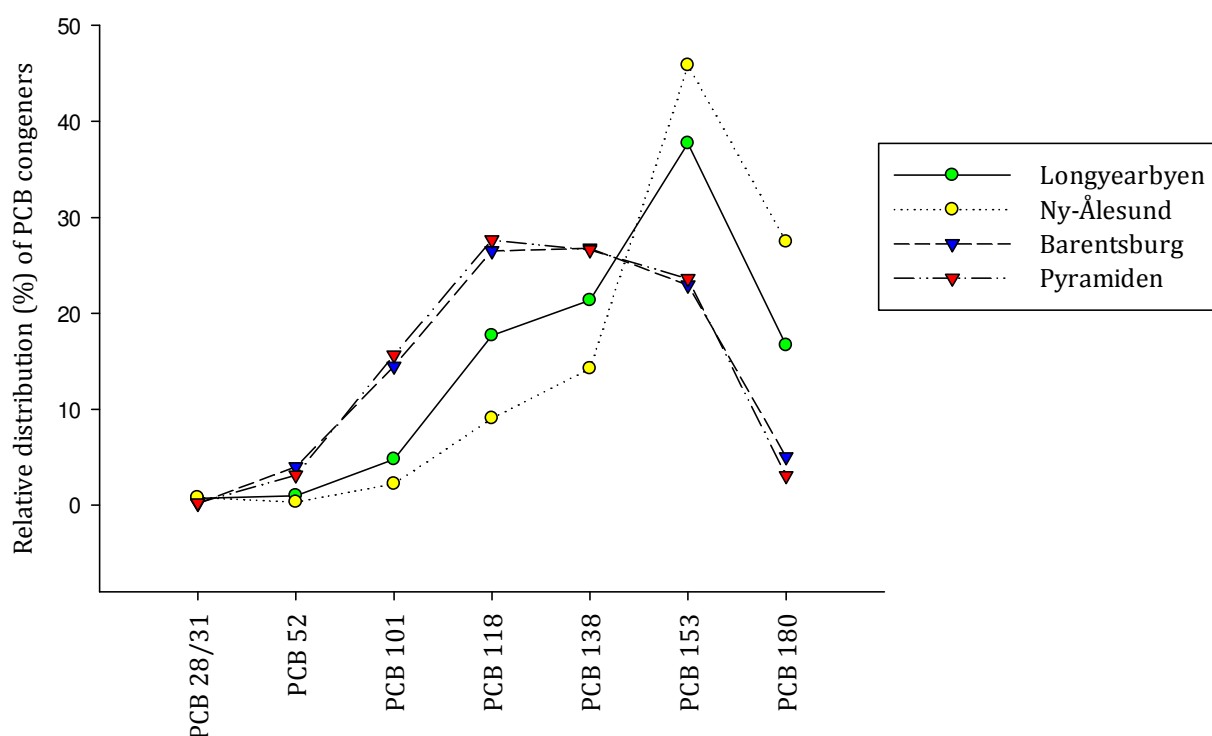


Figure 6. Relative distribution (%) of PCB congeners derived from wet weight mean concentrations in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7).

### 3.4 Principal component analysis

The score plot and the loading plot are presented in Figure 7 and Figure 8. The analysis of the compounds resulted in four different principal components (PC) (eigenvalues > 1), which explained 75.5 % of the variation. The main load was explained by PC1 (30.6 %) and PC2 (25.7 %). The score represents the different individuals from the different locations, LYB=Longyearbyen, NÅ=Ny-Ålesund, BAR=Barentsburg and PYR=Pyramiden. The contaminant burden in each individual represents the diversity and the spread of the contaminant pattern in the different locations. Hence outliers have not been removed. Appendix J, Table J.1 and Table J.2 presents the values of the Spearman's correlation coefficient test.

The score plot indicates how the observations from the respectively location are related to each other based on the different variables. The pattern indicates a separation of the Norwegian settlements (Longyearbyen and Ny-Ålesund), and the Russian settlements (Barentsburg and Pyramiden) along PC1. Longyearbyen and Ny-Ålesund are located on the left side along, whereas Barentsburg and Pyramiden are located on the right side

(Figure 7). Further on, the score plot indicates a separation between the two Russian settlements, where Barentsburg eggs and Pyramiden eggs are divided into two separate groups. The two Norwegian settlements, on the other hand, are not different from each other in a manner that can be explained by neither PC1 nor PC2.

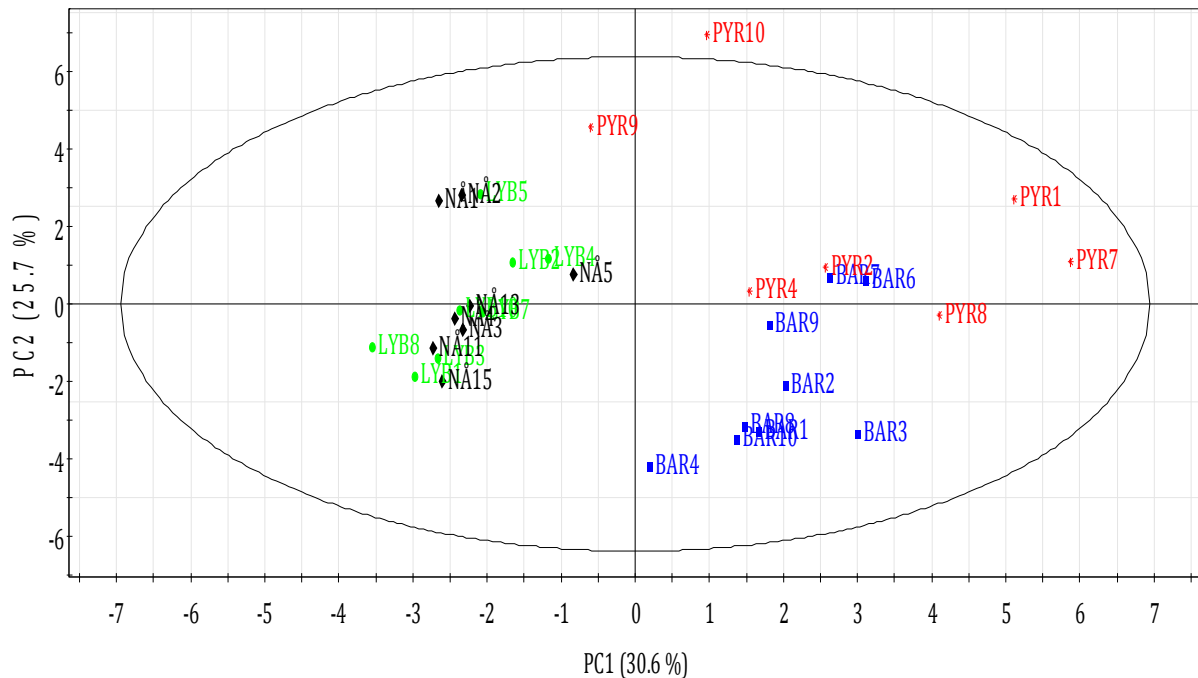


Figure 7. PCA score plot for 32 eggs of snow bunting (*Plectrophenax nivalis*) from Loneyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7). The score plot includes the variables PCB-28/31, PCB-53, PCB-118, PCB-153, PCB-138, PCB-180, PFOS, PFNA, PFDcA, PFUnA, PFDcA, PFTriA, *p,p'*-DDE, *trans*-nonachlor, HCB, lipid content (%), volume (cm<sup>3</sup>) and clutch size. The samples from Loneyearbyen are green and labeled LYB, the samples from Ny-Ålesund are black and labeled NÅ, the samples from Barentsburg are blue and labeled BAR, and the samples from Pyramiden are red and labeled PYR. In addition the samples are labeled with an individual number from 1 to 10, 11, 13 and 15.

The loading plot indicates how the different variables are related to each other (Figure 8). This is visualized in a two dimensional plot that constitute PC1 (range 0.0-0.35) and PC2 (range 0.0-0.20). The individual PCA loadings are presented in Appendix G, Table G.1. The same pattern that was indicated in the score plot (Figure 7) is also evident in the loading plot. The two Russian settlements appear on the right side of the plot, though separated by PC1, and the Norwegian settlements appear on the left side along PC1 (Figure 8). The PCBs (PCB-28/31, PCB-53, PCB-118, PCB-153, PCB-138, PCB-180) were all positively correlated with PC1 (all  $r_s > 0.521$ ,  $p < 0.002$ ). Furthermore, as observed in the loading plot, there was a high positive inter-correlation between the different PCBs (all  $r_s > 0.461$ ,  $p < 0.008$ ), In addition, PCB-28/31 and *p,p'*-DDE were

positively correlated ( $r_s = 0.477$ ,  $p = 0.006$ ). Despite the positive correlation with PC1, PCB-28/31 also correlated negatively with PC2 ( $r_s = -0.351$ ,  $p = 0.049$ ).

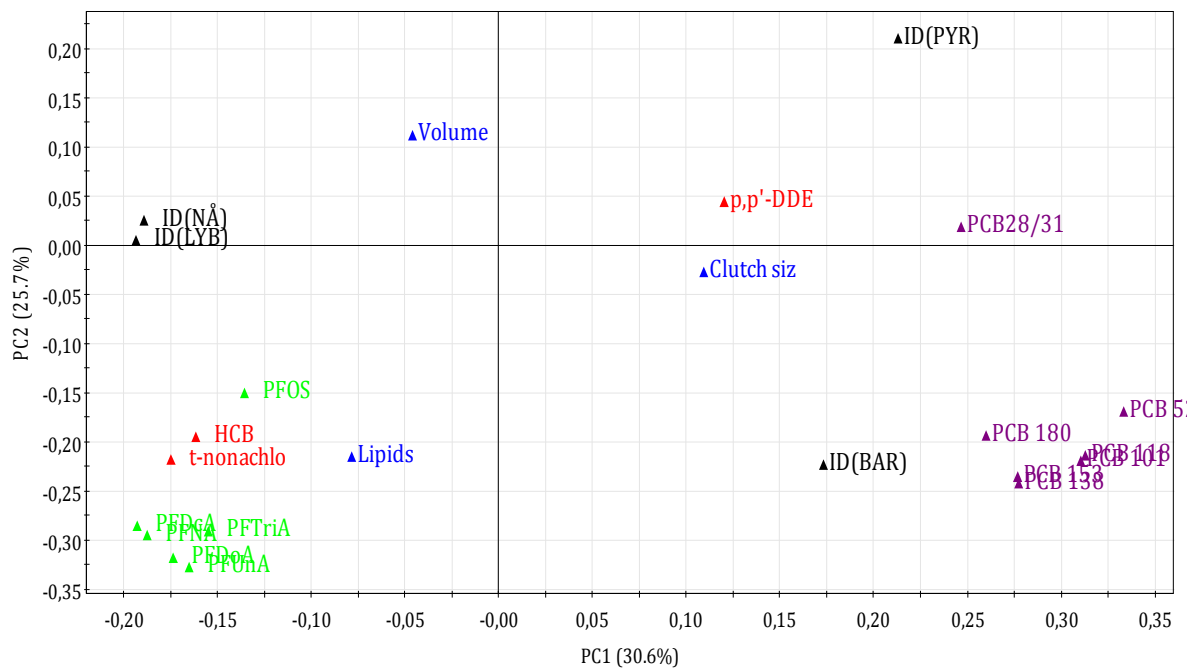


Figure 8. PCA loading plot for 32 eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8), Ny-Ålesund (n=8), Barentsburg (n=9) and Pyramiden (n=7). The loading plot includes the variables PCB-28/31, PCB-53, PCB-118, PCB-153, PCB-138, PCB-180, PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA, *p,p'*-DDE, *trans*-nonachlor, HCB, lipid content (%), volume (cm<sup>3</sup>) and clutch size. The four locations, Longyearbyen (LYB), Ny-Ålesund (NÅ), Barentsburg (BAR) and Pyramiden (PYR) are quantifying x- variables.

The PFASs (PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA) all correlated positively with PC2 (all  $r_s > 0.650$ ,  $p < 0.001$ ), in addition to positively inter-correlate with each other (all  $r_s > 0.461$ ,  $p < 0.008$ ), as visualized in Figure 8. Further on, *trans*-nonachlor correlated positively with all the PFASs (all  $r_s > 0.491$ ,  $p < 0.004$ ), in addition to HCB ( $r_s = 0.777$ ,  $p < 0.001$ ). HCB indicated the same pattern and correlated positively with PFOS, PFNA, PFUnA, PFDoA and PFTriA (all  $r_s > 0.360$ ,  $p < 0.043$ ). Finally, the lipid content did also correlate positively with *trans*-nonachlor, HCB, PFOS, PFNA, PFUnA, PFDoA and PFTriA (all  $r_s > 0.353$ ,  $p < 0.048$ ). These correlations are indicated by the loading plot (Figure 8), where the different PFASs, lipid content, HCB and *trans*-nonachlor appear together.

The two Norwegian settlements are located to the left together with the PFASs, *trans*-nonachlor, HCB, while the Russian settlements are located to the right together with the PCBs and *p,p'*-DDE, indicating a separation of settlements based on the contaminant load

(Figure 8). This further confirms the separation of the settlements in the score plot (Figure 7). The egg volume did not correlate with any of the variables, and could not be explained by the model. Clutch size correlated positively with PCB-52 ( $r_s = 0.504$ ,  $p = 0.003$ ), but with no other variables. Hence, clutch size could not be explained by the model.

### 3.5 Comparison of the Russian and the Norwegian settlements

The score plot (Figure 7) and the loading plot (Figure 8) indicated a separation of the Norwegian and Russian settlements. Consequently, Figure 9 represents a comparison of the contaminant concentrations in eggs of snow buntings in the Russian settlements as one group and the eggs in the Norwegian settlements as one group. The concentration of  $\Sigma_7$ PCB,  $p,p'$ -DDE, HCB, *trans*-nonachlor and  $\Sigma_6$ PFAS at the four locations are presented in Appendix H, Table H.1.

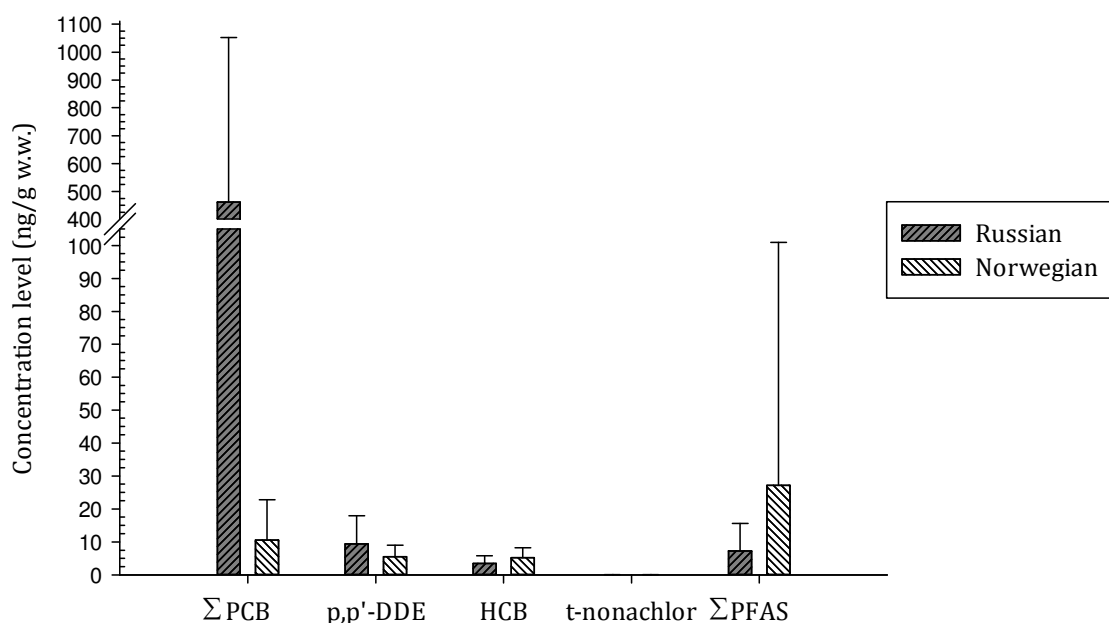


Figure 9. Concentration level (mean and standard deviation, ng/g w.w.) of  $\Sigma_7$ PCB,  $p,p'$ -DDE, HCB, *trans*-nonachlor and  $\Sigma_6$ PFAS in the Norwegian settlements (n=16) and the Russian settlements (n=16).  $\Sigma_7$ PCB includes PCB-28/31, PCB-53, PCB-118, PCB-153, PCB-138 and PCB-180.  $\Sigma_6$ PFASs includes PFOS, PFNA, PFDCa, PFUnA, PFDoA and PFTriA.

The concentration of  $\Sigma$ POP in eggs of snow buntings in the Russian settlements was  $481.42 \pm 609.88$  ng/g w.w. (mean  $\pm$  SD), while in the Norwegian settlements the concentration was  $48.43 \pm 92.63$  ng/g w.w. When compared with the Norwegian settlements, the concentration of  $\Sigma$ POP the Russian settlements are approximately 10



times higher. This further confirms the distinct separation of the two settlements based on contaminant load. Nevertheless, large standard deviations indicate large variations within the locations, with low and extreme values, and the concentration means must be interpreted with regard to the variations.

The details in the statistics show that egg of snow buntings from the Russian settlements have significant higher concentration of  $\sum_7\text{PCB}$  (Mann-Whitney U = 32, all  $p < 0.001$ ), as well as the individual congeners, PCB-28/31, PCB-52, PCB-118, PCB-153, PCB-138, PCB-180 (Mann-Whitney U = 20.5-38, all  $p < 0.001$ ) than the Norwegian settlements.

With respect to the PFASs, the results did not show any significant difference between  $\sum_6\text{PFAS}$  (Mann Whitney U = 89,  $p = 149$ ) in the Russian and the Norwegian settlements. Further on, the results did not show any significant difference between any of the individual PFAS compounds PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA (Mann-Whitney U = 76-192, all  $p > 0.051$ ), when comparing the Russian and the Norwegian settlements.

With respect to HCB and *trans*-nonachlor, the results showed significant higher concentration of both compounds in the Norwegian settlements (Mann-Whitney U = 70-75.5, all  $p < 0.047$ ) compared with the Russian settlements. On the other hand, the Russian settlements had significant higher concentration of *p,p'*-DDE (Mann-Whitney U = 73,  $p = 0.039$ ) than the Norwegian settlements.

With respect to egg volume and egg lipid content, there were no significant difference between the Russian and the Norwegian settlements (Mann-Whitney U = 92-103, all  $p > 0.184$ ). The clutch size are borderline higher in the Russian settlements (Mann-Whitney U = 77,  $p = 0.05$ ). As a consequence of several replaced values with location clutch size mean, clutch size mean is an inaccurate variable, and must be interpreted with regard to this uncertainty.

## 4. Discussion

There are few reports that have reported contaminant levels in snow buntings (Choy et al., 2010), and to my knowledge, this is the first study to report environmental contaminants in snow buntings from Svalbard. This study's main objective was to investigate if the snow buntings breeding in the Russian settlements had higher concentrations of PCB in their eggs than snow buntings breeding in the Norwegian settlements. By utilizing the snow bunting as a sentinel species, distinct differences regarding both the contaminants concentration and contaminant pattern were found in the eggs from the respective locations. The eggs in Barentsburg and Pyramiden were found to have 25-87 times higher mean concentration of  $\sum_7$ PCBs than the eggs in Longyearbyen and Ny-Ålesund. This indicates influence of local pollution. This local influence by contaminants was further confirmed by the PCB congener pattern in the eggs. Local influence of contaminants cannot be excluded in the Norwegian settlement. The PCB concentration in this study was found to be lower or comparable with other birds investigated in Svalbard.

### 4.1 Biological variables

The clutch size was determined by counting the eggs in the nest in the best possible way. Reaching the eggs in the nest was very challenging; sometimes only a few eggs were possible to reach. This resulted in an uncertain estimation of clutch size. Moreover, some eggs were collected before the female had finished her egg laying, resulting in an unknown number of eggs in the clutch. The unknown values were replaced by the clutch size mean from the respective locations, thus making the clutch size an unreliable variable. The egg lipid content (%) was determined by evaporating an aliquot of the extracted egg content. Thus, other organic materials, such as proteins dissolved in the extract, were not taken into consideration. Therefore, the lipid content should be referred to as extracted organic material (EOM), and not pure lipids. Since EOM most frequently are referred to as lipids, I have chosen to call it lipids in this text. The statistical analysis showed that the egg volume was not significantly different between any of the locations (Table 3). Lipid content (%) and clutch size were significantly different between the locations. As a consequence of the uncertainties regarding determination of the variables, clutch size and lipid content will not be further discussed. Verboven et al., (2009) suggested that a high sum of chlordanes ( $\sum$ CHL) and high sum of DDT ( $\sum$ DDT)

concentration in relation to low  $\Sigma$ PCB concentration caused smaller eggs in glaucous gulls from Bjørnøya. However, the egg volume was not different between the locations in this study. This indicates that the egg volume of snow buntings in Svalbard is not affected by OHCs.

#### **4.2 Factors influencing contaminant concentration in eggs**

Collecting representative wildlife data from the Arctic is challenging. The sample size in this study represents only a minor part of the population of snow buntings in Svalbard. Great variation in contaminant concentrations in the eggs within the locations indicates high individual differences within the snow bunting population. These individual differences may be explained by factors such as the physical condition of the female at the time of egg laying, age of the female, the quality of food at the feeding ground and time of arrival at the breeding area. Furthermore, contaminant exposure during migration and in the overwintering areas may contribute to the contaminant burden in snow buntings. Thus, the contaminant burden in the eggs may reflect not only local influence of contaminants in Svalbard, but also exposure from more urban areas. As only one egg was collected from each nest, inter-clutch variation may be a contributing factor to individual differences in contaminant burden. Furthermore, the contaminant burden in the eggs of snow buntings is a reflection of the exposure of contaminants via diet and further distribution to the eggs. As maternal transfer and exposure through diet are two important factors impacting the contaminant concentration in the eggs (Verreault et al., 2006), these factors will be further discussed (see below). It is important to note that this study can only report a status on levels of contaminants in eggs of snow buntings in Svalbard. Potential effects as a consequence of contamination have not been investigated. Thus, the contaminant concentration can only be discussed with respect to previous studies.

##### **Maternal transfer**

In this study, one egg of snow buntings was collected from each of the nests. It was not possible to decide the egg laying sequence when collecting the eggs. As snow buntings only incubate for 12-13 days, the developmental stages of the eggs in this study ranged from undeveloped egg yolk to developed chicks. However, the snow bunting does not start incubating until the last egg have been laid (Hussell, 1972). Thus, all of the eggs in

the clutch are equally developed. Verreault et al., (2006) concluded that the third and last egg laid by the glaucous gull is smaller and contains more lipids than the other eggs in the clutch. Thus, preferably the same egg from each clutch should be collected from the nest. Further would a non-incubated egg be optimal.

Several studies have been conducted on both sea- and passerine birds regarding maternal transfer. Van den Steen et al., (2009a) suggested that maternal transfer to the eggs was related to the investment in the eggs (i.e. number of eggs), as the authors found a decline in concentration from the first to the last laid egg by blue tits (*Cyanistes caeruleus*). However, as the among-clutch variation was greater than the intra-clutch variation in eggs of blue tits, the authors concluded that one randomly collected egg was useful as a biomonitoring tool for PCBs and PBDEs. Organochlorine pesticides, such as DDE, was found to vary within the clutch of warblers (*Protonotaria citrea*) and European starlings (*Sturnus vulgaris*) in Alabama and Colorado (Reynolds et al., 2004). The authors suggested that one random egg from the clutch should not be utilized as a biomonitoring tool, as one egg did not reflect the DDE concentration in the remaining eggs in the clutch. Results contradicting Van den Steen et al., (2009a) and Reynolds et al., (2004) were found by Verreault et al., (2006) and Van den Steen et al., (2006). The authors concluded that there were no laying order effects in eggs of glaucous gull and great tits (*Parus major*). The absence of intra-clutch differences could possibly be explained by the constantly remobilization of the maternal lipids, protein and contaminants during egg formation. Further on, continuously exposure of contaminants through food during the egg production could potentially get transferred to the eggs (Verreault et al., 2006). Small territories could also contribute to an explanation of the absence of intra-clutch variation (Van den Steen et al., 2006). However, as sea birds do not have small territories, whereas great tits do, this may be an explanation of minor importance. When considering that the great tit and blue tit lay twice as many eggs as the snow bunting, and consequently invests more in the eggs, comparison should be done with caution. Nevertheless, when taking species differences into consideration, using a single egg from each snow bunting nest to illustrate contaminant burden in the adult bird is appropriate.

### **Maternal investment in eggs**

Maternal transfer of contaminants is still poorly understood, but different factors influence maternal transfer of contaminants to the eggs. In the present study, the OHC concentration in eggs was investigated. The concentration in the adult bird can only be estimated on the knowledge from previous studies. However, it is challenging to extrapolate egg contaminant burden to maternal exposure. As a consequence of different physical and chemical properties of the contaminants, the distribution will depend on the tissue and contaminant investigated (Van den Steen et al., 2009a). Thus, the egg:maternal tissue ratio varies among different species, depending on contaminant properties and lipid recourses used during egg formation. Drouillard and Norstrom, (2001) suggested that altricial species investing low quantity of maternal lipids in the eggs may exhibit a egg:maternal tissue ratio of 0.3-0.7. As the snow bunting is an altricial species, this indicates that the maternal contaminant burden may be higher than the concentration revealed in the eggs. There are different strategies regarding the use of energy during reproduction, ranging from pure income breeders, where resources are derived from recently ingested resources, to pure capital breeders that uses endogenous reserves (Drent and Daan, 1980). Several passerine birds are known to be income breeders (Meijer and Drent, 1999). The snow bunting females feed on seeds and insects from the respectively locations, and it is assumed that it needs to consume nourishments every day. As a migratory bird, it needs to replenish the energy storage after migration, and is therefore constantly exposed to contaminants during egg formation. Thus, it is highly likely to assume that the snow bunting is an income breeder and transfers its most resent diet to the eggs (Moksnes, (2012), personal comments). Nevertheless, it is important to take into consideration that maternal transfer of contaminants is species specific, depending on several factors such as maternal exposure, diet and lipid investment (Verreault et al., 2006).

With respect to PFASs, there is little knowledge regarding maternal transfer. As PFASs have an affinity to proteins, in contrast to OCs, they are assumed to correlate with yolk proteins (Gebink et al., 2011). There is inconsistency regarding concentration in egg in relation to plasma, as well as preferential accumulation of long chained PFCAs in the egg relative to the liver (Verreault et al., 2005; Holmstrom et al., 2010; Gebink et al., 2011). To my knowledge, intra-clutch variation of PFASs has been reported in neither seabirds

nor in passerine birds. As knowledge regarding maternal transfer of PFASs is insufficient, the concentration in the eggs must be interpreted with respect to this.

## **Diet**

The snow bunting feeds on seeds and insects. Seeds constitute the main diet, but it consumes insects when it is available (Cramp and Perrins, 1994). It is not known whether the snow bunting consume insects prior to egg laying, but it feeds its nestlings with insects such as dipteras (e.g. *chironomidae* and *nematocera*) and spiders (Skjøstad, 2008). The insects possibly accumulate contaminants through its sediment-associated larvae stage, and thus function as a cohesion between the aquatic environment and the terrestrial environment (Larsson, 1984). Bioaccumulation and trophic transfer of PCBs from insects to tree swallows (*Tachycineta bicolor*) have confirmed this relationship (Maul et al., 2006). In contrast to insects, plants are available for the snow bunting early in the spring (e.g. *Cassiope tetragona*, *Poa alpina*, *Bistorta vivipara*, *Saxifraga oppositifolia*). Most of the vascular plants on Svalbard are perennial with nutritious storage compartments. Plants accumulate contaminants by deposition on the surface by particles, uptake of vapors or directly from the soil through the roots by vapors or water phases of the soil. However, uptake via root is thought to be limited (Lovett et al., 1997; AMAP, 1998), and depends on several factors such as lipid composition of the root (Collins et al., 2006), soil composition and compound properties (Higgins and Luthy, 2006). Since uptake via contaminated seeds and insects are the assumed most important route, an investigation of contaminant on the surface of the plants, in the plants and in invertebrates from the settlements is suggested.

## **4.5 Concentrations and patterns**

It is important to emphasize that direct comparison of concentrations from different tissue or different species is not appropriate. Seabirds and terrestrial passerine birds have different feeding habitats that will affect the accumulation of contaminants. Age, gender, physical condition, season for sampling, trophic level and metabolic capability are factors influencing the contaminant concentration at time of sampling. Moreover, migration could contribute to a contaminant load that is not representative for the Arctic environment. Nevertheless, a comparison of previous studies on both passerine birds and Arctic seabirds may be informative in this study.

## Concentration of PCB

In this study, PCBs was the most abundant contaminant in eggs of snow buntings in both of the Russian settlements (Figure 4). Polychlorinated biphenyls constituted more than 80 % of the total contaminant burden in the eggs. In Barentsburg and Pyramiden, mean  $\Sigma_7$ PCB concentration was more than 25 times higher than in Longyearbyen and Ny-Ålesund (Figure 3). The  $\Sigma_7$ PCB concentration, as well as all the individual PCB congeners, was significant higher in Barentsburg compared with the Norwegian settlements. This indicates a local contaminant source in Barentsburg. In eggs from Pyramiden, only two PCB congeners were significant higher compared with eggs from Longyearbyen and Ny-Ålesund. The absence of significant differences between eggs from Pyramiden and the Norwegian settlements regardless of high concentration, may be explained by the high concentration range between the different eggs from Pyramiden (Appendix I, Table I.1), and low sample size (n=7). The high concentration range in the Pyramiden eggs is further explained by the fact that the median is considerable lower than the mean concentration (Appendix F, Table F.2). For two eggs in Pyramiden, all the PCB congeners were below limit of detection. Moreover, in one egg (PYR 7), the PCB concentration was more than twice as high as the egg with the second highest concentration for several of the PCB congeners. Despite this, outliers were not excluded as they merely illustrate the individual variation occurring in nature. By testing the PCB concentrations in eggs of snow buntings in Barentsburg and Pyramiden against each other, and Longyearbyen and Ny-Ålesund against each other, no difference was found. When samples from the Norwegian settlements were combined in one group and samples from the Russian settlements in one group, (Figure 9), there were significant differences between the two groups. All the individual PCB congeners, as well as  $\Sigma_7$ PCB, were significant higher in eggs of snow buntings in the Russian settlements when compared with the Norwegian settlements. These results are further supported by the fact that the Russian settlements are heavily contaminated by PCB (Evenset, 2010; Jartun et al., 2010).

One sample (NÅ5) from Ny-Ålesund have approximately twice as high concentration of the three most chlorinated PCBs (PCB-138, PCB-153, PCB-180), than the sample with the second highest concentration (Appendix I, Table I.1). This egg was collected at Ossian Sars, a bird cliff occupied by black-legged kittiwakes (*Rissa tridactyla*) and

Brünnich's guillemots (*Uria Lomvia*). Choy et al., (2010) reported the same congeners as the dominant congeners in snow buntings that were possibly affected by sea bird guano by a bird cliff at Cape Vera, Canada. Further on, these congeners are known to biomagnify in food chains due to metabolic processes in the organisms (Evenset et al., 2007). Thus, the elevated concentration of PCB in this particular egg (NÅ5) compared with other eggs from Kongsfjorden may be due to input of contaminants by seabird guano. The two eggs (PYR7 and PYR8) with the highest PCBs concentration in Pyramiden were collected north in the settlement, close to the buildings located near the mine (Figure 2A). In a survey conducted by NGU, very high levels of PCBs was found in surface soil at this particular location (Jartun et al., 2010). As the snow buntings are territorial birds (Gjershaug et al., 1994), the female may have been feeding in this contaminated area prior egg laying. The soil in both Pyramiden and Barentsburg are heavily contaminated as a result of PCB containing paint and electrical waste in several of the locations where the eggs of snow buntings were collected (Jartun et al., 2008; Jartun et al., 2009c; Jartun et al., 2010). Moreover, the snow buntings may additionally be exposed by feeding on the ground close to buildings with PCB containing paint during snow melt. However, without observing the female in the period prior egg laying, it can only be assumed that the females were feeding in these contaminated areas when developing the eggs.

Both black-legged kittiwakes and glaucous gulls are nesting on buildings within Barentsburg and Pyramiden. However, this is not the situation in the Norwegian settlements. As seabirds have shown to be carriers of contaminants to pristine areas, (Evenset et al., 2007; Choy et al., 2010), the snow buntings in the Russian settlements may be influenced by seabirds breeding in the settlements. However, Miljeteig and Gabrielsen, (2009) showed that the black-legged kittiwakes breeding in Barentsburg and Pyramiden not were affected by local pollution as the more heavy PCB congeners, and not PCB-118, was dominant in their eggs. As a PCB-118 is the dominant congener in eggs from the Russian settlements (Figure 6), influence by PCB contaminated seabird guano in the settlements is not a likely explanation.



Table 4. Concentration of organochlorines and perfluorinated compounds in selected seabird eggs and liver, and whole passerine birds and eggs. Concentrations are presented in mean  $\pm$  SD, mean  $\pm$  SE or median and range in ng/g w.w..

Species	n	Matrix	$\Sigma$ PCB	DDE	$\Sigma$ DDT	HCB	<i>t</i> -nonachlor	$\Sigma$ PFAS	Reference
Snow bunting ( <i>Plectrophenax nivalis</i> ), Svalbard									
- Longyearbyen	8	Egg	6.93 $\pm$ 4.02	4.29 $\pm$ 2.79		4.34 $\pm$ 3.10	0.07 $\pm$ 0.03	16.43 $\pm$ 18.04	Present study 2012
- Ny-Ålesund	8		14.12 $\pm$ 16.23	6.67 $\pm$ 4.01		6.10 $\pm$ 2.78	0.11 $\pm$ 0.05	37.8 $\pm$ 91.21	
- Barentsburg	9		349.61 $\pm$ 326.76	6.69 $\pm$ 3.32		4.0 $\pm$ 2.17	0.08 $\pm$ 0.05	9.89 $\pm$ 8.76	
- Pyramiden	7		604.84 $\pm$ 822.77	12.87 $\pm$ 11.99		2.75 $\pm$ 2.59	0.04 $\pm$ 0.02	3.82 $\pm$ 5.76	
Snow bunting ( <i>Plectrophenax nivalis</i> )* - Canada	18	Whole bird	168 (11.7-601)	98.4 (4.3-380)	105.9 $\pm$ 29.2				Choy et al., (2010)
Great tit ( <i>Parus major</i> ), Belgium									
- Site 1**	22	Egg	298 (209-406)	35.6 (30-69)		1.82 (1.3-2.09)	0.99 (0.7-2.5)		Dauwe et al., (2006)
- Site 2**	22		179 (113-331)	36.9 (21-65)		1.63 (0.8-3.5)	0.68 (0.43-2.46)		
Clauous gull ( <i>Larus hyperboreus</i> )*** - Bear Island									
	32	Egg	1151 $\pm$ 72.5		343 $\pm$ 15.7	20.1 $\pm$ 1.12			Verreault et al., (2004a)
Black legged kittiwake ( <i>Rissa tridactyla</i> ), Svalbard									
- Kongsfjorden	10	Egg	423 $\pm$ 83	84.5 $\pm$ 56	91.5 $\pm$ 56.8	32.1 $\pm$ 5.5	5.17 $\pm$ 2.32	37.8 $\pm$ 12.5	Miljeteig and Gabrielsen, (2009)
- Barentsburg	10		918 $\pm$ 1470	331 $\pm$ 852	339 $\pm$ 855	46.6 $\pm$ 19.4	5.14 $\pm$ 3.9	62.9 $\pm$ 33.6	
- Pyramiden	10		428 $\pm$ 280	67.4 $\pm$ 23.9	77.5 $\pm$ 25.2	35.5 $\pm$ 9.9	6.79 $\pm$ 4.00	77.7 $\pm$ 36.3	
Brünnich's guillemot ( <i>Uria lomvia</i> ), Svalbard									
- Kongsfjorden 1993	5	Egg	447 $\pm$ 214	227 $\pm$ 112		54.1 $\pm$ 20.4	-	23.2 $\pm$ 3.7	Miljeteig and Gabrielsen, (2010)
- Kongsfjorden 2002	5		222 $\pm$ 60	129 $\pm$ 22		43.9 $\pm$ 6.3	-	29.6 $\pm$ 5.2	
- Kongsfjorden 2007	5		145 $\pm$ 29	111 $\pm$ 18		42.0 $\pm$ 4.0	-	21.9 $\pm$ 5.9	
- Bjørnøya 2003	5		189 $\pm$ 112	131 $\pm$ 27		51.3 $\pm$ 15.4	-	45.8 $\pm$ 15.3	
- Bjørnøya 2007	5		132 $\pm$ 6	103 $\pm$ 8.50		49.0 $\pm$ 2.01	-	64.8 $\pm$ 17.3	
Glaucous gull ( <i>Larus hyperboreus</i> ) Svalbard									
- Barentsburg	20	Liver	854 $\pm$ 401 (female)	270.8 $\pm$ 251.5	205 $\pm$ 85 (female)	22.2 $\pm$ 12.8	0.2 $\pm$ 0.3		Sagerup et al., (2009)

- not detected

\* Concentrations are given in mean and range

\*\* Concentrations given in median and range

\*\*\* Concentrations given in mean  $\pm$  SE

Choy et al., (2010) reported total body concentrations of OCs in snow buntings from Cape Vera, in the northern part of Canada (Table 4). The snow buntings were feeding on insects with an aquatic phase in ponds that were contaminated with organic contaminants transported by seabirds to the Arctic environment. The whole body  $\Sigma$ PCB concentration reported by the authors was 10-20 times higher when compared with eggs of snow buntings from the Norwegian settlements, and 2-3 times lower when compared with the Russian settlements. As the Russian settlements are heavily influenced by human activity, in contrary to Cape Vera, this result is not unforeseen. Moreover, the concentration of PCB in snow buntings from Cape Vera indicates that seabird guano is a greater contributor of PCB than human influence in the Norwegian settlements. As passerine birds are suitable as monitoring tools (Dauwe et al., 2006), several studies regarding contaminants in passerines have been conducted. At the most contaminated sites such as by the Hudson River, New York,  $\Sigma$ PCB concentration up to 24,000 ng/g w.w. have been reported in eggs of tree swallows (*Tachycineta bicolor*) (Echols et al., 2004). However, at more moderate contaminated sites such as in Belgium, the  $\Sigma$ PCB concentration in great tits from is comparable with the concentrations in the eggs of snow buntings in the Russian settlements in this study (Dauwe et al., 2006; Van den Steen et al., 2008). When comparing the  $\Sigma$ PCB concentrations in eggs of snow buntings in the Norwegian settlement with previous studies on passerines in less contaminated areas in Mexico and Belgium (Mora, 2008; Van den Steen et al., 2008), the concentration in the Norwegian settlements is in the lower range. The  $\Sigma$ PCB concentration in eggs of snow buntigs the Russian settlements in this study is comparable with the concentration in eggs of black-legged kittiwakes and Brünnich's guillemots in Svalbard (Table 4).

When comparing the concentrations in the current snow buntings with  $\Sigma$ PCB ( $\mu\text{g/g}$  w.w.) for avian effects (AMAP, 1998), the mean concentration in Barentsburg (0.350  $\mu\text{g/g}$  w.w.) and Pyramiden (0.605  $\mu\text{g/g}$  w.w.) are near and exceeding the NOAEL of hatching success in white leghorn chicken (0.360  $\mu\text{g/g}$  w.w.). On the other hand, the  $\Sigma$ PCB concentration in eggs of snow buntings in Longyearbyen and Ny-Ålesund are lower than these reported NOAEL thresholds (0.007  $\mu\text{g/g}$  w.w. and 0.014  $\mu\text{g/g}$  w.w. respectively). This means that toxicological implications may occur for snow buntings feeding and breeding in Barentsburg and Pyramiden. It should be noted that comparison

of effects derived from other species must be done with caution, as there are many factors in that could influence the effect of contaminants on the individual. Moreover, it is important to take into consideration the interaction between the different contaminants present in the organism, and possibly synergetic or additive effects they could pose on each other (Bustnes, 2006). As the concentration in the eggs are postulated to reflect the maternal concentration (Drouillard and Norstrom, 2001), the developing chick is exposed to the same concentrations as adults. Thus, potentially toxic effects could occur at embryonic stage (Van den Steen et al., 2009a).

### **PCB pattern**

Variation in PCB congener pattern in passerine birds as a result of different anthropogenic exposure, have previously been reported (Van den Steen et al., 2008; Van den Steen et al., 2009b). The PCB congener pattern found in the eggs in the Russian settlements (Figure 6) is comparable with the pattern found in surface soil in the settlements (Jartun et al., 2010). The technical PCB-mixtures, such as Svovol, Chlophen A50 or Arochlor 1254, could possibly be the source of this congener pattern, as PCB-118 is dominant in these mixtures (Figure 10). The PCB congener pattern in the eggs from the Norwegian settlements (Figure 6) appear to be more influenced by the heavier chlorinated PCB-mixtures, such as Arochlor 1260, Arochlor 1262 or Chlophen A60 (Figure 10). The higher contribution of PCB-118 and dominance of the lower chlorinated congeners in the eggs from Barentsburg and Pyramiden, are a very strong indications of local influence of PCB from the Russian settlements. Moreover, Hop et al., (2001) reported that the PCB congener profile found in macro-benthos in Grønfjorden and Billefjorden possibly originated from the technical mixtures Arochlor 1254, Chlophen A50 or Svovol as a result of PCB leaking from the settlements (Figure 11). The same PCB congener pattern was found in liver of glaucous gulls in Barentsburg, which were feeding in Grønfjorden (Sagerup et al., 2009). Miljeteig and Gabrielsen, (2009) did not report a higher contribution of PCB-118 in eggs of black-legged kittiwakes breeding in Pyramiden. The authors concluded that this could be explained by the kittiwakes feeding pelagic and at glacier fronts, and that these environments were not affected by the local pollution. The congener pattern in the eggs from the Norwegian settlements is similar to the pattern found in seabirds outside the settlements. It is therefore not possible to conclude whether the snow buntings are influenced by the small elevation of PCB in

these settlements. The PCB load in these eggs might be a result of long range transport, contribution from sea bird guano, or from sources in its wintering area and during its migration route.

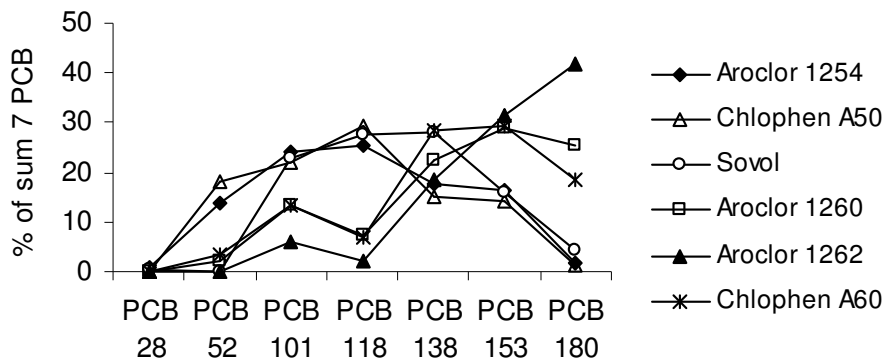


Figure 10. The relative mean distribution of PCB congeners in the PCB-mixtures Arochlor 1254, Chlophen A50, Sovol, Arochlor 1260, Arochlor 1262 and Chlophen A6. Figure from Hop et al., (2001).

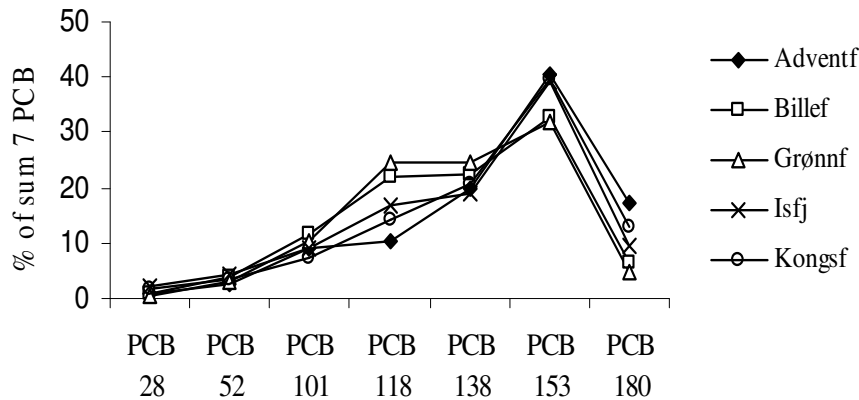


Figure 11. The relative mean distribution of PCB congeners found in macro benthos in Adventfjorden, Billefjorden, Grønfjorden, Isfjorden and Kongsfjorden, Svalbard. Figure from Hop et al., (2001).

### Concentration of HCB and pesticides

The concentrations of HCB and *trans*-nonachlor (Figure 3) in eggs of snow buntings were significantly higher in eggs from Ny-Ålesund than Pyramiden. Furthermore, these compounds were significantly higher in the Norwegian settlements as one group when

compared with the Russian settlements as one group (Figure 9). As HCB and *trans*-nonachlor are a result of industrial processes and have formerly been utilized as pesticides (Barrie et al., 1992; Bailey, 2001), they have no local source in the Arctic environment. Hence, the difference between the locations is not a result of local pollution of these compounds. As a result of the high volatility of HCB, it is found in similar or higher concentrations in the Arctic environment compared with areas closer to the source (Burkow and Kallenborn, 2000). This further makes it prevalent in soil and lower trophic terrestrial feeders (AMAP, 2002). No significant difference was found between the settlements regarding *p,p'*-DDE (Figure 3). When eggs from the Norwegian settlements were combined in one group and eggs from the Russian settlements in one group, significant higher concentration was found in the Russian settlements (Figure 9). It has previously been reported fresh sources of DDT in soil in Barentsburg (Evenset and Christensen, 2009a) as well as in Billefjorden and Grønfjorden (Evenset et al., 2009b). It has been suggested that DDT was used as delousing agent, however, this is only assumptions (Evenset, 2010). As little is known about the fresh sources of DDT, it is not possible to conclude whether the snow buntings are influenced by these local sources of DDT in the Russian settlements. Therefore, the occurrence of *p,p'*-DDE, HCB and *trans*-nonachlor in the eggs in this study may be explained by long range transport, as these compounds are transported to the Arctic terrestrial environment via the atmosphere (Barrie et al., 1992). Further more, contribution from seabird guano or exposure during migration and overwintering area may be additionally sources of these compounds in the eggs. The concentrations of DDE and HCB in this study are 5-1,000 times lower than concentrations shown to cause adverse affects in glaucous gulls and peregrine falcons, such as eggshell thinning and wing asymmetry (Johnstone et al., 1996; Bustnes et al., 2002). The concentrations of DDE and *trans*-nonachlor in Svalbard seabirds and other passerines (Table 4) are more than twice as high as the concentration in eggs of snow buntings in this study. The concentration of HCB is lower than Arctic seabirds (Table 4). However, the concentration is comparable with previous studies conducted on great tits (Dauwe et al., 2006; Van den Steen et al., 2006).

## Concentration of PFAS

The PFASs were the most abundant compounds in the eggs of snow buntings from the Norwegian settlements, constituting more than 50 % of the total contaminant burden (Figure 4). The high standard deviation (Figure 3) of the Ny-Ålesund samples is explained by one egg (NÅ15). This egg has a PFOS concentration more than 100 times higher than the sample with the second highest concentration from Ny-Ålesund. The outlier was not excluded as it was assumed to represent individual variation. Therefore, the concentration mean in the Ny-Ålesund samples must be interpreted with respect of the outlier. When comparing the concentration mean of PFAS, and the concentration median of PFAS, the mean is 6 times higher than the median in the Ny-Ålesund samples (Appendix F, Table F.1). In situations where the mean is affected by extreme outliers, the median may be a more suitable measurement. When considering the concentrations with respect to the median,  $\sum_6$ PFAS constitutes merely 22 % of the total contaminant burden in the Ny-Ålesund samples. In this study, the concentration of  $\sum_6$ PFAS in eggs of snow buntings (Figure 3) was not significantly different between the locations. Further on, no significant difference was found when comparing the Norwegian settlements and the Russian settlements (Figure 9). This is explained by the fact that although  $\sum_6$ PFAS contributes to a relative higher distribution of the contaminant burden in eggs of snow buntings from the Norwegian settlements, the concentrations are comparable with the  $\sum_6$ PFAS in the Russian settlements. However, some individual PFASs compounds were significantly higher in Barentsburg, Longyearbyen and Ny-Ålesund when compared with Pyramiden, indicating a smaller distribution of PFASs to Pyramiden. As Pyramiden have been abandoned since 1998, a minor distribution of PFASs in this location cannot be excluded as PFASs are used in a variety of products, such as paper coatings, fire-fighting foam, in carpets and textiles (Hekster and Voogt, 2002; Houde et al., 2006). However, a majority of the samples from Ny-Ålesund were collected at several other locations in Kongsfjorden that were distant from the community, and are therefore not likely affected by the community. This means that other sources than local pollution in Svalbard was the origin of PFASs in these specific samples. PFOSA was only detected in two samples. A minor contribution of PFOSA in this study is in accordance with previous studies (Verreault et al., 2005; Holmstrom and Berger, 2008), indicating possibly biotransformation of PFOSA to PFOS

either in the organism via metabolism (Tomy et al., 2004; Xu et al., 2004) or via abiotic processes (D'Eon et al., 2006).

The high PFOS concentration in one egg (NÅ15; 247.92 ng/g w.w.) from Ny-Ålesund may be explained by exposure during migration or overwintering area. However, local exposure can not be excluded. Formerly, waste was burned in Ny-Ålesund at several locations, contributing to local sources of pollution. At the major dump-site in Ny-Ålesund, both industrial and domestic waste was burned until 1995. This dumpsite was located on the west side of town, in close proximity to the community (Kovacs, 1996). As this egg (247.92 ng/g w.w.) was sampled from a nest within the settlement, the female may be more influenced by human activity compared with snow buntings breeding distant from the settlement. It has been suggested that PFOS has a half-life of 2-3 weeks in some bird species (Newsted et al., 2006; Yeung et al., 2009), indicating that the snow buntings are exposed to PFOS in the respectively locations. However, it is important to emphasize that elimination may be very species specific, and thereby it is not possible to conclude whether the snow buntings are influenced by local pollution of PFOS. The concentration of PFASs found in eggs of snow buntings from Svalbard is lower than reported in other Svalbard seabirds (Table 4) and peregrine falcons feeding terrestrial (Holmstrom et al., 2010). Possible correlation of PFOS and liver weight, as well as cholesterol and triglyceride concentration in great tits and blue tits nestlings have been suggested by Hoff et al., (2005). However, as those particular nestlings were situated in the proximity of a fluorochemical plant, the concentrations of PFOS reported were up to several thousand times higher than the concentrations of PFOS in this study.

### **PFAS pattern**

Despite the phase-out of PFOS in 2000 (3M, 2012), PFOS is the dominant PFASs in wild-life (Houde et al., 2011). This is in agreement with the patterns reported herein in eggs of snow buntings from Barentsburg, Pyramiden and Ny-Ålesund (Figure 5), where PFOS is the dominating PFASs. In the same settlements in this study, PFUnA and PFTriA was the dominant PFCA, while short chained PFCA was not detected in any of the samples. This is in agreement with previous studies on the glaucous gull (Verreault et al., 2005; Verreault et al., 2007b), common guillemot (Holmstrom et al., 2010) and the peregrine falcon (Holmstrom et al., 2010), where PFUnA and PFTriA was the dominating PFCA.

However, in the samples from Longyearbyen, PFNA and PFUnA were the dominating PFASs (Figure 5). Furthermore, PFNA and PFUnA were more abundant than PFOS. These results are contradicting previous studies on Arctic birds. However, when assessing the concentrations with respect to the median (Appendix F, Table F.1), PFOS is the dominating PFAS in the Longyearbyen samples. The concentration of PFNA is higher than PFOS in only two samples (LYB1 and LYB3), thus, it is not reasonable to conclude that PFNA is the dominating PFASs in the Longyearbyen samples. The two samples with the dominating PFNA concentration were collected in the same area. This area is located at the waterfront in the center of the community, and have previous been used as a deposition site for domestic and industrial waste. However, the landfill was covered by several layers of material when closed (Kovacs, 1996). Thus, it is not possible to conclude whether the snow buntings are influenced by this old dump site. Further more, when assessing the PFCA pattern in eggs of snow buntings from Longyearbyen with respect to the median, the PFCA pattern in Longyearbyen is similar to the other locations (Appendix F, Table F.1). The source of PFASs in the Arctic environment is suggested to be the degradation of perfluorinated sulfonamides (D'Eon et al., 2006) and fluorotelomer alcohols (FTOH) in the atmosphere (Ellis et al., 2004). The degradation 8:2 FTOH is known to yield PFOA and PFNA and the degradation of 10:2 FTOH is known to yield PFDcA and PFUnA. Atmospheric transport of these precursors is a likely contributor of the PFASs burdens in eggs of snow buntings this study. However, influence of local contamination of PFASs cannot be excluded as PFASs are found in a variety of products in a modern society. Thus, the PFASs burden in this study may be explained by atmospheric transport and local pollution, as well as exposure during migration and exposure in overwintering areas.

### **Principal component analysis**

The score plot (Figure 7) and loading plot (Figure 8) illustrates a distinct separation of the settlements based on the contaminant burden in the settlements. The Norwegian and the Russian settlements are clearly separated from each other, illustrated in Figure 7, and Figure 8 further confirms this separation based on the contaminant burden. These results are clearly illustrating the dominating PCB burden in the two Russian settlements, as both Barentsburg and Pyramiden appear together with the PCB congeners (Figure 8). Further on, Longyearbyen and Ny-Ålesund appear together with



the PFASs, illustrating that these compounds are constituting a major part of the contaminant burden in the Norwegian settlements (Figure 8). The concentration of  $\Sigma_7$ PCB concentration in the Russian settlements as one group was significant higher than the Norwegian settlements as one group (Figure 9). Thus, Figure 7 and Figure 8 are supporting the strong indication of local influence of PCB in the two Russian settlements. The individual PFASs were positively correlating with HCB and *trans*-nonachlor (Figure 8). In contrast to legacy POPs, PFASs are known to partition into blood where they bind to blood proteins, as well as partitioning into the liver and kidney (Butt et al., 2010). As HCB and *trans*-nonachlor have lipophilic properties, they were expected to correlate with PCBs and *p,p'*-DDE that exert the same lipophilic properties (Haukas et al., 2007). This means that positively correlation between HCB, *trans*-nonachlor and PFASs were not expected. These correlations are challenging to explain, and may be a result of several factors such as tissue investigated, composition of the egg regarding lipids and proteins, maternal transfer, species differences and low sample size.

## 5. Conclusion

The present study is the first to investigate contaminants in snow buntings in Svalbard. Significant higher concentrations of PCB were found in the eggs from the Russian settlements (Barentsburg and Pyramiden) than in eggs from the Norwegian settlements (Longyearbyen and Ny-Ålesund). Further on, the PCB congener composition in the eggs from Barentsburg and Pyramiden was comparable with the technical PCB-mixtures previously used in the Russian settlements. These findings are strong indications of local anthropogenic pollution influencing the concentrations of PCB in the eggs from the Russian settlements. Further on, local influence of *p,p'*-DDE and PFASs cannot be excluded. However, the contaminant burden of HCB, *trans*-nonachlor, *p,p'*-DDE and PFASs in the eggs of snow buntings in Svalbard are mainly explained by; I: atmospheric transport of contaminants to the Arctic environment, II: transport of contaminants by sea birds, III: exposure during migration, IV: exposure in overwintering areas.

As toxicological implications was not the aim of the present study, the results can only report a status regarding contaminants in snow buntings in Svalbard. Despite the fact that direct comparison between different species is not appropriate, the results show that the concentration OHCs in general are low in eggs of snow bunting in Svalbard. However, the  $\sum$ PCB concentration in eggs of snow buntings in the Russian settlements was comparable with eggs of black-legged kittiwakes and Brünnich's guillemot from Svalbard. Further was the mean  $\sum$ PCB concentration in the Russian settlements near and exceeding NOAEL for hatching success in leghorn chicken.

As the concentrations of OHCs in the eggs are dependent of several factors, such as maternal transfer and diet, this study show that more research of OHCs in the snow bunting are needed. However, the results in this study indicate that the snow bunting may be utilized as a sentinel of local pollution on Svalbard. As the Governor in Svalbard has requested the removal of sources of PCB in the Russian settlements, the snow bunting is suggested as a future bioindicator for local pollution.

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## Appendix A- Internal standard POP

Table A.1. Internal standard (POP I (34.10)) for analysis of PCB, DDT/HCH – and pesticides in eggs of snow bunting (*Plectrophenax nivalis*).

Compound group	Individual <sup>13</sup> C compounds
PCBs	<sup>13</sup> C PCB-28
	<sup>13</sup> C PCB-52
	<sup>13</sup> C PCB-101
	<sup>13</sup> C PCB-105
	<sup>13</sup> C PCB-114
	<sup>13</sup> C PCB-118
	<sup>13</sup> C PCB-123
	<sup>13</sup> C PCB-138
	<sup>13</sup> C PCB-153
	<sup>13</sup> C PCB-156
	<sup>13</sup> C PCB-157
	<sup>13</sup> C PCB-167
	<sup>13</sup> C PCB-180
	<sup>13</sup> C PCB-189
	<sup>13</sup> C PCB-209
OCP	<sup>13</sup> C <i>trans</i> -Chlordane
	<sup>13</sup> C <i>cis</i> -Chlordane
	<sup>13</sup> C <i>oxy</i> -Chlordane
	<sup>13</sup> C <i>trans</i> -Nonachlor
	<sup>13</sup> C <i>cis</i> -Nonachlor
	<sup>13</sup> C Mirex
	<sup>13</sup> C α-HCH
	<sup>13</sup> C β-HCH
	<sup>13</sup> C γ-HCH
	<sup>13</sup> C p,p'-DDT
	<sup>13</sup> C p,p'-DDE
	<sup>13</sup> C Endosulfan α
	<sup>13</sup> C Endosulfan β
	<sup>13</sup> C Endosulfan sulfate
	<sup>13</sup> C Trifluralin
	<sup>13</sup> C Aldrin
	<sup>13</sup> C Eldrin
	<sup>13</sup> C Isodrin
<sup>13</sup> C Dieldrin	
<sup>13</sup> C Heptachlor epoxide	
<sup>13</sup> C Heptachlor	
<sup>13</sup> C Delta-BHC	
Industrial chlorinated by-products	<sup>13</sup> C HCB
	<sup>13</sup> C Pentachlorobenzene

## Appendix B- Limit of detection POP

Table B.1. Limit of detection (LOD) for OCs in eggs of snow bunting (*Plectrophenax nivalis*). LOD are calculated as 3\*blank or 3\*signal/noise.

Compound	Detection limit range (ng/g w.w.)
PCB-28/31	0.01 - 0.08
PCB-52	0.01 - 0.7
PCB 101	0.04 - 1.4
PCB 118	0.02 - 0.29
PCB 138	0.02 - 0.35
PCB 153	0.02 - 0.37
PCB 180	0.03 - 0.13
HCB	0.03 - 0.36
$\alpha$ -HCH	0.01 - 1.16
$\beta$ -HCH	0.06-0.52
$\gamma$ -HCH	0.01-0.09
<i>trans</i> -Chlordane	0.01-0.08
<i>trans</i> -Nonachlor	0.01 - 0.07
<i>cis</i> -Chlordane	0.01-0.15
<i>oxy</i> -Chlordane	0.14-1.08
<i>cis</i> -Nonachlor	0.02 - 0.25
Mirex	0.04-1.02

## Appendix C- Internal standard PFAS

Table C.1. Internal standard (allPFC) for analysis of PFASs in eggs of snow bunting (*Plectrophenax nivalis*).

Compound group	Individual <sup>13</sup> C compounds
PFCA	<sup>13</sup> C PFBA
	<sup>13</sup> C PFPA
	<sup>13</sup> C PFH <sub>x</sub> A
	<sup>13</sup> C PFOA
	<sup>13</sup> C PFNA
	<sup>13</sup> C PFDcA
	<sup>13</sup> C PFUnA
	<sup>13</sup> C PFD <sub>o</sub> A
PFSA	<sup>13</sup> C PFH <sub>x</sub> A
	<sup>13</sup> C PFOS
	<sup>13</sup> C PFOSA

## Appendix D- Limit of detection PFAS

Table D.1. Limit of detection (LOD) for PFASs in eggs of snow bunting (*Plectrophenax nivalis*). LOD are calculated as 3\*blank or 3\*signal/noise.

Compound group	Compound	Limit of detection (ng/g)
PFCA	PFBA	0.02
	PFPA	0.04
	PFHxA	0.004
	PFHpA	0.01
	PFOA	0.05
	PFNA	0.04
	PFDCa	0.05
	PFUnA	0.03
	PFDoA	0.02
	PFTriA	0.06
PFTeA	0.08	
PFSA	PFBS	0.01
	PFHxS	0.10
	LIN-PFOS	0.04
	PFDCs	0.50
PASF	PFOSA	0.50

## Appendix E- Individual biological measurements

Table E.1. Individual biological measurements of egg volume, egg lipid content (%) and clutch size in eggs of snow buntings (*Plectrophenax nivalis*).

ID	Volume (cm <sup>3</sup> )	Lipids (%)	Clutch size
LYB1	3,24	4,13	5,67*
LYB2	3,06	8,27	4,00
LYB3	3,05	9,75	6,00
LYB4	3,06	6,10	7,00
LYB5	4,15	6,23	5,00
LYB7	2,34	6,56	7,00
LYB8	2,88	5,86	5,00
LYB10	3,09	9,73	5,67*
BAR1	2,75	12,62	5,40*
BAR2	2,48	8,46	5,00
BAR3	2,98	6,71	6,00
BAR4	2,79	8,73	6,00
BAR6	2,90	4,56	5,00
BAR7	2,59	7,77	5,00
BAR8	2,54	7,52	5,40*
BAR9	2,85	4,63	5,40*
BAR10	3,27	6,77	5,40*
PYR1	3,31	5,31	6,00
PYR2	3,16	5,90	6,00
PYR4	3,21	4,25	5,00
PYR7	2,99	5,19	5,00
PYR8	2,70	3,77	6,00
PYR9	2,89	4,50	5,00
PYR10	2,85	4,59	6,00
NÅ1	3,04	4,06	5,00
NÅ2	2,91	4,97	4,50*
NÅ3	2,62	8,38	4,50*
NÅ4	3,22	6,82	4,50*
NÅ5	3,52	6,14	4,50*
NÅ11**	2,83	6,98	4,00
NÅ13**	3,24	7,73	4,00
NÅ15**	2,67	7,41	5,00

\* Value derived from mean clutch size at the respectively location

\*\* Samples from 2010

## Appendix F- Concentration of individual compounds

Table F.1. Concentration of compounds (ng/g w.w.), egg volume (cm<sup>3</sup>), clutch size and lipid content (%) in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (n=8) and Ny-Ålesund (n=8). Concentration below the detection limit (LOD) is reported as 0.5\*LOD.

Analyte	Longyearbyen					Ny-Ålesund				
	n	Mean	SD	Median	Range min-max	n	Mean	SD	Median	Range min-max
PCB 28/31	8	0.05	0.06	0.03	0.01 - 0.15	8	0.11	0.18	0.06	0.01 - 0.55
PCB 52	8	0.07	0.02	0.07	0.02 - 0.10	8	0.05	0.03	0.04	0.03 - 0.11
PCB 101	8	0.33	0.20	0.29	0.08 - 0.72	8	0.32	0.20	0.35	0.01 - 0.60
PCB 118	8	1.23	0.77	0.94	0.43 - 2.51	8	1.28	0.69	1.41	0.11 - 2.01
PCB 138	8	1.48	0.60	1.34	0.73 - 2.42	8	2.01	1.69	1.84	0.01 - 5.59
PCB 153	8	2.62	1.31	2.45	1.21 - 5.54	8	6.48	7.80	4.03	0.1 - 24.66
PCB 180	8	1.16	1.06	1.11	0.05 - 3.40	8	3.88	5.64	2.03	0.02 - 17.33
$\Sigma_7$ PCB	8	6.93	4.02	6.22	2.53 - 14.48	8	14.12	16.23	9.74	0.28 - 50.85
<i>p,p'</i> -DDE	8	4.29	2.79	3.21	2.53 - 10.50	8	6.67	4.01	5.77	2.87 - 16.1
HCB	8	4.34	3.10	3.11	1.82 - 11.50	8	6.10	2.78	5.60	2.54 - 9.81
<i>trans</i> -nonachlor	8	0.07	0.03	0.07	0.02 - 0.12	8	0.11	0.05	0.12	0.05 - 0.18
PFOS	8	3.75	1.93	4.14	1.21 - 5.82	8	31.81	87.32	0.96	0.44 - 247.92
PFNA	8	4.78	6.45	0.98	0.28 - 15.45	8	0.85	0.66	0.57	0.20 - 2.17
PFDCa	8	1.76	2.79	0.65	0.34 - 8.47	8	0.43	0.33	0.31	0.08 - 1.00
PFUnA	8	3.93	5.00	1.55	0.41 - 13.55	8	1.97	1.16	1.73	0.83 - 4.27
PFDoA	8	0.93	0.86	0.66	0.19 - 2.91	8	0.75	0.49	0.59	0.30 - 1.54
PFTriA	8	1.28	1.02	0.99	0.34 - 3.03	8	1.99	1.24	1.82	0.57 - 4.36
$\Sigma_6$ PFAS	8	16.43	18.04	8.97	2.77 - 49.23	8	37.80	91.21	5.98	2.42 - 261.26
$\Sigma$ POP	8	32.06	27.98	21.57	9.67 - 85.83	8	64.80	114.28	27.21	8.16 - 338.20



Table F.2. Concentration of compounds (ng/g w.w.), egg volume (cm<sup>3</sup>), clutch size and lipid content (%) in eggs of snow bunting (*Plectrophenax nivalis*) from Barentsburg (n=9) and Pyramiden (n=7). Concentration below the detection limit (LOD) is reported as 0.5\*LOD.

Analyte	Barentsburg					Pyramiden				
	n	Mean	SD	Median	Range min-max	n	Mean	SD	Median	Range min-max
PCB 28/31	9	0.61	0.56	0.48	0.01 - 1.69	7	1.43	2.55	0.55	0.01 - 7.17
PCB 52	9	14.03	19.12	8.39	1.93 - 63.39	7	19.04	30.60	2.18	0.04 - 82.03
PCB 101	9	50.72	63.02	32.64	11.22 - 215.00	7	94.77	138.84	17.79	0.02 - 370.00
PCB 118	9	92.67	74.78	70.05	25.97 - 275.88	7	167.24	227.91	42.02	0.1 - 639.24
PCB 138	9	93.64	83.11	69.18	22.90 - 302.26	7	160.93	216.60	43.02	0.02 - 593.68
PCB 153	9	80.25	65.07	63.78	20.12 - 238.28	7	142.79	183.53	55.74	0.08 - 507.62
PCB 180	9	17.69	21.09	12.32	3.04 - 72.41	7	18.64	22.75	9.79	0.51 - 64.21
$\Sigma_7$ PCB	9	349.61	326.76	256.84	85.19 - 1168.91	7	604.84	822.77	171.09	0.77 - 2263.95
<i>p,p'</i> -DDE	9	6.69	3.32	6.23	2.88 - 12.32	7	12.87	11.99	8.16	2.47 - 38.56
HCB	9	4.00	2.17	3.51	1.66 - 7.29	7	2.75	2.59	1.68	1.40 - 8.55
<i>trans</i> -nonachlor	9	0.08	0.05	0.08	0.03 - 0.20	7	0.04	0.02	0.04	0.02 - 0.07
PFOS	9	3.53	3.66	2.20	0.58 - 11.99	7	2.13	4.32	0.55	0.25 - 11.90
PFNA	9	0.92	0.74	0.75	0.14 - 2.25	7	0.23	0.20	0.17	0.02 - 0.62
PFDCa	9	0.65	0.48	0.55	0.03 - 1.43	7	0.14	0.20	0.03	0.03 - 0.53
PFUnA	9	2.08	1.62	1.64	0.32 - 5.26	7	0.56	0.49	0.39	0.02 - 1.33
PFDoA	9	0.94	0.70	0.65	0.16 - 2.10	7	0.21	0.19	0.24	0.01 - 0.51
PFTriA	9	1.76	1.56	1.30	0.03 - 4.50	7	0.54	0.37	0.71	0.06 - 1.05
$\Sigma_6$ PFAS	9	9.89	8.76	7.09	1.26 - 27.54	7	3.82	5.76	2.08	0.39 - 15.94
$\Sigma$ POP	9	370.27	341.06	273.75	91.02-1216.26	7	624.33	843.12	183.05	5.05 - 2327.07

## Appendix G- PCA loadings

Table G.1. PCA loadings for the individual variables, yielding 4 Principal Components.

	Component			
	1	2	3	4
Volume (cm <sup>3</sup> )	-0.097	-0.250	-0.528	-0.274
Lipids (%)	-0.193	0.497	0.405	-0.304
Clutch size	0.275	0.068	0.113	0.788
PCB 28/31	0.647	-0.066	0.117	0.167
PCB 52	0.882	0.392	0.010	0.109
PCB 101	0.837	0.524	-0.056	0.000
PCB 118	0.845	0.511	-0.070	-0.009
PCB 138	0.763	0.582	-0.122	-0.082
PCB 153	0.766	0.570	-0.102	-0.177
PCB 180	0.700	0.479	0.084	-0.228
<i>p,p'</i> -DDE	0.290	-0.087	0.829	0.126
HCB	-0.416	0.498	0.394	-0.458
<i>trans</i> -nonachlor	-0.463	0.545	0.453	-0.289
PFOS	-0.379	0.361	0.470	0.489
PFNA	-0.483	0.744	-0.230	0.214
PFDCa	-0.506	0.698	-0.232	0.285
PFUnA	-0.423	0.815	-0.288	0.094
PFDoA	-0.456	0.775	-0.191	0.116
PFTriA	-0.406	0.744	-0.009	-0.060

## Appendix H- Concentration of individual compounds in Russian and Norwegian settlements

Table H.1 Concentration of compounds (ng/g w.w.), volume (cm<sup>3</sup>), lipid content (%) and clutch size in eggs of snow bunting (*Plectrophenax nivalis*) from the Norwegian settlements (n=16) and the Russian settlements (n=16). Concentration below the detection limit (LOD) is reported as 0.5\*LOD.

Analyte	Norwegian					Russian				
	n	Mean	SD	Median	Range min-max	n	Mean	SD	Median	Range min-max
Volume (cm <sup>3</sup> )	16	3.06	0.40	3.06	2.34-4.15	16	2.89	0.25	2.87	2.48-3.31
Lipids (&)	16	6.82	1.70	6.69	4.06-9.75	16	6.33	2.30	5.61	3.77-12.62
Clutch size	16	5.08	0.96	5.00	4.00-7.00	16	5.48	0.45	5.40	5.00-6.00
PCB28/31	16	0.08	0.13	0.05	0.01-0.55	16	0.97	1.72	0.53	0.01-7.17
PCB 52	16	0.06	0.03	0.06	0.02-0.11	16	16.22	24.00	6.90	0.04-82.3
PCB 101	16	0.32	0.19	0.31	0.01-0.72	16	69.99	101.68	32.26	0.02-370
PCB 118	16	1.25	0.71	1.01	0.11-2.51	16	125.29	158.81	69.33	0.10-630.24
PCB 138	16	1.75	1.25	1.68	0.01-5.59	16	123.08	153.75	65.86	0.02-593.68
PCB 153	16	4.55	5.76	2.73	0.10-24.66	16	107.61	129.45	60.09	0.08-507.62
PCB 180	16	2.52	4.17	1.26	0.02-17.33	16	18.10	21.08	11.18	0.51-72.41
Σ <sub>7</sub> PCB	16	10.53	12.24	7.08	0.27-51.47	16	461.27	590.48	246.13	0.76-2263.15
<i>p,p'</i> -DDE	16	5.48	3.55	4.83	2.53-16.10	16	9.40	8.57	6.91	2.47-38.56
HCB	16	5.22	2.99	4.25	1.82-11.50	16	3.46	2.36	2.47	1.40-8.55
<i>trans</i> -nonachlor	16	0.09	0.05	0.08	0.02-0.18	16	0.06	0.05	0.05	0.02-0.20
PFOS	16	17.78	61.40	1.49	0.44-247.92	16	2.92	3.89	1.02	0.25-11.99
PFNA	16	2.81	4.87	0.71	0.20-15.45	16	0.62	0.66	0.43	0.02-2.25
PFDCa	16	1.09	2.04	0.41	0.08-8.47	16	0.43	0.45	0.37	0.03-1.43
PFUnA	16	2.95	3.65	1.66	0.41-13.55	16	1.42	1.45	1.02	0.02-5.26
PFDoA	16	0.84	0.69	0.64	0.19-2.91	16	0.62	0.64	0.44	0.01-2.10
PFTriA	16	1.64	1.16	1.36	0.34-4.36	16	1.23	1.32	0.75	0.03-4.50
Σ <sub>6</sub> PFC	16	27.12	73.80	6.26	1.67-292.65	16	7.23	8.42	4.02	0.35-27.54
ΣPOP	16	48.43	92.63	22.49	6.31-371.90	16	481.42	609.88	259.57	5.00-2338

## Appendix I- Individual contaminant concentration

Table I.1. Individual concentrations (ng/g w.w.) of PCBs and pesticides in eggs of snow bunting (*Plectrohenax nivalis*) from Longyearbyen (LYB), Barentsburg (BAR), Pyramiden (PYR) and Ny-Ålesund (NÅ), sampled in 2010 and 2011.

ID	PCB-28/31	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180	Σ <sub>7</sub> PCB	trans-nonachlor	HCB	p,p'-DDE
LYB1	0.12	0.06	0.54	2.51	2.42	2.58	1.11	9.34	0.06	3.16	2.57
LYB2	0.01*	0.06*	0.21	1.04	1.59	5.54	3.40	11.85	0.07	5.54	3.42
LYB3	0.15	0.08	0.28	0.90	1.08	2.31	1.42	6.22	0.07	3.00	3.27
LYB4	0.05	0.09	0.30	0.98	1.87	2.69	1.10	7.08	0.04	2.49	2.53
LYB5	0.05	0.02	0.08	0.43	0.73	1.21	0.05	2.57	0.02	1.82	2.62
LYB7	0.01*	0.08*	0.72	2.38	2.06	2.76	0.06*	8.07	0.07	3.06	10.50
LYB8	0.01*	0.06*	0.32	0.79	1.01	1.52	0.71	4.42	0.12	11.50	3.14
LYB10	0.01*	0.10*	0.22*	0.79	1.09	2.31	1.40	5.92	0.10	4.14	6.25
BAR1	0.58	13.90	48.80	98.79	99.40	90.35	16.84	368.66	0.08	6.22	6.23
BAR2	0.48	9.72	40.50	70.05	69.18	51.85	10.03	251.81	0.06	2.61	5.80
BAR3	1.69	63.39	215.00	275.88	302.26	238.28	72.41	1168.91	0.20	4.30	11.30
BAR4	0.01*	8.39	31.88	58.60	62.53	56.39	12.55	230.35	0.12	7.29	6.52
BAR6	0.21	5.41	32.64	68.60	58.77	63.78	8.38	237.79	0.03	1.68	3.58
BAR7	0.25	4.28	17.26	25.97	22.90	20.12	3.04	93.82	0.03	2.33	3.76
BAR8	1.06	1.93	15.08	119.13	112.22	104.02	12.32	365.76	0.09	6.42	12.32
BAR9	0.15	3.14	11.22	32.03	35.37	26.56	5.48	113.95	0.04	1.66	2.88
BAR10	1.10	16.08	44.06	85.00	80.14	70.93	18.12	315.43	0.08	3.51	7.84
PYR1	0.76	10.82	76.45	195.53	171.22	143.52	19.50	617.80	0.02	2.67	8.16
PYR2	0.14	2.18	17.79	40.82	40.08	44.58	5.87	151.46	0.04	8.55	13.40
PYR4	0.01*	2.12	11.14	42.02	43.02	55.74	9.79	163.84	0.05	1.40	2.47
PYR7	7.17	82.03	370.00	630.24	593.68	507.62	64.21	2254.95	0.03	1.65	13.73
PYR8	0.88	36.04	188.00	261.85	278.49	247.87	30.05	1043.18	0.04	1.59	6.51
PYR9	0.51*	0.04*	0.03*	0.10*	0.02*	0.08*	0.51*	1.27	0.03	1.68	7.29
PYR10	0.55*	0.05*	0.02*	0.11*	0.02*	0.09*	0.55*	1.38	0.07	1.73	38.56
NÅ1	0.55*	0.05*	0.01*	0.11*	0.01*	0.10*	0.58*	1.40	0.05	3.15	6.83
NÅ2	0.01*	0.03*	0.06*	0.56	0.64	1.18	0.02*	2.49	0.06	2.54	2.87
NÅ3	0.01*	0.05*	0.39	1.47	1.91	6.34	3.26	13.43	0.18	8.96	6.35
NÅ4	0.09	0.04*	0.49	1.79	1.76	3.19	1.02	8.38	0.15	9.81	4.37
NÅ5	0.05	0.03*	0.33	1.98	5.59	24.66	17.33	49.97	0.08	4.35	5.29
NÅ11**	0.01*	0.04*	0.28	1.35	2.14	8.29	4.75	16.86	0.14	5.56	6.06
NÅ13**	0.14	0.04*	0.36	0.98	1.25	3.71	2.34	8.82	0.15	8.78	5.48
NÅ15**	0.06	0.11	0.60	2.01	2.80	4.34	1.72	11.64	0.10	5.64	16.10

\* Samples under the limit of detection are given the value 0.5\*LOD

\*\* Samples from 2010

Table I.2. Individual concentrations (ng/g w.w.) of PFASs in eggs of snow bunting (*Plectrophenax nivalis*) from Longyearbyen (LYB), Barentsburg (BAR), Pyramiden (PYR) and Ny-Ålesund (NÅ), sampled in 2010 and 2011.

ID	PFOS	PFNA	PFDCa	PFUnA	PFDoA	PFTriA	ΣPFC
LYB1	5.78	14.31	8.47	13.5	2.91	3.03	48.04
LYB2	1.22	0.45	0.34	0.41	0.19	0.34	2.96
LYB3	2.36	15.45	0.90	10.0	0.72	2.53	31.96
LYB4	5.35	0.52	0.56	0.60	0.39	0.37	7.79
LYB5	1.21	0.28	0.35	0.80	0.41	0.52	3.56
LYB7	4.26	1.20	0.73	1.67	1.11	1.21	10.19
LYB8	5.82	5.27	2.32	2.98	1.11	0.76	18.26
LYB10	4.03	0.76	0.39	1.42	0.61	1.50	8.71
BAR1	11.99	0.75	0.48	2.14	0.65	1.29	17.29
BAR2	2.20	0.56	0.43	1.38	0.64	1.30	6.52
BAR3	1.53	0.79	0.55	1.64	0.73	1.45	6.69
BAR4	5.86	2.25	1.36	5.26	1.73	4.50	20.96
BAR6	1.20	0.17	0.21	0.84	0.30	0.03*	2.75
BAR7	0.58	0.14	0.03*	0.32	0.16	0.51	1.73
BAR8	2.71	1.00	0.85	2.10	1.67	2.12	10.45
BAR9	0.77	0.60	0.55	0.94	0.52	0.57	3.94
BAR10	4.93	2.01	1.43	4.14	2.10	4.07	18.69
PYR1	0.27	0.12	0.03*	0.17	0.01*	0.18	0.78
PYR2	0.55	0.28	0.03*	0.67	0.24	0.71	2.48
PYR4	0.58	0.62	0.53	1.32	0.51	0.73	4.30
PYR7	0.25*	0.17	0.03*	0.27	0.12	0.29	1.12
PYR8	0.84	0.29	0.32	1.09	0.37	1.05	3.97
PYR9	0.48	0.12	0.06	0.39	0.24	0.76	2.06
PYR10	11.90	0.02*	0.03*	0.02*	0.01*	0.03*	12.00
NÅ1	0.81	0.66	0.25	1.32	0.46	0.94	4.45
NÅ2	0.44	0.20	0.08	0.83	0.30	0.57	2.42
NÅ3	1.31	0.48	0.36	1.81	0.67	1.57	6.19
NÅ4	1.12	1.28	0.42	2.03	0.52	2.08	7.44
NÅ5	0.55	0.31	0.19	0.86	0.34	1.17	3.43
NÅ11**	1.67	1.20	0.89	2.98	1.49	3.09	11.31
NÅ13**	0.69	0.48	0.24	1.65	0.70	2.13	5.88
NÅ15**	247.92***	2.17***	1.00***	4.27**	1.54***	4.36***	261.26***

\* Samples under the limit of detection are given the value 0.5\*LOD

\*\* Samples from 2010

\*\*\* Individuals with extreme high concentration

### Appendix J- Spearman's correlation coefficient

Table J.1. Spearman's correlation coefficient between PCB-28/31. PCB-52. PCB-101. PCB-118. PCB-138. PCB-153. PCB-180, *trans*-nonachlor, *p,p'*-DDE, HCB, principal component 1 (PC1), principal component 2 (PC2), egg volume, lipid content and clutch size in eggs of snow bunting (*Plectrophenax nivalis*) (n=32).

ID	PCB-28/31	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180	<i>trans</i> -nonachlor	<i>p,p'</i> -DDE	HCB	Volume	Lipids	Clutch size	PC1	PC2
PCB-28/31	-	0.544**	0.494**	0.497**	0.482**	0.461**	0.484**	-	0.477**	-	-	-	-	0.521**	-0.351*
PCB-52	0.544**	-	0.878**	0.852**	0.847**	0.803**	0.753**	-	-	-	-	-	0.504**	0.799**	-
PCB-101	0.494**	0.878**	-	0.968**	0.953**	0.915**	0.821**	-	-	-	-	-	-	0.923**	-
PCB-118	0.497**	0.852**	0.968**	-	0.989**	0.959**	0.873**	-	-	-	-	-	-	0.946**	-
PCB-138	0.482**	0.847**	0.953**	0.989**	-	0.972**	0.908**	-	-	-	-	-	-	0.956**	-
PCB-153	0.461**	0.803**	0.915**	0.959**	0.972**	-	0.947**	-	-	-	-	-	-	0.978**	-
PCB-180	0.484**	0.753**	0.821**	0.873**	0.908**	0.947**	-	-	-	-	-	-	-	0.945**	-
<i>trans</i> -nonachlor	-	-	-	-	-	-	-	-	-	0.777**	-	0.538**	-	-	0.435*
<i>p,p'</i> -DDE	0.477**	-	-	-	-	-	-	-	-	-	-	0.562**	-	-	-
HCB	-	-	-	-	-	-	-	0.777**	-	-	-	-	-	-	-
PFOS	-	-	-	-	-	-	-	0.491**	-	0.360*	-	0.396*	-	-	0.650**
PFNA	-	-	-	-	-	-	-	0.623**	-	0.515**	-	0.353*	-	-	0.922**
PFDCa	-	-	-	-	-	-	-	0.505**	-	-	-	-	-	-	0.964**
PFUnA	-	-	-	-	-	-	-	0.680**	-	0.368**	-	0.402*	-	-	0.854**
PFDoA	-	-	-	-	-	-	-	0.657**	-	0.510**	-	0.369*	-	-	0.874**
PFTriA	-	-	-	-	-	-	-	0.708**	-	0.574**	-	0.476**	-	-	0.688**
Volume	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lipids	-	-	-	-	-	-	-	0.538**	-	0.562**	-	-	-	-	-
Clutch size	-	0.504**	-	-	-	-	-	-	-	-	-	-	-	-	-
PC1	0.521**	0.799**	0.923**	0.946**	0.956**	0.978**	0.945**	-	-	-	-	-	-	-	-
PC2	-	-	-	-	-	-	-	0.435*	-	-	-	-	-	-	-

\* Significance at  $p < 0.05$  (2-tailed)

\*\* Significance at the  $p < 0.001$  (2-tailed)

Table J.2. Spearman's correlation coefficient between PFOS, PFNA, PFDcA, PFUnA, PFDoA, PFTriA, principal component 1 (PC1), principal component 2 (PC2), egg volume, lipid content and clutch size in eggs of snow bunting (*Plectrophenax nivalis*) (n=32).

ID	PFOS	PFNA	PFDcA	PFUnA	PFDoA	PFTriA	Volume	Lipids	Clutch size	PC1	PC2
PCB-28/31	-	-	-	-	-	-	-	-	-	0.521**	-0.351*
PCB-52	-	-	-	-	-	-	-	-	0.504*	0.799**	-
PCB-101	-	-	-	-	-	-	-	-	-	0.923**	-
PCB-118	-	-	-	-	-	-	-	-	-	0.946**	-
PCB-138	-	-	-	-	-	-	-	-	-	0.956**	-
PCB-153	-	-	-	-	-	-	-	-	-	0.978**	-
PCB-180	-	-	-	-	-	-	-	-	-	0.945**	-
<i>trans</i> -nonachlor	0.491**	0.623**	0.505**	0.680**	0.657**	0.708**	-	0.538**	-	-	0.435*
HCB	0.360*	0.515**	-	0.568**	0.510**	0.574**	-	0.562**	-	-	-
<i>p,p'</i> -DDE	-	-	-	-	-	-	-	-	-	-	-
PFOS	-	0.638**	0.720**	0.614**	0.646**	0.461**	-	0.396*	-	-	0.650**
PFNA	0.638**	-	0.920**	0.924**	0.897**	0.788**	-	0.353*	-	-	0.922**
PFDcA	0.720**	0.920**	-	0.853**	0.902**	0.686**	-	-	-	-	0.964**
PFUnA	0.614**	0.924**	0.853**	-	0.944**	0.895**	-	0.402*	-	-	0.854**
PFDoA	0.646**	0.897**	0.902**	0.944**	-	0.873**	-	0.369*	-	-	0.874**
PFTriA	0.461**	0.788**	0.686**	0.895**	0.873**	-	-	0.476**	-	-	0.688**
Volume	-	-	-	-	-	-	-	-	-	-	-
Lipids	0.396*	0.353*	-	0.402*	0.369*	0.476**	-	-	-	-	-
Clutch size	-	-	-	-	-	-	-	-	-	-	-
PC1	-	-	-	-	-	-	-	-	-	-	-
PC2	0.650**	0.922**	0.964**	0.854**	0.874**	0.688**	-	-	-	-	-

\* Significance at  $p < 0.05$  (2-tailed)

\*\* Significance at the  $p < 0.001$  (2-tailed)