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Screening of PFAS and Dechlorane compounds in selected Arctic top predators



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Screening av PFAS og Dekloran forbindelser i utvalgte arktiske toppredatorer Screening of PFAS and Dechlorane compounds in selected Arctic top predators

Summary - sammendrag

This report summarizes the findings of a screening study into the occurrence of selected perfluorinated compounds (PFCs) and dechloranes in Arctic top predators. The emerging PFCs F53 F53B, and PFBS were not detected neither in bird eggs nor in mammals. However, different dechloranes were detected in all samples.

Denne rapporten oppsummerer resultatene av en screeningundersøkelse om forekomst av utvalgte perfluorerte forbindelser i Arktiske toppredatorer. PFOS erstatningsstoffer kunne ikke påvises i noen av de undersøkte prøver, verken i fuglegg eller pattedyr. Flere forskjellige dekloraner ble påvist i alle prøver.

4 emneord

PFAS, Dechlorane, Arctic, Top predators

PFAS, Dekloran, Arktis, Toppredatorer

4 subject words

Front page photo

Geir Wing Gabrielsen

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Summary

On behalf of the Norwegian Environment Agency NILU - Norwegian Institute for Air Research in collaboration with the Norwegian Polar Institute studied the new emerging PFAS F53 and F53B, and Dechlorane compounds in selected Arctic top predators in comparison with well-known pollutants perfluorinated sulfonic and carboxylic acids and PCB 153.

In all samples, it was possible to detect PFOS, PFOA, PCB-153, and some dechloranes. It was not possible to detect the emerging PFAS compounds F53, F53B, and PFBS above the limit of detection (LoD). The pattern of detected dechlorane(s) is depending on the studied species, with Dec 602 found in all samples except of ringed seal. DP syn and anti were only found in mammal samples.

In eggs from glaucous gull, the mean PFOS concentration was 4.5 ng/g ww. PFOA was also present, however, at a much lower concentration of 0.51 ng/g ww. Dec 602 was possible to detect above LoD with mean concentrations of 0.21 ng/g ww, which is much lower than PCB-153 which showed a concentration of 166 ng/g ww.

In eggs from kittiwake, mean PFOS concentration was 6.3 ng/g ww. PFOA was also present, however, with a much lower concentration of 0.03 ng/g ww. Of the selected dechloranes, only Dec 602 was possible to detect above LoD with concentration of 0.26 ng/g ww, which is much lower than PCB-153 with a concentration of 160 ng/g ww.

In liver samples of ringed seal, mean PFOS concentration was 2.8 ng/g ww. PFHxS was also present in five of ten samples, however, with a much lower concentration of 0.08 ng/g ww. No PFBS, or other fluorinated sulfonic acids were found in samples of ringed seal. Of the analysed perfluorinated carboxyl acids, PFNA and PFUnA were found with the highest concentrations at 0.77 and 0.69 ng/g ww respectively. In addition, three more long chained carboxylic acids were detected in all samples (PFDcA, PFDoA, and PFTriA). The sum of the C9 to C14 carboxylic acids is 2.21 ng/g ww and in the same range as the PFOS concentration. PFOA was also present in 7 of 10 samples, however, with a much lower concentration of 0.05 ng/g ww. In contrast to the avian samples, it was possible to detect DP syn and DP anti, together with PCB-153 in seal. The concentrations of the other measured dechloranes were below LoD (0.02 - 0.2 ng/g ww). The DP syn concentrations were 0.10 ng/g ww on mean, and DP anti 0.17 ng/g ww on mean, which is lower than PCB-153 with a mean of 1.6 ng/g ww. These DP concentrations are in the same range as what was found in ringed seal blubber from Eastern Greenland.

In whole blood samples of polar bear, mean PFOS concentration was 84 ng/g ww. PFHxS was also present in all samples, with a mean concentration of 18 ng/g ww. It was not possible to detect any of the other fluorinated sulfonic acids. Of the analysed perfluorinated carboxyl acids, PFNA and PFUnA were found with the highest mean concentrations of 18 and 12 ng/g ww respectively. In addition, four more long chain carboxylic acids were detected in all samples (PFDcA, PFDoA, PFTriA, and PFTeA). PFOA was also present in all samples with a mean concentration of 6.3 ng/g ww. Of the dechloranes, Dec 602, DP syn, and DP anti, together with PCB-153 were detect above LoD. The dechloranes were detected at much lower mean concentrations well below 1 ng/g compared to 7 ng/g ww for PCB-153.

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Sammendrag

På vegne av Miljødirektoratet undersøkte NILU - Norsk institutt for luftforskning sammen med Norsk Polarinstituttet forekomsten av to nye perfluorerte alkylstoffer F53 og F53B, forskjellige dekloran forbindelser samt de mer kjente miljøgiftene PFOS, PFOA og PCB-153 i et utvalg av arktiske toppredatorer.

I alle undersøkte prøver ble det påvist PFOS, PFOA, PCB-153 og noen dekloraner. Det ble ikke påvist F53 og F53B over deteksjonsgrensen. Dekloran-mønsteret, det vil si den relative fordelingen mellom de forskjellige dekloraner, er forskjellig i de undersøkte artene. Dekloran Dec 602 ble funnet i alle eggprøver og i blod fra isbjørn, men ikke i lever fra ringsel. Dechlorane plus, både syn og anti isomer, ble bare funnet i prøver fra pattedyr.

I alle polarmåkeegg ble PFOS funnet med høyest konsentrasjon av alle målte stoffer med en gjennomsnittskonsentrasjon på 4,5 ng/g våt vekt. Også PFOA ble påvist i alle polarmåkeprøver, men med en mye lavere gjennomsnittskonsentrasjon på 0,51 ng/g våt vekt. Av dekloranene var det mulig å påvise Dec 602 med en gjennomsnittskonsentrasjon på 0,21 ng/g våt vekt som er en mye lavere konsentrasjon enn PCB-153 med 166 ng/g våt vekt.

I alle krykkjeegg ble PFOS funnet med høyest konsentrasjon av alle målte stoffer med en gjennomsnittskonsentrasjon på 6,3 ng/g våt vekt. Også PFOA ble påvist i alle krykkjeprøver, men med en mye lavere gjennomsnittskonsentrasjon på 0,03 ng/g våt vekt. Av dekloranene var det mulig å påvise Dec 602 med en gjennomsnittskonsentrasjon på 0,26 ng/g våt vekt som er en mye lavere konsentrasjon enn PCB-153 med 160 ng/g våt vekt.

I alle leverprøver fra ringsel var det mulig å påvise PFOS hvor gjennomsnittskonsentrasjonen var 2,8 ng/g våt vekt. I fire av ti prøver ble også PFHxS påvist, med konsentrasjon på 0,08 ng/g våt vekt. Det ble ikke detektert andre fluorerte sulfonsyrer. Av de analyserte perfluorerte karboksylsyrene ble de høyeste konsentrasjonene funnet for PFNA og PFUnA, med henholdsvis 0,77 og 0,69 ng/g våt vekt. I tillegg ble også tre langkjedede karboksylsyrer påvist i alle prøvene (PFDcA, PFDoA og PFTriA). Summen av C9-C14 karboksylsyrene er 2,21 ng/g våt vekt, og er i det sammen konsentrasjonsområdet som for PFOS. PFOA ble påvist i syv av ti prøver med en noe lavere gjennomsnittskonsentrasjon på 0,05 ng/g våt vekt. I motsetning til eggprøver var det mulig å påvise syn og anti dekloran plus (DP syn og DP anti) med en gjennomsnittskonsentrasjon på 0,10 ng/g våt vekt (DP syn) og 0,17 ng/g våt vekt. (DP syn) som er noe lavere konsentrasjon enn PCB-153 som ble funnet med 1,6 ng/g våt vekt. Tilsvarende DP konsentrasjoner ble også funnet i ringselspekk fra Østgrønland.

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I alle blodprøver fra isbjørn var det mulig å påvise PFOS med en gjennomsnittskonsentrasjon på var 84 ng/g våt vekt. PFHxS ble også påvist i alle prøvene med en

gjennomsnittskonsentrasjon på 18 ng/g våt vekt. Ingen av de andre fluorerte sulfonsyrene ble påvist. Av de analyserte perfluorerte karboksylsyrene ble de høyeste konsentrasjonene funnet for PFNA og PFUnA, med henholdsvis 18 og 12 ng/g våt vekt. I tillegg ble også fire langkjedede karboksylsyrer påvist i alle prøvene (PFDcA, PFDoA, PFTriA og PFTeA). Også PFOA ble påvist i alle isbjørnblodprøver, med en gjennomsnittskonsentrasjon på 4,1 ng/g våt vekt. Som hos ringsel var det mulig å påvise syn og anti dekloran plus (DP syn og DP anti), men også Dec 602. Alle dekloraner hadde en vesentlig lavere konsentrasjon enn PCB-153, under 1 ng/g våt vekt, mens gjennomsnittlig PCB-153 konsentrasjon var 7 ng/g våt vekt.

1. Background and introduction

1.1 General

The goal of this project was to study the occurrence of potentially long-range transported compounds in Arctic biota. Such data are very useful for the evaluation of the environmental risk of chemicals and an important input to the negotiations leading to international regulations. In this study, two emerging PFAS and a group of chlorinated flame-retardants were in focus and the following top predators and matrices were selected based on relevance and availability: Egg samples of glaucous gull and kittiwake, liver samples of ringed seal, and whole blood samples of polar bear.

1.2 Selected compounds

Per- and polyfluorinated alkylated compounds shown in Table 1 were analysed in this study. For the mammal samples, the complete list of compounds will be reported in this report. However, the selected egg samples are a part of another study and will be reported later.

| Table 1: PFAS Name, Acronym, CAS, Function | | | |
|--|---------|--|---------------------------|
| Name | Acronym | Structure | CAS |
| Perfluorooctane sulfonamide | PFOSA | O F F F F F F F F H ₂ N-S H + H + H + H F O F F F F F F F F | 754-91-6 |
| Perfluorobutane sulfonic acid | PFBS | 0 F F F F HO-S + + + F 0 F F F F | 375-73-5 or 59933-66-3 |
| Perfluoropentane sulfonic acid | PFPS | 0 F F F F F HO-S <mark>+++++</mark> F Ö F F F F F | 2706-91-4 |
| Perfluorohexane sulfonic acid | PFHxS | 0 F F F F F F HO-S H F F F F F F F F F F F F F F F F F F | 355-46-4 |
| Perfluoroheptane sulfonic acid | PFHpS | 0 F F F F F F F HO-S + + + + + + + F 0 F F F F F F F | 375-92-8 |
| Perfluorooctansulfonate | PFOS | 0 HO-S HO-S HO-S HO-S HO-S HO-S HO-S HO-S | 2795-39-3 |

| Table 1: PFAS Name, Acronym, CAS, Function | | | |
|---|---------|---|-------------|
| Name | Acronym | Structure | CAS |
| Branched Perfluorooctan- sulfonate* | brPFOS | F F F F HO-S HO-S F F F F F F O F F F F F F | |
| Perfluorononane sulfonic acid | PFNS | 0 F F F F F F F F F HO-\$ + + + + + + + F 0 F F F F F F F F F F | 474511-07-4 |
| Perfluorodecane sulfonic acid | PFDcS | 0 F F F F F F F F F F F HO-S + + + + + + + + + + + + + + + + + + + | - 335-77-3 |
| Perfluorohexanoic acid | PFHxA | O F F F F F HO F F F F F | 307-24-4 |
| Perfluoroheptanoic acid | PFHpA | O F F F F F F HO F F F F F F | 375-85-9 |
| Perfluorooctanoic acid | PFOA | 0 F F F F F F F | 335-67-1 |
| Perfluorononanoic acid | PFNA | 0 F F F F F F F F HO F F F F F F F F F F F F F F F F F F F | 375-95-1 |
| Perfluorodecanoic acid | PFDcA | 0 F F F F F F F F F HO F F F F F F F F F F F F F F F F F F F | 335-76-2 |
| Perfluoroundecanoic acid | PFUnA | 0 F F F F F F F F F F F F F F F F F F F | 2058-94-8 |
| Perfluorododecanoic acid | PFDoA | 0 F F F F F F F F F F F F F F F F F F F | 307-55-1 |
| Perfluorotridecanoic acid | PFTriA | 0 F F F F F F F F F F F F F F F F F F F | 72629-94-8 |

| Table 1: PFAS Name, Acronym, CAS, Function | | | |
|--|---------|---|-------------|
| Name | Acronym | Structure | CAS |
| Perfluorotetradecanoic acid | PFTeA | 0 F F F F F F F F F F F F F F HO F F F F F F F F F F F F F F F F F F F | 376-06-7 |
| 6:2 Fluorotelomer sulfonic acid | 6:2FTS | HO-S FFFFFF FFFFFF FFFFFFF | 27619-97-2 |
| 8:2 Fluorotelomer sulfonic acid | 8:2 FTS | HO-S HO-S O FFFFFFFFFFF FFFFFFFFFFFFFFFFFFFFFF | 39108-34-4 |
| Potassium 1,1,2,2- tetrafluoro-2- (perfluorohexyloxy) ethane sulfonate | F53 | $F F F F F F F$ $F F F F F F F$ $F F F F F F F F$ $O S F$ $K^+ O$ | 754925-54-7 |
| Potassium 2-(6-chloro- 1,1,2,2,3,3,4,4,5,5,6,6- dodecafluorohexyloxy)- 1,1,2,2-tetrafluoroethane sulfonate | F53B | $ \begin{array}{c} F F F F F F F F F F F F F F F F F F F $ | 73606-19-6 |

*One of several possible structures

PFAS have been in use for over 60 years for various industrial purposes such as in electronic devices, fire-fighting foam, hydraulic fluids, metal plating and textiles. In 2000, the major producer of PFOS voluntarily started to phase-out the use of this compound. Today PFOS, its salts and PFOSF are included in Annex B of the Stockholm Convention. On the other hand, widespread manufacturing of PFOS and related substances started in China in the first decade of this century. The other important PFAS group are the perfluoroalkyl carboxylates (PFCAs). Production and use of perfluorooctanoate (PFOA) and its homologues have been phased out in the western countries following agreements with manufacturers. Today, PFOA is being considered as a candidate for the "substances of very high concern" by The European Chemicals Agency (Z. Wang, Cousins, Scheringer, Buck, & Hungerbuhler, 2014; Zhanyun Wang, Cousins, Scheringer, Buck, & Hungerbühler, 2014). There are also planned restrictions under REACH, and global restriction are prepared under the Stockholm convention.

Some of the major alternatives to PFOS in the chrome plating industry are perfluorobutane sulfonate (PFBS) based substances, 6:2 fluorotelomer sulfonate (6:2 FTS) and 2-[(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)oxy]-1,1,2,2-tetrafluoroethanesulfonate, typically referred to by its trade name F-53B (CAS No. 73606-19-6).(S. Wang et al., 2013; Zhanyun Wang, Cousins, Scheringer, & Hungerbühler, 2013; Xie, Lu, et al., 2013; Xie, Wang, et al., 2013; Yang et al., 2014; Zhang et al., 2012). The F53, is structurally similar to the F53B without the chlorine. The relatively high detection frequency of F-53B at comparable concentrations to those of PFOS, reported by Wang et al., 2016, suggests a widespread use of this fluorinated alternative in China (T. Wang, Vestergren, Herzke, Yu, & Cousins, 2016).

Samples with detectable levels of F-53B and 6:2 FTS were positively correlated with PFOS (Spearman's rho 0.75 and 0.66, respectively, p <0.01; Table S6). The positive correlation between these substances probably reflect similar emission sources originating from the usage in metal plating processes as mist suppressant (S. Wang et al., 2013). This conclusion is consistent with the ubiquitous detection of F-53B in sewage sludge and strong correlation with PFOS (Ruan, Lin, Wang, Liu, & Jiang, 2015).

| Table 2: Dechloranes Name, Acronym, CAS, Function, and Log Kow | | | | | |
|--|---------|--|-------------------|--------------------|---------------------|
| Name | Acronym | Structure | CAS | Function | Log K _{ow} |
| Dechlorane plus | DP | $\begin{array}{c c} CI & CI & CI & CI \\ CI & CI & CI & CI \\ CI & CI &$ | 13560-89-9 | Flame retardant | 8.85 |
| Dechlorane plus is exist approximate ratio of 1: | | different isomers, syn and a | nti, which are fo | ormed in the | |
| Dechlorane plus syn | DP syn | | 135821-03-3 | Flame retardant | 8.85 |
| Dechlorane plus anti | DP anti | | 135821-74-8 | Flame retardant | 8.85 |
| Dechlorane 601 | Dec 601 | | 13560-90-2 | Flame retardant | 9.22 |
| Dechlorane 602 | Dec 602 | | 31107-44-5 | Flame retardant | 7.37 |
| Dechlorane 603 | Dec 603 | | 13560-92-4 | Flame retardant | 8.24 |

| Table 2: Dechloranes Name, Acronym, CAS, Function, and Log Kow | | | | | |
|--|---------|----------------------|------------|--------------------|---------------------|
| Name | Acronym | Structure | CAS | Function | Log K _{ow} |
| Dechlorane 604 | Dec 004 | Br Br Br Br | 34571-16-9 | Flame retardant | 8.84 |
| Dibromoaldrin | DBALD | | 20389-65-5 | Flame retardant | 5.77 |

Under the heading dechlorane we find different dechlorane structures and the closely related dibromoaldrine (DBALD). All of them are used as flame retardants or are impurities of DP and are polycyclic and highly chlorinated (or partly brominated) compounds. As the production of these compounds start with hexachlorocyclopentadiene (HCCP) they are chemically closely related to Mirex and a lot of other pesticides.

There is a growing international interest in dechlorane related compounds with an increasing number of scientific papers and reports on this compound group. A review study in 2011 on Dechlorane Plus (DP) summarized the available information as following: Dechlorane Plus (DP) is a high production volume and very persistent compound. DP is a global contaminant and has recently been detected along a pole-to-pole transect of the Atlantic Ocean. There seems to be one production site in North America and at least one in China. Beside DP there are other closely related compounds in the environment. These DP analogs have also been detected globally. Modeling data are in agreement with available environmental data, proposing DP and analogs to be persistent, bioaccumulative, and long-range transported (Sverko et al., 2011).

2. Materials and Methods

2.1 Sampling stations and sample collection

Sample collection, transport and storage before analysis was done under the responsibility of the Norwegian Polar Institute.

Eggs from kittiwakes and Glaucous gulls were sampled at the Islands Observasjonsholmen, Kapp Guissez and Krykkjefjellet in Kongsfjorden, Svalbard. A total of 10 eggs of black-legged kittiwake (n= 10) and glaucous gulls (n=5) were collected randomly in 2013 and 2014 respectively. The sampling of eggs were performed in June both years. The eggs were wrapped in aluminium foil and stored frozen until laboratory analysis (Lucia, Gabrielsen, Herzke, & Christensen, 2016).

Ringed seals were shot on the sea ice. The samples were taken from the carcasses on the ice. The liver sample was cut out and placed on an aluminium foil before stored in a ziplock bag and frozen (-20 $^{\circ}$ C). Samples (n=10) were stored frozen at -20 $^{\circ}$ C until analysis.

Blood from polar bears were collected during the spring sampling (April) in 2016 at the northeastern part of Svalbard (n = 5 females and n= 5 males). Blood from polar bears was centrifuged in the field. Plasma was transferred to cryogenic vials and immediately frozen (-20 °C). Samples (n=10) were stored frozen at -20 °C until analysis.

The selected species were recently described in detail in public reports (Lucia et al., 2016; Sagerup et al., 2011).

2.2 Chemical analysis

All chemical analyses were done by NILU.

2.2.1 PFAS

Sample extraction and clean-up

Prior to extraction, a mixture of isotope labelled perfluorinated sulfonic acids and PFCAs was added to the samples. The samples were extracted with acetonitrile. The obtained sample extract was concentrated under vacuum and treated with an emulsive clean-up. Egg samples were processed by Randi Rodvelt, NTNU. All other samples were processed by NILU staff.

Instrumental analysis

The instrumental analysis were performed on a Thermo UPLC-MS/MS in ESI(-) mode.

2.2.2 Dechlorane compounds

Sample extraction and clean-up

Prior to extraction, the samples were added a mixture of isotope labelled PCB and dechloranes for quantification purposes. The water-, sediment-and biota-samples were extracted with organic solvents and concentrated under nitrogen flow, followed by a clean-up procedure using concentrated sulphuric acid and a silica column to remove lipids and other interferences prior to analysis.

Analysis

Prior to analysis, all samples were concentrated to ~150 μ L sample volume. The extracts were injected into an Agilent 7890N GC system coupled to an Agilent 7200 QToF mass spectrometer operated in electron capture negative ionization mode (GC-ECNI-HRMS) and PCB-153 and the dechlorane compounds were quantified based on the use of internal standards.

3. Results and discussion

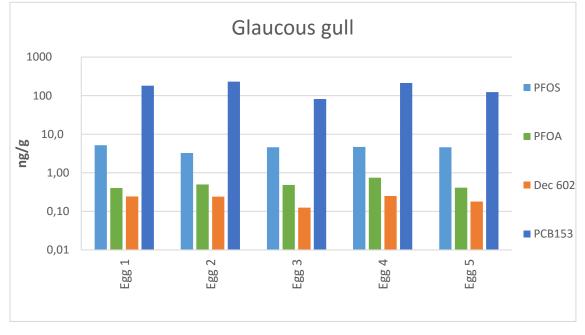
A complete data table with all analytical results is attached in the appendix. A summary of the results showing the mean concentration of all studied compounds in all matrices is shown in Table 3. When calculating mean concentration, non-detects were replaced by $\frac{1}{2}$ *LoD and included into the calculation.

| Table 3: Mean concentration of all studied compounds in all samples | | | | |
|---|------------------|----------------------|--------------------|---------------|
| Concentration in ng/ | g ww, Red shadin | g indicating the rel | ative distribution | |
| Compound | Glaucous Gull | Kittiwake | Ringed Seal | Polar bear |
| PFOSA | n.a. | n.a. | 0.03 | 2.19 |
| PFBS | n.a. | n.a. | n.f. | n.f. |
| PFPS | n.a. | n.a. | n.f. | 0.05 |
| PFHxS | n.a. | n.a. | 0.06 | 17.6 |
| PFHpS | n.a. | n.a. | n.f. | 2.86 |
| PFOS | 4.46* | 6.34* | 2.76 | 83.7 |
| brPFOS | n.a. | n.a. | 0.69 | 27.3 |
| PFNS | n.a. | n.a. | n.f. | n.f. |
| PFDcS | n.a. | n.a. | n.f. | n.f. |
| PFHxA | n.a. | n.a. | n.f. | n.f. |
| PFHpA | n.a. | n.a. | n.f. | 0.49 |
| PFOA | 0.51* | 0.03* | 0.05 | 4.10 |
| PFNA | n.a. | n.a. | 0.77 | 18.2 |
| PFDcA | n.a. | n.a. | 0.37 | 6.32 |
| PFUnA | n.a. | n.a. | 0.69 | 12.0 |
| PFDoA | n.a. | n.a. | 0.10 | 1.53 |
| PFTriA | n.a. | n.a. | 0.23 | 3.01 |
| PFTeA | n.a. | n.a. | n.f. | 0.30 |
| 6:2FTS | n.a. | n.a. | 0.05 | n.f. |
| 8:2 FTS | n.a. | n.a. | n.f. | n.f. |
| F53 | n.f. | n.f. | n.f. | n.f. |
| F53B | n.f. | n.f. | n.f. | n.f. |
| Dibromoaldrin | n.f. | n.f. | n.f. | n.f. |
| Dec 601 | n.f. | n.f. | n.f. | n.f. |
| Dec 602 | 0.21 | 0.26 | n.f. | 0.08 |
| Dec 603 | n.f. | n.f. | n.f. | n.f. |
| Dec 604 | n.f. | n.f. | n.f. | n.f. |
| DPsyn | n.f. | n.f. | 0.10 | 0.07 |
| DPanti | n.f. | n.f. | 0.17 | 0.14 |
| PCB153 | 166 | 160 | 1.65 | 7.15 |

*: Data Randi Rodvelt

n.a.: not analysed.

n.f.: not found



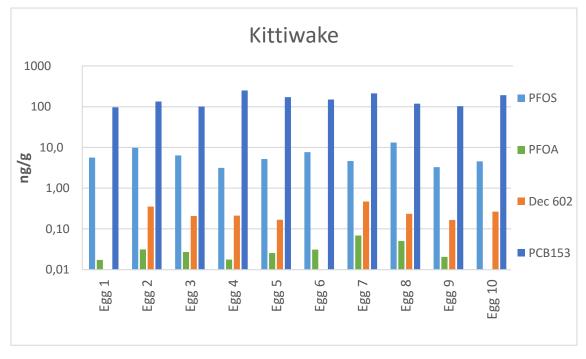
3.1 Glaucous gull eggs

Figure 1: Concentration of PFOS, PFOA, Dec602, and PCB-153 in egg samples from glaucous gulls. Concentration given in ng/g ww on a logarithmic scale.

Of the measured PFAS compounds, PFOS was found with the highest concentration for the five samples (see Table 4 and Figure 1). PFOA was also present, however, with a much lower concentration. In glaucous gull eggs it was not possible to detect the two emerging PFAS compounds F53 and F53B above the limit of detection (LoD), which was 0.05 and 0.02 ng/g ww for F53 and F53B respectively.

| Table 4: Detected analyte concentrations in glaucous gull eggs | | | | | |
|--|--------------------------------------|---------------------------------------|-----------------------------------|--|--|
| PFOS | PFOA | Dec 602 | PCB-153 | | |
| me | 'max ean requency % | ng/g | ww | | |
| (3.2 - 5.2) 4.5 100 % | (0.40 - 0.74) 0.5 100 % | (0.12 - 0.25) 0.21 100 % | (82 - 231) 166 100 % | | |

The following seven dechlorane related compounds together with PCB-153 were measured: Dec 601, Dec 602, Dec 603, Dec 604, DP syn, DP anti, and DBALD. In glaucous gull only Dec 602 and PCB-153 was possible to detect above LoD (0.1 - 0.2 ng/g ww). The Dec 602 concentration was 0.21 ng/g ww on mean and much lower than PCB-153 with a mean of 166 ng/g ww. In liver samples of glaucous gulls from Greenland, however, it was possible to detect DP syn and DP anti with an mean of 0.023 and 0.11 ng/g ww (Vorkamp et al., 2015). If this is due to different levels in egg and liver or due to a higher contamination of the glaucous gulls from Greenland is not possible to conclude from the present study. In a recent study of legacy and new POPs in avian tissues from King George Island, Antarctica, it was also Dec 602, which showed the highest concentration of all measured dechloranes, about threefold higher than the sum of the DPs (Kim et al., 2015).



3.2 Kittiwake eggs

Figure 2: Concentration of PFOS, PFOA, Dec602, and PCB-153 in egg samples from kittiwakes. Concentration given in ng/g ww on a logarithmic scale.

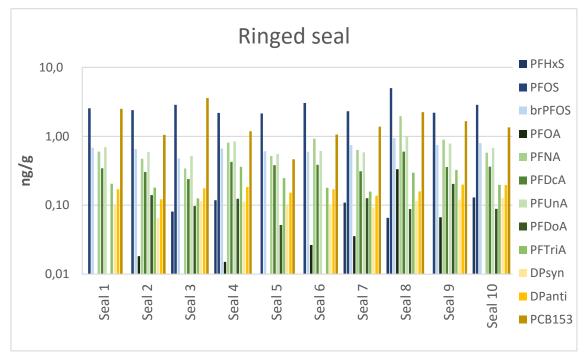
Of the measured PFAS compounds, PFOS was found with the highest concentration for the ten measured samples (see Table 5 and Figure 2). PFOA was also present, however, with a much lower concentration. It was not possible to detect the two emerging PFAS compounds F53 and F53B in kittiwake eggs above the limit of detection (LoD), which was 0.05 and 0.02 ng/g ww for F53 and F53B respectively.

| Table 5: Detected analyte concentrations in kittiwake eggs | | | | | |
|--|---------------------------------------|---------------------------------------|-----------------------------------|--|--|
| PFOS | PFOA | Dec 602 | PCB-153 | | |
| me | 'max ean requency % | ng/g | ww | | |
| (3.1 - 13) 6.3 100 % | (<0.15 - 0.07) 0.03 90 % | (0.16 - 0.47) 0.26 100 % | (96 - 250) 160 100 % | | |

The following seven dechlorane related compounds together with PCB-153 were measured: Dec 601, Dec 602, Dec 603, Dec 604, Dechlorane plus syn, Dechlorane plus anti, and DBALD. Only Dec602 and PCB-153 was possible to detect above LoD (0.1 - 0.2 ng/g ww). The Dec602 concentration was 0.26 ng/g ww on mean and much lower than PCB-153, which showed an mean of 160 ng/g ww. For two of the 10 samples it was not possible to determine the dechloranes, since the stored extracts were completely evaporated under storage.

3.3 Ringed seal liver

In Figure 3 the concentration of the most prominent of the detected compounds in liver samples of ringed seal is shown.



In almost all samples PFOS shows the highest concentration, closely followed by PCB-153.

Figure 3: Concentration of all detected compounds in liver samples from ringed seal. Concentration given in ng/g ww on a logarithmic scale.

Of the measured PFAS compounds, PFOS was found with the highest mean concentration with 2.8 ng/g ww of the 10 samples. Roughly 25 % of the total PFOS were related to the branched PFOS (br PFOS) derivatives. PFHxS was also present in five of ten samples, however, with a much lower concentration of 0.08 ng/g ww on mean of 10 samples. No other fluorinated sulfonic acids were found in samples of ringed seal (see Figure 4 and Table 6).

The emerging PFAS compounds F53 and F53B, and PFBS could not be detected above the limit of detection (LoD), which was between 0.05 and 0.02 ng/g ww.

| Table 6: Concentration of perfluorinated sulfonic acids in ringed seal liver | | | | | |
|--|--|------------------------------------|---------------------------------------|--|--|
| PFOSA | PFHxS | PFOS | br-PFOS | | |
| Detec | min/max Mean tion frequency % | | ng/g ww | | |
| (<0.05 - 0.06) 0.03 10 % | (<0.05 - 0.13) 0.06 100 % | (2.1 - 5.0) 2.8 100 % | (0.48 - 0.94) 0.69 100 % | | |

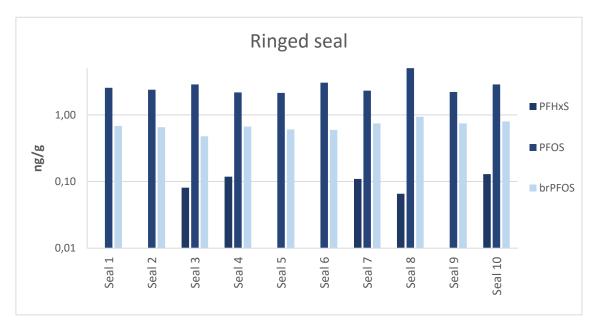


Figure 4: Concentration of all detected perfluorinated sulfonic acids (PFHxS and PFOS) in liver samples from ringed seal. Concentration are given in ng/g ww on a logarithmic scale.

Of the analysed perfluorinated carboxyl acids PFNA and PFUnA were found with the highest concentrations 0.77 and 0.69 ng/g ww respectively. In addition, three more long chain carboxylic acids were detected in all samples (PFDcA, PFDoA, and PFFriA). The sum of the mean concentration of C9 to C14 carboxylic acids is 2.21 ng/g ww and in the same range as the mean PFOS concentration. PFOA was also present in 7 of 10 samples, however, with a much lower concentration of 0.05 ng/g ww on mean (see Figure 5 and Table 1). The PFAS pattern is in agreement with a study on plasma from ringed seals sampled from Svalbard (H. Routti, Gabrielsen, Herzke, Kovacs, & Lydersen, 2016).

| Table 7: Concentration of perfluorinated carboxylic acids in ringed seal liver | | | | | | | |
|--|--|---------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|--|--|
| PFOA | PFNA | PFDcA | PFUnA | PFDoA | PFTriA | | |
| De | min/max ng/g ww Mean Detection frequency % | | | | | | |
| (<0.015 - 0.33) 0.05 100 % | (0.34 - 2.0) 0.77 100 % | (0.24 - 0.60) 0.37 100 % | (0.52 - 1.0) 0.69 100 % | (<0.05 - 0.20) 0.10 80 % | (0.13 - 0.36) 0.23 100 % | | |

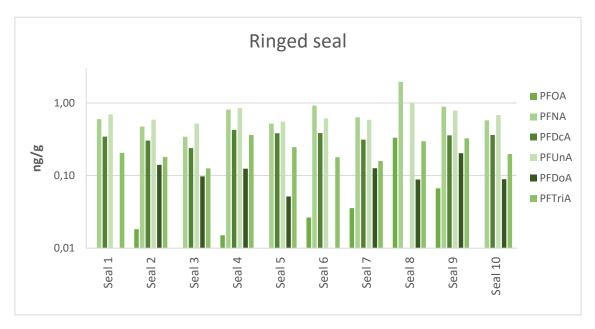


Figure 5: Concentration of all detected perfluorinated carboxylic acids in liver samples from ringed seal. Concentration given in ng/g ww on a logarithmic scale.

The following seven dechlorane related compounds were measured together with PCB-153: Dec 601, Dec 602, Dec 603, Dec 604, Dechlorane plus syn, Dechlorane plus anti, and DBALD. In contrast to the avian samples, it was possible to detect DP syn and DP anti in seal liver, together with PCB-153. The concentration of the other measured dechloranes was below LoD (0.02 - 0.2 ng/g ww). The DP syn and DP anti concentration were 0.10 ng/g ww on mean for DP syn and 0.17 ng/g ww on mean for DP anti, which is lower than PCB-153 with a mean of 1.6 ng/g ww (see Table 8 and Figure 6).

This DP concentrations are in the same range as what was found in ringed seal blubber from Eastern Greenland (0.096/0.42 ng/g ww DP syn/DP anti) (Vorkamp et al., 2015).

| Table 8: Concentration of dechloranes in ringed seal liver | | | | | |
|--|---|-------------------------------------|--|--|--|
| DPsyn | DPanti | PCB-153 | | | |
| Me | min/max Mean ng/g ww Detection frequency % | | | | |
| (0.06 - 0.13 0.10 100 % | (0.12 - 0.20) 0.17 100 % | (0.47 - 3.6) 1.6 100 % | | | |

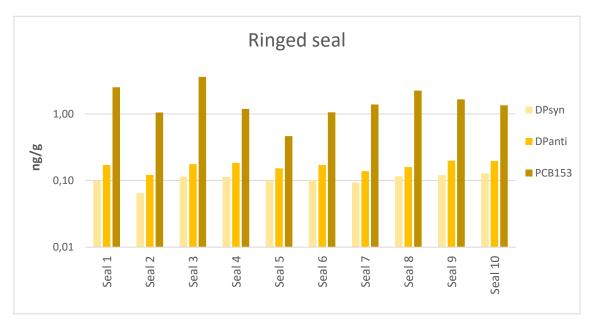


Figure 6: Concentration of detected dechloranes (DPsyn and DPanti) and PCB-153 in liver samples from ringed seal. Concentration given in ng/g ww on a logarithmic scale.

3.4 Polar bear blood

In Figure 7 the concentration of the most prominent of the detected compounds in whole blood samples of polar bear is shown.

In all samples PFOS shows the highest concentration, followed by PCB-153.

Whereas PFOS shows a very narrow sample-to-sample variation (Coefficient of variation: CV = 0.37), we observe a much higher degree of sample-to-sample variation for PCB-153 (CV = 1.2). With only ten samples the statistical basis is too limited to speculate on explanations for this observation.

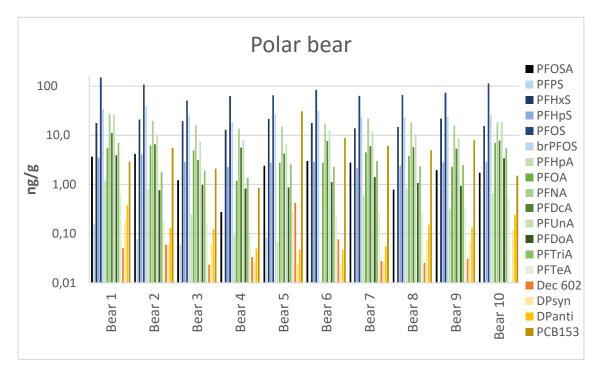


Figure 7: Concentration of all detected compounds in whole blood samples of polar bear from Spitsbergen. Concentration given in ng/g ww.

Of the measured perfluorinated sulfonic acids, PFOS was found with the highest concentration of 84 ng/g ww on mean of the 10 samples (Table 9 and Figure 8). Roughly 30 % of the total PFOS were related to the branched PFOS (br PFOS) derivatives. PFHxS was also present in all samples, with a concentration of 18 ng/g ww on mean for all samples. It was not possible to detect PFBS above LoD (< 0.05 ng/g ww). In contrast, PFBS was detected in all polar bear plasma samples analysed for this compound (n=70) (Heli Routti et al., 2017).

The emerging PFAS compounds F53 and F53B, and PFBS could not be detected above the limit of detection (LoD), which was between 0.05 and 0.02 ng/g ww.

| Table 9: Con | Table 9: Concentration of perfluorinated sulfonic acids in polar bear blood | | | | | | | | | | | |
|-------------------------------------|---|---------------------------------|----------------------------------|----------------------------------|---------------------------------|--|--|--|--|--|--|--|
| PFOSA PFPS PFHxS PFHpS PFOS br-PFOS | | | | | | | | | | | | |
| D | min/max Mean ng/g ww Detection frequency % | | | | | | | | | | | |
| (0.3 - 4) 2.2 100 % | (<0.05 - 0.16) 0.03 40 % | (13 - 22) 18 100 % | (2.1-4.1) 2.9 100 % | (51 - 149) 84 100 % | (18 - 39) 27 100 % | | | | | | | |

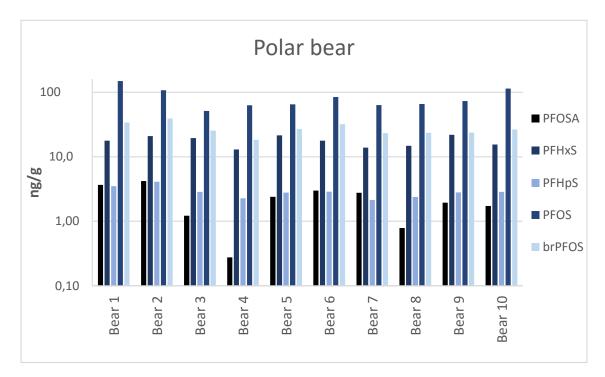


Figure 8: Concentration of the detected perfluorinated sulfonic acids (PFHxS and PFOS) in whole blood samples of polar bear from Spitsbergen. Concentration given in ng/g ww.

Even with still high PFOS concentrations in polar bears, concentrations found in this study are considerably lower than what was found earlier. In the screening report from 2013, PFOS in polar bear plasma was reported with a mean of 205 ng/g, about two times higher, fitting well with the expected plasma versus full blood ratio (Harju, Herzke, & Kaasa, 2013). A study on temporal trends of PFAS in polar bear plasma samples (n=192), which also takes into account biological and ecological effects, shows that PFOS concentrations have declined during the period 2003-2009 after which the decline has stabilized (Heli Routti et al., 2017).

Of the analysed perfluorinated carboxyl acids PFNA and PFUnA were found with the highest concentrations 18 and 12 ng/g ww respectively (Table 10 and Figure 9). In addition, three more long chain carboxylic acids were detected in all samples (PFDcA, PFDoA, PFTriA, and PFTeA). The sum of the mean concentration of C9 to C14 carboxylic acids is 41 ng/g ww and about half of the mean PFOS concentration.

PFOA was also present in all samples, however, with a much lower concentration of 6.3 ng/g ww on mean.

The PFAS patterns are in agreement with previous studies on PFAS in polar bear plasma from Svalbard (Bytingsvik et al., 2012; Heli Routti et al., 2017; Tartu et al., 2017).

| Table 10: | Table 10: Concentration of perfluorinated carboxylic acids in polar bear blood | | | | | | | | | | | |
|--|--|---------------------------------|-----------------------------------|----------------------------------|------------------------------------|------------------------------------|-------------------------------------|--|--|--|--|--|
| PFHpA PFOA PFNA PFDcA PFUnA PFDoA PFTriA PFTeA | | | | | | | | | | | | |
| | min/max ng/g ww Mean Detection frequency % | | | | | | | | | | | |
| (<0.05 - 1.2) 0.49 90 % | (1.2 - 7.0) 4.1 100 % | (14 - 27) 18 100 % | (3.1 - 11) 6.3 100 % | (6.8 - 26) 12 100 % | (0.8 - 3.9) 1.5 100 % | (1.4 - 7.0) 3.0 100 % | (0.09 - 0.7) 0.3 100 % | | | | | |

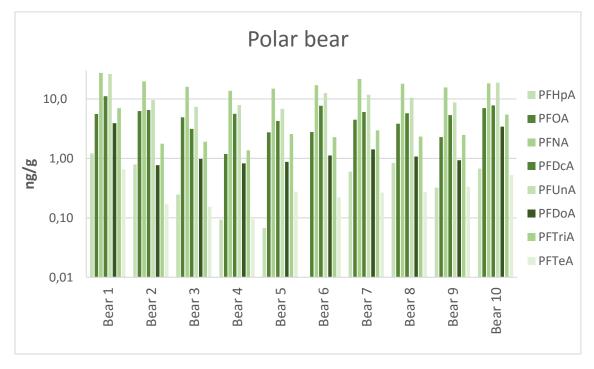


Figure 9: Concentration of the detected perfluorinated carboxylic acids in whole blood samples of polar bear from Spitsbergen. Concentration given in ng/g ww.

The following seven dechlorane related compounds together with PCB-153 were measured in polar bear samples: Dec 601, Dec 602, Dec 603, Dec 604, Dechlorane plus syn, Dechlorane plus anti, and DBALD.

Dec 602, DP syn, and DP anti, together with PCB-153 were detect above LoD (0.1 - 0.2 ng/g ww) as shown in Table 11. The concentration of the three detected dechlorane compounds with 0.07 to 0.14 ng/g ww were much lower than PCB-153 with a mean of 7.1 ng/g ww.

The measured concentrations of DP syn and DP anti are slightly higher compared to what measured in polar bear adipose tissue from Greenland (0.021/0.055 ng/g ww DPsyn/DPanti) (Vorkamp et al., 2015)).

| Table 11: Concentration of dechloranes in polar bear blood | | | | | | | | | | |
|--|--|------------------------------|----------------------------|--|--|--|--|--|--|--|
| Dec 602 DPsyn DPanti PCB-153 | | | | | | | | | | |
| Me | min/max Mean ng/g ww Detection frequency % | | | | | | | | | |
| (<0.02 - 0.42) 0.08 | (0.02 - 0.17) | (0.05 - 0.38) 0.14 | (0.86 - 31) 7 .1 | | | | | | | |

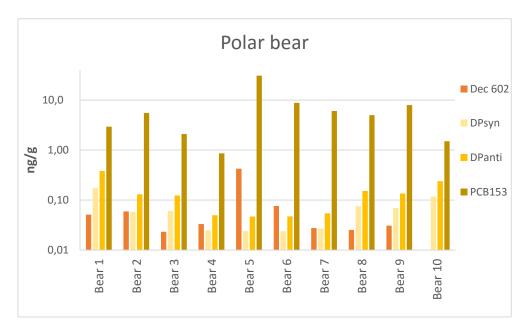


Figure 10: Concentration of the detected dechloranes (DPsyn and DPanti) and PCB-153 in whole blood samples of polar bear from Spitsbergen. Concentration given in ng/g ww.

4. Conclusion

In all samples, it was possible to detect PFOS, PFOA, PCB-153, and some dechloranes. It was not possible to detect the emerging PFAS compounds F53, F53B, and PFBS above the limit of detection (LoD). The pattern of detected dechlorane(s) is depending on the studied species, with Dec 602 found in all samples except of ringed seal. DP syn and anti were only found in mammal samples.

In eggs from glaucous gull, PFOS was found with a concentration of 4.5 ng/g ww. PFOA was also present, however, with a much lower concentration of 0.51 ng/g ww. Dec 602 was possible to detect above LoD with concentration of 0.21 ng/g ww, which is much lower than PCB-153 with a concentration of 166 ng/g ww.

In eggs from kittiwake, PFOS was found with a concentration of 6.3 ng/g ww on mean of the 10 samples. PFOA was also present, however, with a much lower concentration of 0.03 ng/g ww. Of the selected dechloranes, only Dec 602 was possible to detect above LoD with concentration of 0.26 ng/g ww, which is much lower than PCB-153 with a concentration of 160 ng/g ww.

In liver samples of ringed seal, PFOS was found with concentration of 2.8 ng/g ww. PFHxS was also present in five of ten samples, however, with a much lower concentration of 0.08 ng/g ww. No PFBS, PFHxS, or other fluorinated sulfonic acids were found in samples of ringed seal. Of the analysed perfluorinated carboxyl acids, PFNA and PFUnA were found with the highest concentrations 0.77 and 0.69 ng/g ww respectively. In addition, three more long chain carboxylic acids were detected in all samples (PFDcA, PFDoA, and PFFriA). The sum of the C9 to C14 carboxylic acids is 2.21 ng/g ww and in the same range as the PFOS concentration. PFOA was also present in 7 of 10 samples, however, with a much lower concentration of 0.05 ng/g ww. In contrast to the avian samples, it was possible to detect DP syn and DP anti, together with PCB-153 in seal. The concentrations of the other measured dechloranes were below LoD (0.02 - 0.2 ng/g ww). The DP syn concentrations were 0.10 ng/g ww on mean, and DP anti 0.17 ng/g ww on mean, which is lower than PCB-153 with a mean of 1.6 ng/g ww. These DP concentrations are in the same range as what was found in ringed seal blubber from Eastern Greenland.

In whole blood samples of polar bear, PFOS was found with a concentration of 84 ng/g ww. PFHxS was also present in all samples, with a concentration of 18 ng/g ww. It was not possible to detect PFBS above LoD. Of the analysed perfluorinated carboxyl acids PFNA and PFUnA were found with the highest concentrations 18 and 12 ng/g ww respectively. In addition, three more long chain carboxylic acids were detected in all samples (PFDcA, PFDoA, PFTriA, and PFTeA). PFOA was also present in all samples with a concentration of 6.3 ng/g ww. Of the dechloranes Dec 602, DP syn, and DP anti, together with PCB-153 were detect above LoD. The dechloranes were detected at much lower concentration well below 1 ng/g compared to 7 ng/g ww on mean for PCB-153.

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6. References

- Bytingsvik, J., van Leeuwen, S. P. J., Hamers, T., Swart, K., Aars, J., Lie, E., . . . Jenssen, B. M. (2012). Perfluoroalkyl substances in polar bear mother-cub pairs: A comparative study based on plasma levels from 1998 and 2008. *Environment International*, 49, 92-99. doi:10.1016/j.envint.2012.08.004
- Harju, M., Herzke, D., & Kaasa, H. (2013). Perfluorinated alkylated substances, brominated flame retardants and chlorinated paraffins in the Norwegian environment : screening 2013 (9788242525970). Retrieved from Kjeller:
- Kim, J.-T., Son, M.-H., Kang, J.-H., Kim, J.-H., Jung, J.-W., & Chang, Y.-S. (2015). Occurrence of Legacy and New Persistent Organic Pollutants in Avian Tissues from King George Island, Antarctica. *Environmental Science & Technology*, 49(22), 13628-13638. doi:10.1021/acs.est.5b03181
- Lucia, M., Gabrielsen, G. W., Herzke, D., & Christensen, G. (2016). Screening of UV chemicals, bisphenols and siloxanes in the Arctic.
- Routti, H., Aars, J., Fuglei, E., Hanssen, L., Lone, K., Polder, A., . . . Yoccoz, N. G. (2017). Emission Changes Dwarf the Influence of Feeding Habits on Temporal Trends of Perand Polyfluoroalkyl Substances in Two Arctic Top Predators. *Environmental Science & Technology*, 51(20), 11996-12006. doi:10.1021/acs.est.7b03585
- Routti, H., Gabrielsen, G. W., Herzke, D., Kovacs, K. M., & Lydersen, C. (2016). Spatial and temporal trends in perfluoroalkyl substances (PFASs) in ringed seals (Pusa hispida) from Svalbard. *Environmental Pollution*, 214, 230-238. doi:10.1016/j.envpol.2016.04.016
- Ruan, T., Lin, Y., Wang, T., Liu, R., & Jiang, G. (2015). Identification of Novel Polyfluorinated Ether Sulfonates as PFOS Alternatives in Municipal Sewage Sludge in China. Environmental Science & Technology, 49(11), 6519-6527. doi:10.1021/acs.est.5b01010
- Sagerup, K., Leonards, P., Routti, H., Fuglei, E., Aars, J., Strøm, H., . . . Gabrielsen, G. W. (2011). Organophosphorous flame retardants in Arctic biota.
- Sverko, E., Tomy, G. T., Reiner, E. J., Li, Y.-F., McCarry, B. E., Arnot, J. A., . . . Hites, R. A. (2011). Dechlorane Plus and Related Compounds in the Environment: A Review. *Environmental Science & Technology*, 45(12), 5088-5098. doi:10.1021/es2003028
- Tartu, S., Bourgeon, S., Aars, J., Andersen, M., Lone, K., Jenssen, B. M., . . . Routti, H. (2017). Diet and metabolic state are the main factors determining concentrations of perfluoroalkyl substances in female polar bears from Svalbard. *Environmental Pollution*, 229, 146-158. doi:10.1016/j.envpol.2017.04.100
- Vorkamp, K., Bossi, R., Riget, F. F., Skov, H., Sonne, C., & Dietz, R. (2015). Novel brominated flame retardants and dechlorane plus in Greenland air and biota. *Environmental Pollution*, 196, 284-291. doi:10.1016/j.envpol.2014.10.007

- Wang, S., Huang, J., Yang, Y., Hui, Y., Ge, Y., Larssen, T., . . . Harman, C. (2013). First Report of a Chinese PFOS Alternative Overlooked for 30 Years: Its Toxicity, Persistence, and Presence in the Environment. *Environmental Science & Technology*, 47(18), 10163-10170. doi:10.1021/es401525n
- Wang, T., Vestergren, R., Herzke, D., Yu, J., & Cousins, I. T. (2016). Levels, Isomer Profiles, and Estimated Riverine Mass Discharges of Perfluoroalkyl Acids and Fluorinated Alternatives at the Mouths of Chinese Rivers. Environmental Science & Technology, 50(21), 11584-11592. doi:10.1021/acs.est.6b03752
- Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerbuhler, K. (2014). Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environment International, 70, 62-75. doi:10.1016/j.envint.2014.04.013
- Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerbühler, K. (2014). Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: The remaining pieces of the puzzle. *Environment International*, 69, 166-176. doi:<u>http://dx.doi.org/10.1016/j.envint.2014.04.006</u>
- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environment International*, 60(0), 242-248. doi:<u>http://dx.doi.org/10.1016/j.envint.2013.08.021</u>
- Xie, S., Lu, Y., Wang, T., Liu, S., Jones, K., & Sweetman, A. (2013). Estimation of PFOS emission from domestic sources in the eastern coastal region of China. *Environment International*, 59, 336-343. doi:10.1016/j.envint.2013.06.015
- Xie, S., Wang, T., Liu, S., Jones, K. C., Sweetman, A. J., & Lu, Y. (2013). Industrial source identification and emission estimation of perfluorooctane sulfonate in China. *Environment International*, 52, 1-8. doi:10.1016/j.envint.2012.11.004
- Yang, X., Huang, J., Zhang, K., Yu, G., Deng, S., & Wang, B. (2014). Stability of 6:2 fluorotelomer sulfonate in advanced oxidation processes: degradation kinetics and pathway. *Environmental Science and Pollution Research*, 21(6), 4634-4642. doi:10.1007/s11356-013-2389-z
- Zhang, L., Liu, J., Hu, J., Liu, C., Guo, W., Wang, Q., & Wang, H. (2012). The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. *Environmental Pollution*, 165, 193-198. doi:10.1016/j.envpol.2011.09.001

7. Appendix

| Tat | Table 12: Analyte concentrations in egg samples of glaucous gull | | | | | | | | | | | | | |
|---------------|--|------|------|-------|-------|-------|---------|---------|---------|---------|--------|---------|--------|--|
| Anal | Analyte concentration given in ng/g wet weight | | | | | | | | | | | | | |
| Sample number | OI AN | PFOS | PFOA | F53 | F53B | DBALD | Dec 601 | Dec 602 | Dec 603 | Dec 604 | nya 90 | DP anti | PCB153 | |
| 1 | GG-02-15 | 5,18 | 0,40 | <0,05 | <0,02 | <0,1 | <0,1 | 0,24 | <0,1 | <0,2 | <0,1 | <0,1 | 182 | |
| 2 | GG-05-15 | 3,24 | 0,50 | <0,05 | <0,02 | <0,1 | <0,1 | 0,24 | <0,1 | <0,2 | <0,1 | <0,1 | 231 | |
| 3 | GG-10-15 | 4,57 | 0,48 | <0,05 | <0,02 | <0,1 | <0,1 | 0,12 | <0,1 | <0,2 | <0,1 | <0,1 | 82,1 | |
| 4 | GG-11-15 | 4,69 | 0,74 | <0,05 | <0,02 | <0,1 | <0,1 | 0,25 | <0,1 | <0,2 | <0,1 | <0,1 | 213 | |
| 5 | GG-13-15 | 4,60 | 0,41 | <0,05 | <0,02 | <0,1 | <0,1 | 0,18 | <0,1 | <0,2 | <0,1 | <0,1 | 124 | |

| Tal | Table 13: Analyte concentrations in egg samples of kittiwake | | | | | | | | | | | | |
|---------------|--|-------------|----------|----------|--------|-------|---------|---------|---------|---------|--------|---------|--------|
| Anal | yte concent | ration give | en in ng | /g wet v | veight | | | | | | | | |
| Sample number | QI dN | PFOS | PFOA | F53 | F53B | DBALD | Dec 601 | Dec 602 | Dec 603 | Dec 604 | DP syn | DP anti | PCB153 |
| 1 | KW-01-15 | 5,66 | 0,02 | <0,05 | <0,02 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| 2 | KW-02-15 | 9,81 | 0,03 | <0,05 | <0,02 | <0,1 | <0,1 | 0,35 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 3 | KW-03-15 | 6,38 | 0,03 | <0,05 | <0,02 | <0,1 | <0,1 | 0,21 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 4 | KW-04-15 | 3,14 | 0,02 | <0,05 | <0,02 | <0,1 | <0,1 | 0,21 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 5 | KW-05-15 | 5,19 | 0,03 | <0,05 | <0,02 | <0,1 | <0,1 | 0,17 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 6 | KW-07-15 | 7,65 | 0,03 | <0,05 | <0,02 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| 7 | KW-09-15 | 4,63 | 0,07 | <0,05 | <0,02 | <0,1 | <0,1 | 0,47 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 8 | KW-10-15 | 13,1 | 0,05 | <0,05 | <0,02 | <0,1 | <0,1 | 0,23 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 9 | KW-16-15 | 3,28 | 0,02 | <0,05 | <0,02 | <0,1 | <0,1 | 0,16 | <0,1 | <0,2 | <0,1 | <0,1 | |
| 10 | KW-17-15 | 4,56 | 0,01 | <0,05 | <0,02 | <0,1 | <0,1 | 0,26 | <0,1 | <0,2 | <0,1 | <0,1 | |

The eggs were collected in the field in 2013 and 2014 and analyzed for other parameters in 2015 (Lucia et al., 2016). Missing results marked n.a. (not analyzed) are due to the fact that sample extracts were completely evaporated during storage.

Table 14: Concentrations of perfluorinated sulfonic acids in liver samples of ringed seal

| Ana | yte concentratio | | | | | | | | | |
|---------------|------------------|-----|-------|-------|-------|-------|------|--------|-------|-------|
| Sample number | QI AN | Sex | PFBS | PFPS | PFHxS | PFHpS | PFOS | brPFOS | PFNS | PFDcS |
| 1 | MM 0909-02 | | <0.05 | <0.05 | <0.05 | <0.05 | 2.55 | 0.68 | <0.10 | <0.10 |
| 2 | MM 0909-03 | | <0.05 | <0.05 | <0.05 | <0.05 | 2.39 | 0.65 | <0.10 | <0.10 |
| 3 | MM 0909-05 | | <0.05 | <0.05 | 0.08 | <0.05 | 2.87 | 0.48 | <0.10 | <0.10 |
| 4 | MM 0909-06 | | <0.05 | <0.05 | 0.12 | <0.05 | 2.18 | 0.67 | <0.10 | <0.10 |
| 5 | MHM 170916-1 | | <0.05 | <0.05 | <0.05 | <0.05 | 2.14 | 0.61 | <0.10 | <0.10 |
| 6 | MHM 170916-3 | | <0.05 | <0.05 | <0.05 | <0.05 | 3.05 | 0.60 | <0.10 | <0.10 |
| 7 | MHM 240916-2 | | <0.05 | <0.05 | 0.11 | <0.05 | 2.31 | 0.75 | <0.10 | <0.10 |
| 8 | MHM 240916-3 | | <0.05 | <0.05 | 0.07 | <0.05 | 5.02 | 0.94 | <0.10 | <0.10 |
| 9 | MHM 240916-4 | | <0.05 | <0.05 | <0.05 | <0.05 | 2.21 | 0.75 | <0.10 | <0.10 |
| 10 | MHM 240916-6 | | <0.05 | <0.05 | 0.13 | <0.05 | 2.87 | 0.80 | <0.10 | <0.10 |

Analyte concentration given in ng/g wet weight

| | ringeo | d sea | | | o f perfluc et weight | orinated | carboxy | lic acids | in liver s | amples o | of |
|---------------|--------------|-------|-------|-------|---------------------------------|----------|---------|-----------|------------|----------|-------|
| Sample number | QI AN | Sex | PFHxA | PFHpA | PFOA | PFNA | PFDcA | PFUnA | PFDoA | PFTriA | PFTeA |
| 1 | MM 0909-02 | | <0.10 | <0.05 | <0.015 | 0.60 | 0.34 | 0.69 | <0.05 | 0.21 | <0.10 |
| 2 | MM 0909-03 | | <0.10 | <0.05 | 0.02 | 0.47 | 0.30 | 0.59 | 0.14 | 0.18 | <0.10 |
| 3 | MM 0909-05 | | <0.10 | <0.05 | <0.015 | 0.34 | 0.24 | 0.52 | 0.10 | 0.13 | <0.10 |
| 4 | MM 0909-06 | | <0.10 | <0.05 | 0.02 | 0.81 | 0.43 | 0.85 | 0.12 | 0.36 | <0.10 |
| 5 | MHM 170916-1 | | <0.10 | <0.05 | <0.015 | 0.52 | 0.38 | 0.55 | 0.05 | 0.25 | <0.10 |
| 6 | MHM 170916-3 | | <0.10 | <0.05 | 0.03 | 0.92 | 0.38 | 0.61 | <0.05 | 0.18 | <0.10 |
| 7 | MHM 240916-2 | | <0.10 | <0.05 | 0.04 | 0.63 | 0.31 | 0.59 | 0.13 | 0.16 | <0.10 |
| 8 | MHM 240916-3 | | <0.10 | <0.05 | 0.33 | 1.96 | 0.60 | 1.01 | 0.09 | 0.30 | <0.10 |
| 9 | MHM 240916-4 | | <0.10 | <0.05 | 0.07 | 0.89 | 0.36 | 0.79 | 0.20 | 0.33 | <0.10 |
| 10 | MHM 240916-6 | | <0.10 | <0.05 | <0.015 | 0.58 | 0.36 | 0.68 | 0.09 | 0.20 | <0.10 |

Table 16: Concentrations of different per- and polyfluorinated alkylated compounds in liver samples of ringed seal

| | , | 5 | | | | | |
|---------------|--------------|-----|-------|--------|---------|-------|-------|
| Sample number | QI AN | Sex | PFOSA | 6:2FTS | 8:2 FTS | F53 | F538 |
| 1 | MM 0909-02 | | <0.05 | 0.01 | <0.10 | <0.05 | <0.02 |
| 2 | MM 0909-03 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 3 | MM 0909-05 | | 0.06 | <0.10 | <0.10 | <0.05 | <0.02 |
| 4 | MM 0909-06 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 5 | MHM 170916-1 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 6 | MHM 170916-3 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 7 | MHM 240916-2 | | <0.05 | 0.10 | <0.10 | <0.05 | <0.02 |
| 8 | MHM 240916-3 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 9 | MHM 240916-4 | | <0.05 | <0.10 | <0.10 | <0.05 | <0.02 |
| 10 | MHM 240916-6 | | <0.05 | 0.01 | <0.10 | <0.05 | <0.02 |

| | Table 17: Concentrations of dechloranes and PCB-153 in liver samples of ringed seal Analyte concentration given in ng/g wet weight | | | | | | | | | | | |
|---------------|--|-----|---------------|---------|---------|---------|---------|-------|--------|--------|--|--|
| Sample number | | Sex | Dibromoaldrin | Dec 601 | Dec 602 | Dec 603 | Dec 604 | DPsyn | DPanti | PCB153 | | |
| 1 | MM 0909-02 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.10 | 0.17 | 2.51 | | |
| 2 | MM 0909-03 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.06 | 0.12 | 1.05 | | |
| 3 | MM 0909-05 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.11 | 0.18 | 3.59 | | |
| 4 | MM 0909-06 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.11 | 0.18 | 1.19 | | |
| 5 | MHM 170916-1 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.10 | 0.15 | 0.47 | | |
| 6 | MHM 170916-3 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.10 | 0.17 | 1.06 | | |
| 7 | MHM 240916-2 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.09 | 0.14 | 1.38 | | |
| 8 | MHM 240916-3 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.12 | 0.16 | 2.24 | | |
| 9 | MHM 240916-4 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.12 | 0.20 | 1.66 | | |
| 10 | MHM 240916-6 | | <0.2 | <0.02 | <0.02 | <0.02 | <0.05 | 0.13 | 0.20 | 1.35 | | |

Table 18: Concentrations of perfluorinated sulfonic acids in samples of whole blood of polar bears

Analyte concentration given in ng/g wet weight

| | yte concentratio | 511 511 | | | | | | | | |
|---------------|------------------|---------|-------|-------|-------|-------|------|--------|-------|-------|
| Sample number | QI dN | Sex | PFBS | PFPS | PFHxS | PFHpS | PFOS | brPFOS | PFNS | PFDcS |
| 1 | N23475 | м | <0.05 | 0.16 | 17.8 | 3.50 | 149 | 34.0 | <0.10 | <0.10 |
| 2 | N23688 | F | <0.05 | 0.08 | 20.8 | 4.10 | 108 | 39.2 | <0.10 | <0.10 |
| 3 | N23689 | F | <0.05 | 0.06 | 19.4 | 2.86 | 51.1 | 25.4 | <0.10 | <0.10 |
| 4 | N23802 | F | <0.05 | <0.05 | 12.9 | 2.26 | 63.0 | 18.4 | <0.10 | <0.10 |
| 5 | N23803 | F | <0.05 | 0.08 | 21.5 | 2.78 | 64.8 | 26.8 | <0.10 | <0.10 |
| 6 | N23882 | F | <0.05 | <0.05 | 17.8 | 2.87 | 84.5 | 32.0 | <0.10 | <0.10 |
| 7 | N26043 | м | <0.05 | <0.05 | 13.8 | 2.14 | 63.4 | 23.2 | <0.10 | <0.10 |
| 8 | N26126 | м | <0.05 | <0.05 | 14.8 | 2,38 | 65.9 | 23.5 | <0.10 | <0.10 |
| 9 | N26264 | м | <0.05 | <0.05 | 21.9 | 2.81 | 73.1 | 23.7 | <0.10 | <0.10 |
| 10 | N26268 | м | <0.05 | <0.05 | 15.4 | 2.86 | 114 | 26.5 | <0.10 | <0.10 |

Table 19: Concentrations of perfluorinated carboxylic acids in samples of whole blood of polar bears

| | Analyte | conce | ntration give | en in ng/g w | et weight | | | | | | |
|---------------|---------|-------|---------------|--------------|-----------|------|-------|-------|-------|--------|-------|
| Sample number | CI dN | Sex | PFHxA | PFHpA | PFOA | PFNA | PFDcA | PFUnA | PFDoA | PFTriA | PFTeA |
| 1 | N23475 | Μ | <0.10 | 1.21 | 5.59 | 27.4 | 11.1 | 26.3 | 3.90 | 6.99 | 0.66 |
| 2 | N23688 | F | <0.10 | 0.79 | 6.23 | 19.7 | 6.53 | 9.56 | 0.77 | 1.76 | 0.17 |
| 3 | N23689 | F | <0.10 | 0.25 | 4.92 | 16.0 | 3.13 | 7.35 | 0.98 | 1.90 | 0.15 |
| 4 | N23802 | F | <0.10 | 0.09 | 1.18 | 13.6 | 5.60 | 7.89 | 0.82 | 1.37 | 0.09 |
| 5 | N23803 | F | <0.10 | 0.07 | 2.73 | 14.9 | 4.26 | 6.80 | 0.87 | 2.56 | 0.28 |
| 6 | N23882 | F | <0.10 | <0.05 | 2.79 | 17.1 | 7.68 | 12.5 | 1.12 | 2.28 | 0.22 |
| 7 | N26043 | м | <0.10 | 0.60 | 4.48 | 21.6 | 6.02 | 11.8 | 1.41 | 2.96 | 0.27 |
| 8 | N26126 | м | <0.10 | 0.83 | 3.81 | 18.0 | 5.73 | 10.5 | 1.07 | 2.33 | 0.27 |
| 9 | N26264 | м | <0.10 | 0.32 | 2.27 | 15.7 | 5.33 | 8.73 | 0.93 | 2.48 | 0.33 |
| 10 | N26268 | м | <0.10 | 0.67 | 7.00 | 18.2 | 7.81 | 18.8 | 3.42 | 5.47 | 0.52 |

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Table 20: Concentrations of different per- and polyfluorinated alkylated compounds in samples of whole blood of polar bears

Analyte concentration given in ng/g wet weight

| Sample number | QI dN | Sex | PFOSA | 6:2FTS | 8:2 FTS | F53 | F538 | | | | |
|---------------|--------|-----|-------|--------|---------|-------|-------|--|--|--|--|
| 1 | N23475 | м | 3.66 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 2 | N23688 | F | 4.19 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 3 | N23689 | F | 1.22 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 4 | N23802 | F | 0.28 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 5 | N23803 | F | 2.39 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 6 | N23882 | F | 2.99 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 7 | N26043 | м | 2.77 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 8 | N26126 | Μ | 0.79 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 9 | N26264 | м | 1.94 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |
| 10 | N26268 | м | 1.73 | <0.10 | <0.10 | <0.05 | <0.02 | | | | |

Table 21: Concentrations of dechloranes and PCB-153 in samples of whole blood of polar bears

Analyte concentration given in ng/g wet weight

| Sample number | CI dN | Sex | Dibromoaldrin | Dec 601 | Dec 602 | Dec 603 | Dec 604 | uksdQ | DPanti | PCB153 | |
|---------------|--------|-----|---------------|---------|---------|---------|---------|-------|--------|--------|--|
| 1 | N23475 | м | <0.2 | <0.02 | 0.05 | <0.02 | <0.02 | 0.17 | 0.38 | 2.93 | |
| 2 | N23688 | F | <0.2 | <0.02 | 0.06 | <0.02 | <0.02 | 0.06 | 0.13 | 5.54 | |
| 3 | N23689 | F | <0.2 | <0.02 | 0.02 | <0.02 | <0.02 | 0.06 | 0.12 | 2.10 | |
| 4 | N23802 | F | <0.2 | <0.02 | 0.03 | <0.02 | <0.02 | 0.02 | 0.05 | 0.86 | |
| 5 | N23803 | F | <0.2 | <0.02 | 0.42 | <0.02 | <0.02 | 0.02 | 0.05 | 30.8 | |
| 6 | N23882 | F | <0.2 | <0.02 | 0.08 | <0.02 | <0.02 | 0.02 | 0.05 | 8.77 | |
| 7 | N26043 | м | <0.2 | <0.02 | 0.03 | <0.02 | <0.02 | 0.03 | 0.05 | 6.05 | |
| 8 | N26126 | м | <0.2 | <0.02 | 0.03 | <0.02 | <0.02 | 0.08 | 0.15 | 4.97 | |
| 9 | N26264 | м | <0.2 | <0.02 | 0.03 | <0.02 | <0.02 | 0.07 | 0.13 | 7.96 | |
| 10 | N26268 | м | <0.2 | <0.02 | <0.02 | <0.02 | <0.02 | 0.12 | 0.24 | 1.51 | |

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The Norwegian Environment Agency is working for a clean and diverse environment. Our primary tasks are to reduce greenhouse gas emissions, manage Norwegian nature, and prevent pollution.

We are a government agency under the Ministry of Climate and Environment and have 700 employees at our two offices in Trondheim and Oslo and at the Norwegian Nature Inspectorate's more than sixty local offices.

We implement and give advice on the development of climate and environmental policy. We are professionally independent. This means that we act independently in the individual cases that we decide and when we communicate knowledge and information or give advice.

Our principal functions include collating and communicating environmental information, exercising regulatory authority, supervising and guiding regional and local government level, giving professional and technical advice, and participating in international environmental activities.