



# GEOGRAPHICAL TRENDS OF SHORT-CHAIN CHLORINATED PARAFFINS (SCCPS) IN RINGED SEALS FROM THE ARCTIC

Scientific Report from DCE - Danish Centre for Environment and Energy

No. 582

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# Data sheet

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Abstract:	<p>Chlorinated paraffins are high production volume chemicals used in a variety of commercial and industrial applications, e.g. as lubricants, flame retardants and metal working fluids. They are commonly divided into short-, medium and long-chain chlorinated paraffins (C<sub>10</sub>–C<sub>13</sub> (SCCPs), C<sub>14</sub>–C<sub>17</sub> (MCCPs) and ≥ C<sub>18</sub> (LCCPs), respectively), of which SCCPs are regulated via the Stockholm Convention on Persistent Organic Pollutants (POPs). Due to their complexity, the analytical chemistry is challenging, and different studies often lack comparability. The objective of this project was to study spatial differences in ΣSCCPs in ringed seals from Canada, Greenland and Svalbard. Blubber of juvenile ringed seals (N=4-5 per location) from a total of eight locations (Canada: 4; Greenland: 3; Svalbard: 1) were analysed with gas chromatography with Orbitrap high-resolution mass spectrometry (GC-Orbitrap MS). As blanks showed quantifiable levels of SCCPs, all concentrations were blank corrected. Mean ΣSCCPs ranged between 16 and 142 ng/g lipid weight, without statistically significant differences between locations. Standard deviations exceeded 100% in some cases, but were considerably lower for data without blank correction. ΣSCCP concentrations were generally lower than those of other POPs available for the same individuals from East and West Greenland. However, compared with previous studies from the 1990s to early 2000s, this difference seemed smaller, possibly indicating different temporal developments for SCCPs and other POPs. The applicability of the current analytical method for routine monitoring still poses challenges, in particular regarding sensitivity and blank occurrences.</p>
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## Dansk resumé

Klorerede paraffiner produceres i store mængder, ca. 1 million tons om året, og har et stort spektrum af kommercielle og industrielle anvendelser, f.eks. som smøremidler, flammehæmmere, blødgørere og i metalforarbejdning. Ud fra længden af alkankæden opdeles de klorerede paraffiner typisk i tre grupper: Kortkædede paraffiner ( $C_{10}$ – $C_{13}$ ; short-chain chlorinated paraffins (SCCP'er)), mediumkædede paraffiner ( $C_{14}$ – $C_{17}$ ; medium-chain chlorinated paraffins (MCCP'er)) og langkædede paraffiner ( $\geq C_{18}$ ; long-chain chlorinated paraffins (LCCP'er)). SCCP-gruppen er under global udfasning som følge af reguleringen gennem Stockholm Konventionen<sup>1</sup>.

Stofgruppens kompleksitet gør den analysekemiske bestemmelse af miljøkoncentrationer for klorerede paraffiner vanskelig. Sammenligneligheden mellem studier, der anvender forskellige analysemetoder, er typisk begrænset, hvilket gør det svært at undersøge trends. Formålet med dette projekt var at undersøge potentielle geografiske forskelle i  $\Sigma$ SCCP-koncentrationer i ringsæler fra Canada, Grønland og Svalbard. Til dette formål blev der udviklet en analysemetode til SCCP'er, der baserer sig på gaskromatografi med højopløsende massespektrometer, her konkret Orbitrap-teknologien (GC-Orbitrap HRMS). Denne metode blev anvendt til at bestemme  $\Sigma$ SCCP-koncentrationer i spækprøver fra unge ringsæler (N=4-5 per lokalitet). Prøverne stammede fra i alt otte forskellige lokaliteter, heraf fire lokaliteter i Canada, tre i Grønland og en fra Svalbard (hvor der ikke blev skelnet mellem forskellige prøvetagningssteder).

Analysen inkluderede en række prøver til kvalitetssikring og kvalitetskontrol. Da SCCP'er blev påvist i alle blindprøverne, blev koncentrationen i sælprøverne korrigeret for indholdet i blindprøverne. Middelkoncentrationen for  $\Sigma$ SCCP lå mellem 16 og 142 ng/g lipidvægt for de forskellige lokaliteter. Der var ingen statistisk signifikant forskel mellem  $\Sigma$ SCCP-koncentrationen for de forskellige lokaliteter. I nogle tilfælde lå standardafvigelsen på > 100%, mens den var betydelig lavere for de ikke-blindkorrigerede rådata.

$\Sigma$ SCCP-koncentrationen var generelt lavere end koncentrationer for andre POP-forbindelser (såsom polychlorerede biphenyler (PCB'er) og p,p'-DDE) målt i de samme ringsælprøver fra Øst- og Vestgrønland. Differencen i forhold til andre POP-koncentrationer var dog lavere nu end i ældre undersøgelser fra 1990'erne og 2000'erne, muligvis som en følge af forskelle i den tidsmæssige koncentrationsudvikling for SCCP'er sammenlignet med andre POP'er. Anvendelsen af den valgte ekstraktionsmetode og metoden til instrumentel analyse (GC-Orbitrap HRMS) set i en mere rutinemæssig POP-overvågning indebærer fortsat nogle udfordringer, bl.a. mht. metodens følsomhed og tilstedeværelsen af blindværdier.

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<sup>1</sup> Stockholm Convention on Persistent Organic Pollutants (POPs). [www.pops.int](http://www.pops.int)

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The ringed seal samples from Canada and Svalbard were kindly provided by Environment and Climate Change Canada and the Norwegian Polar Institute, respectively. Besides Magali Houde and Heli Routti who have contributed to this project as co-authors, the project group would like to acknowledge Derek Muir (Environment and Climate Change Canada) as well as Geir Wing Gabrielsen, Christian Lydersen and Kit Kovacs (Norwegian Polar Institute) for their collaboration.

The ringed seal samples from Greenland originated from the Environmental Specimen Bank of the AMAP<sup>2</sup> Core Programme. This programme has been in operation since 1994, also funded by the Danish Environmental Protection Agency (project leaders: Frank Rigét and Jens Søndergaard), and regularly collects biota samples from Central East Greenland, Central West Greenland and Northwest Greenland, for monitoring of POPs and chemical elements as well as for specimen banking.

The project group would further like to thank Rossana Bossi for assistance with the GC-Orbitrap HRMS, as well as Annegrete Ljungqvist and Birgit Groth for the chemical analyses of the samples in the laboratory and the calculations on the GC-Orbitrap HRMS.

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<sup>2</sup> Arctic Monitoring and Assessment Programme (AMAP)



# 1 Introduction

## 1.1 Chlorinated paraffins

Approximately 1 million metric tons of chlorinated paraffins are produced each year through the chlorination of mixtures of n-alkanes (Krätschmer et al., 2018; Schinkel et al., 2018). They are widely used in commercial and industrial applications, including as lubricants, flame retardants, plasticizers, and metal working fluids (Schinkel et al. 2018).

Chlorinated paraffins (CPs) comprise complex mixtures of thousands of isomers with different carbon chain lengths ( $C_{10}$ – $C_{30}$ ) and degrees of chlorination (30–70 wt% Cl) (Schinkel et al., 2018). They are commonly divided into short-chain chlorinated paraffins ( $C_{10}$ – $C_{13}$ , SCCPs), medium-chain chlorinated paraffins ( $C_{14}$ – $C_{17}$ , MCCPs), and long-chain chlorinated paraffins ( $\geq C_{18}$ , LCCPs) (Krätschmer et al., 2018). In addition, individual CP congeners are commonly referred to by their carbon and chlorine numbers (e.g., “ $C_{10}Cl_7$ ” =  $C_{10}H_{15}Cl_7$ ). Due to their persistence in the environment, long-range transport potential, bioaccumulation, and high toxicity to many laboratory model organisms, SCCPs have been listed in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) since 2017 (Xu et al., 2019). SCCPs are also the focus of this report.

Frequently, gas chromatography-mass spectrometry (GC-MS) is used to analyse SCCPs and MCCPs and liquid chromatography-mass spectrometry (LC-MS) is used to analyse LCCPs, which are less volatile (van Mourik et al., 2015; Schinkel et al., 2018). The response of CPs is low for most detection systems (van Mourik et al., 2015; 2018). For example, it has been reported that the electron capture detector response of CPs is 500 times lower than that of hexachlorobenzene (HCB) (van Mourik et al., 2018). To further complicate the analysis, commercial and technical CP mixtures are practically impossible to separate chromatographically (Rusina et al., 2011; van Mourik et al., 2018). As a result, short columns and direct injection are often used to enhance sensitivity and reduce analysis time (Ceolhan, 1999; Bogdal et al., 2015; van Mourik et al., 2015) and high-resolution mass spectrometry (HRMS) and sample fractionation are used to minimize interferences (Tomy et al., 1997; Reth & Oehme, 2004; van Mourik et al., 2018).

Technical mixtures with different degrees of chlorination (e.g., 55.5 or 63 wt% Cl) are used to quantify CPs (Schinkel et al., 2018). The exact composition of each technical mixture is unknown, in part because the chlorination process is nonspecific (Schinkel et al., 2018). As a result, CPs are commonly analysed as a group, and reported as sum quantities (e.g., “ $\Sigma$ SCCPs”).

Various methods are used to ionize CPs for mass spectrometry (MS) analysis, including electron ionization (EI) (Nicholls et al., 2001; Zencak et al., 2004) and electron capture negative ionization (ECNI) (Tomy et al., 1997; Reth et al., 2005). Where EI-MS is used, strong fragmentation gives mass spectra without congener-specific information, such as carbon or chlorine number (Zencak et al., 2004). With methane as the reagent gas, ECNI produces  $[M - Cl]^-$ ,  $[M - HCl]^-$ ,  $[M + Cl]^-$ ,  $[Cl_2]^-$  and  $[HCl_2]^-$  ions in varying abundances based on the degree of chlorination, the temperature of the ion source, and the amount of sample injected (Zencak & Oehme, 2006). In general, CP mass spectra are dominated by  $[M - Cl]^-$  ions at low ion source temperatures (e.g.,

120 °C), and dominated by  $[\text{Cl}_2]^{\bullet -}$  and  $[\text{HCl}_2]^-$  ions at high ion source temperatures (e.g., 220 °C) (Tomy et al., 1997; van Mourik et al., 2015). Because other chlorinated compounds also produce  $[\text{Cl}_2]^{\bullet -}$  and  $[\text{HCl}_2]^-$  ions during ECNI-MS analysis (Castells et al., 2004; van Mourik et al., 2015),  $[\text{M} - \text{Cl}]^-$  ions are preferred for CP quantitation (Tomy et al., 1997; Reth et al., 2005; Rusina et al., 2011). In this study, ECNI-GC-HRMS was used with settings to enhance the  $[\text{M} - \text{Cl}]^-$  ions of the targeted SCCPs.

The ECNI-MS responses of CP congeners have been reported to increase with their degree of chlorination and corresponding electron affinities (Reth et al., 2005; Zencak et al., 2005). As a result of this, congeners with less than five chlorine atoms are difficult or impossible to detect, and congeners with high chlorine numbers (e.g., ten chlorine atoms) may be overestimated in abundance (Reth et al., 2005; van Mourik et al., 2015). Another result is that less chlorinated CP technical mixtures (e.g., 51.5 wt% Cl) have lower responses than more chlorinated technical mixtures (e.g., 63 wt% Cl) at the same concentration. In fact, it has previously been suggested that 30% to 60% of the CP congener groups are invisible to ECNI-MS (Yuan et al., 2019).

## 1.2 SCCPs in the Arctic

The occurrence of SCCPs in samples from Arctic wildlife collected in remote areas demonstrates their persistence, long-range transport, and bioaccumulation. Arctic monitoring can also be used to document the global effects of SCCP regulation, in accordance with the Stockholm Convention on POPs, as monitoring strategies have been developed that include samples from remote locations unaffected by local industrial or urban emission sources (Rigét et al., 2016; 2019).

The presence of chlorinated paraffins in the Arctic environment was reviewed a few years ago (Vorkamp et al., 2019). The data were examined from the perspective of the atmosphere as well as terrestrial, freshwater and marine ecosystems. The ecosystem data included samples from water, sediments, and biota. The review noted that comparability between studies was limited by analytical challenges, temporal differences, and the lack of a systematic geographical study. The following paragraphs summarize some results from the review.

In the atmosphere, SCCP concentrations generally exceeded MCCP and legacy POP concentrations. In recent studies, the average  $\Sigma$ SCCPs concentration in air was in the order of hundreds of  $\text{pg}/\text{m}^3$ . In a study at the Alert Arctic monitoring station (Nunavut, Canada), ten air samples and two field blanks were collected from January to August 2011. The mean and median  $\Sigma$ SCCP concentrations were 913 and 685  $\text{pg}/\text{m}^3$ , respectively. In the air monitoring carried out at the Zeppelin Arctic monitoring station (Svalbard, Norway) from 2013 to 2017, the annual average SCCP concentrations in air ranged from ~210 to ~420  $\text{pg}/\text{m}^3$ . For some of these years, the SCCP concentrations were deemed “semi-quantitative” due to high and variable background values. Compilation of air data from these monitoring stations indicated an increase of  $\Sigma$ SCCPs from the early 1990s to recent measurements performed in 2010-2015.

In biota, different trends characterized the SCCP concentrations. MCCP concentrations often exceeded SCCP concentrations. The total SCCP concentrations in biota often ranged from tens to hundreds of  $\text{ng}/\text{g}$  tissue (lipid weight). When freshwater fish studies from Canada and Norway were compared, the

SCCP concentrations in the Canadian fish were lower (Reth et al., 2006; Basconcillo et al., 2015). However, the studies included different species collected about 10 years apart, meaning that comparability is limited. Ringed seal blubber samples from Canada, Norway and Greenland were also examined, but comparisons were difficult to make as the sampling periods ranged from 1994 to 2012. During this period, the total SCCP concentrations varied from 11 ng/g wet weight (ww) (West Greenland, 1999-2001) to 530 ng/g ww (Nunavut, Canada, 1994) (Tomy et al., 2000; Johansen et al., 2004).

The review concluded that challenges associated with the analysis of SCCPs still limited comparability across studies, times and regions. To illustrate this point, the review referenced an interlaboratory comparison which reported  $\Sigma$ SCCP concentrations from 8.5 and 3200  $\mu\text{g}/\text{mL}$  for a soil extract (Pellizzato et al., 2009). Specifically, several authors have expressed concerns over the reliability of low-resolution mass spectrometry (LRMS) during SCCP analysis (Sverko et al. 2012; van Mourik et al., 2018).

### 1.3 Objectives of this study

This study builds on previous work under the AMAP Core Programme, which highlighted uncertainty about the accuracy of preliminary screening data and their comparability to other studies (Vorkamp et al., 2017). The current study therefore aimed to improve the comparability of SCCP data across studies by addressing some of the challenges associated with SCCP analysis. It also aimed to provide a geographical comparison of SCCP concentrations in ringed seal (*Pusa hispida*) blubber across the Arctic.

The original plan was for Aarhus University and Environment and Climate Change Canada, two main contributors to the work on POPs in the AMAP network, to jointly develop and test a common method for SCCP analysis. The resulting method would then be used to jointly generate the data for a spatial comparison of SCCP concentrations in ringed seals across parts of the Arctic. The resulting method was also expected to form the basis for future routine SCCP analyses.

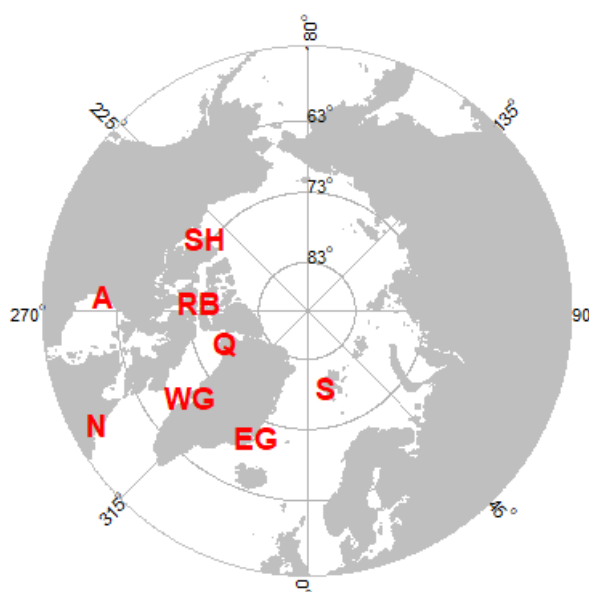
As both institutions acquired a state-of-the-art GC-Orbitrap HRMS, Aarhus University and Environment and Climate Change Canada elected to develop a new HRMS method to perform the proposed analyses of ringed seals. The new method would replace the previously used LRMS method and was expected to eliminate some of the analytical challenges that limited data reliability and comparability. Subject to continuing improvements, the new HRMS method could be used for future SCCP analyses and form the basis for potential extensions to MCCP studies. However, because of organizational challenges in Canada and difficulties to align timelines, the method was eventually developed in Denmark in collaboration with the Canadian partners.

## 2 Materials and methods

### 2.1 Samples

The ringed seal samples were collected from locations in Canada and Greenland in 2016 and from locations in Svalbard in 2017 (Figure 1). Juveniles (0-4 years) were generally used to reduce the natural variation originating from different age groups (Rigét et al., 2016). Samples from Canada were provided by Environment and Climate Change Canada, while samples from Svalbard were provided by the Norwegian Polar Institute. The samples from East and West Greenland constituted a subset of the samples analysed for other POPs in the AMAP Core Programme. All samples were stored at -20°C until analysis and re-homogenized prior to sub-sampling for extraction.

**Figure 1** Sampling locations. SH = Sachs Harbour, Canada, N=5; A = Arviat, Canada, N=4; RB = Resolute Bay, Canada, N=4; N = Nain, Canada, N=5; Q = Qaanaaq, Northwest Greenland, N=5; WG = West Greenland (Qeqertarsuaq), N=5; EG = East Greenland (Ittoqqortoormiit), N=5; S = Svalbard (Ekmanfjorden, Yoldiabugten), N=4.



### 2.2 Sample preparation

The ringed seal blubber samples were prepared in two batches: The first one included the 18 samples from Canada originating from four different locations (Figure 1). The second batch included the 15 samples from Greenland, representing three locations, and four samples from Svalbard. Each batch included blanks and a duplicate analysis of the in-house reference material (fish oil) spiked with SCCPs, as further described in section 4.5.

For the analysis, approximately 0.7 g of the blubber samples was homogenized, dried with diatomaceous earth, spiked with tetrachloronaphthalene <sup>13</sup>C-PCN-27 (40 and 4 ng for the first and second batch, respectively) for recovery determination, and Soxhlet extracted with hexane:dichloromethane (1:1). The extracts were reduced in volume by rotary evaporation to approximately 1 mL, and then cleaned on columns containing aluminum oxide, silica, and acidic silica to remove lipids. Next, the columns were eluted with hexane:dichloromethane (1:1), and evaporated again to approximately 1 mL. To eliminate interferences, the extracts were fractionated on an activated Florisil column (8 g) and eluted in two fractions. The first fraction, eluted with 50 mL of hexane, contained PCBs and some chlorinated pesticides. The second fraction, eluted with 200 mL of hexane:dichloromethane (1:1), was expected to

contain SCCPs and the recovery standard ( $^{13}\text{C}$ -PCN-27). The second fraction was concentrated by rotary evaporation, to approximately 1 mL, and transferred to glass vials containing silicone for evaporation to dryness. The silicone, which was used to trap the SCCPs and recovery standard during evaporation, was rinsed with hexane for 15 minutes prior to use. After evaporation to dryness, the samples were redissolved, and extracted from the silicone overnight using 100  $\mu\text{L}$  of isooctane containing 50 ng/mL of  $^{13}\text{C}$ -HCB for use as an injection standard. Each 100  $\mu\text{L}$  sample was expected to contain 4 ng of the recovery standard and 5 ng of the injection standard.

### 2.3 Instrumental analysis and quantification

The instrument used was a Thermo Scientific<sup>TM</sup> Exactive<sup>TM</sup> Orbitrap<sup>TM</sup> mass spectrometer coupled to a Thermo Scientific TRACE<sup>TM</sup> 1310 GC. The GC-column was a TG-5HT column (5% phenyl methyl polysiloxane, 15 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness). Samples were introduced using a 1.5  $\mu\text{L}$  pulsed pressure splitless injections. Helium was used as the carrier gas, at a flow rate of 1.4 mL/min. The GC oven programme started at 60  $^{\circ}\text{C}$  for two minutes, increased to 360  $^{\circ}\text{C}$  at 40  $^{\circ}\text{C}/\text{min}$ , and finished at 360  $^{\circ}\text{C}$  for 4.5 minutes. The total run time was 14 minutes.

The Orbitrap mass spectrometer was operated in full-scan mode (200 to 550  $m/z$ ) at 60,000 mass resolution (resolving power at 200  $m/z$ ) with a four minute solvent delay. The ion source temperature was 150  $^{\circ}\text{C}$ , the automatic gain control was  $3 \times 10^6$  ions, and the maximum injection time was 500 ms. Methane was used as the ECNI reagent gas, at a flow rate of 1.5 mL per minute, and the C trap offset energy is 2V (positive values favour less fragmentation).

The chlorine-dependent ECNI-MS response means that the experimentally determined chlorine contents (experimental wt% Cl) of many SCCP technical mixtures will be higher than the manufacturer-specified chlorine contents (e.g. 51.5 wt% Cl). It also means that different CP technical mixtures used for calibration will lead to different SCCP concentrations for the same sample. For example, a 51.5 wt% Cl technical mixture standard will systematically overestimate the total SCCP concentration of a 55.5 wt% Cl sample because the technical mixture standard has a lower response at the same concentration. Similarly, a 63 wt% Cl technical mixture standard will systematically underestimate the total SCCP concentration of the same 55.5 wt% Cl sample because the technical mixture standard has a higher response at the same concentration (Reth et al., 2005; Bayen et al., 2006). In fact, quantitation errors greater than 100% have been reported (Reth et al., 2005; Zencak et al., 2005).

Different methods have been developed to address the chlorine-dependent ECNI-MS response (Tomy et al., 1997; Reth et al., 2005; Yuan et al., 2017). According to one approach, the ECNI-MS response of a CP mixture is positively correlated with its experimental wt% Cl (Reth et al., 2005; Sprengel & Vetter, 2019). This means that SCCP technical mixtures with a range of chlorine contents can be used to quantify the relationship between ECNI-MS response and experimental wt% Cl.

Using this information, the concentration of  $\Sigma$ SCCPs in a sample was determined in the following three steps:

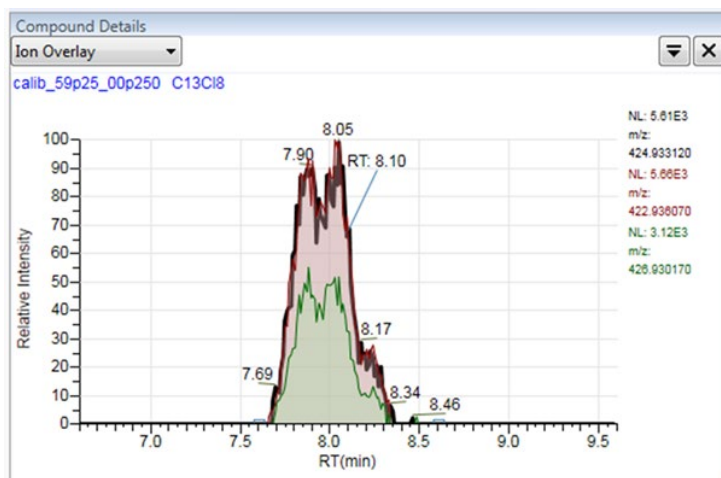
- Compute the experimental wt% Cl of the sample SCCPs.
- Estimate the sample response factor using (i) the sample's experimental wt% Cl and (ii) the chlorine-dependent response relationship determined with the technical mixtures.
- Calculate the sample's total SCCP concentration using its estimated response factor (RF):

$$[SCCP] = \frac{\text{Total Response}_{SCCP \text{ congeners}}}{RF} \quad (1)$$

## 2.4 Data analysis

Thermo Scientific TraceFinder™ 4.1-EFS software was used for peak detection and integration. The most abundant  $[M-Cl]^-$  ion of each of 24 SCCP congeners ( $C_{10-13}Cl_{5-10}$ ) was selected for quantification, and the next two most abundant  $[M-Cl]^-$  ions were used to confirm the quantification ion using isotope abundance ratios. The experimental isotopic abundances were generally deemed acceptable if they were within  $\pm 20\%$  of their expected values. The SCCP congener signals were integrated over 1.5-minute time intervals to account for the complex chromatographic peak produced by multiple unresolvable SCCP isomers from the same congener group (Figure 2). The peak area of every signal was normalized to the peak area of the  $^{13}C$ -HCB injection standard to account for injection variability.

**Figure 2.** Quantification and confirmation ions of the  $C_{13}H_{20}Cl_8$  SCCP congener in a 59.25 wt% Cl technical mixture at a concentration of 250 ng SCCP/mL.



Seven concentration levels (0.1, 0.25, 0.5, 1, 5, 10 and 20  $\mu\text{g}/\text{mL}$ ) of five SCCP technical mixtures with a range of chlorine contents (51.5, 53.5, 55.5, 59.25, and 63 wt% Cl) were used to determine the SCCPs' chlorine-dependent ECNI-MS response. A separate calibration curve was prepared for every SCCP technical mixture. A linear calibration curve was constructed to determine the response factors used to quantify SCCPs in the samples, according to Equation 1 (Reth & Oehme, 2004; Reth et al., 2005). However, as previously discussed for the LRMS approach, there were indications of a non-linear relationship, which needs further study (Vorkamp et al., 2017).

The SCCP amount in ng was related to the sample intake to yield concentrations in ng/g ww. Lipid contents of the samples were available from previous analyses under the AMAP Core Programme. For the samples from Canada and Svalbard, lipid contents were determined using the accredited method

according to Smedes (1999). The SCCP results were corrected for blanks, as further discussed in section 3.1. About 20% of the blank corrected concentrations were below the limit of quantification (LOQ).

In the calculations of means and standard deviations and the statistical analyses of spatial differences, following the method by Loftis et al. (1989), values below LOQ were replaced with  $LOQ/\sqrt{2}$ . Prior to statistical analysis concentration values were log-transformed to approach the assumptions of normal distribution and variance homogeneity. Analysis of variance (ANOVA) was performed to test for differences in  $\Sigma$ SCCP concentrations among the populations including sex and age as explanatory variables. The tests of the explanatory variables were based on Type III Sum of Squares, where every term in the model is tested in light of every other term in the model ("partial"). In addition, a non-parametric Kruskal-Wallis test was performed, as an alternative to ANOVA, but without including the variables age and sex. All statistical analyses were performed using R (R Core Team, 2020).

## 2.5 Quality assurance/quality control (QA/QC)

The laboratory is accredited for the analysis of PCBs and polybrominated diphenyl ethers (PBDEs) in biological materials and has incorporated many QA/QC elements in all chemical analyses, including non-accredited compounds or materials. Procedures applied in all analyses of organic contaminants included the use of glassware (baked at 400°C overnight and covered with aluminium foil until use), the pre-cleaning with dichloromethane of all materials (e.g. those used for the column clean-up), the use of high-grade solvents, the documentation of all steps in the laboratory, the regular calibration of laboratory scales and other equipment etc.

In each batch, a duplicate extraction of 0.4 g fish oil was included. The fish oil samples had been spiked with 100 ng of SCCPs from the 55.5 wt% CI technical mixture (100  $\mu$ L of a 1000 ng/mL solution) prior to extraction. One and three procedural blanks were prepared for the first and second batch, respectively. The spiked samples and procedural blanks were prepared in the same manner as the ringed seal blubber samples and analysed together with them.

In addition, each sample was spiked with a recovery standard, as described in section 2.2. The percentage recovery was calculated relatively to spike solutions, containing the recovery spike and injection standard that were prepared at the same time as the samples and analysed together with the samples. Thus, these spike solutions represent 100% recovery. This procedure has proven more accurate and precise than using a theoretical concentration as 100% as long-term use of standards and other factors may influence the exact concentration of a solution.

## 3 Results and discussion

### 3.1 Quality assurance/Quality control (QA/QC)

As discussed in connection with a previous study and the review of Arctic data on chlorinated paraffins (Vorkamp et al., 2017; 2019), the chemical analysis of this compound group is more challenging than that of other POPs, such as PCBs. This mainly relates to the high complexity of CP mixtures, which does not currently allow congener-specific determinations, the limited availability of analytical standards, the interferences from other chlorinated compounds, and the uncertainties in relation to the determination of response factors. In addition, the use of HRMS instruments such as GC-Orbitrap, is a rapidly developing research field in itself. This type of HRMS has rarely been used in routine analysis for monitoring purposes but found several applications in non-target and suspect screening approaches.

Furthermore, the recent and ongoing use of SCCPs and other CPs increases the risks of sample contamination. The analyses in this study included procedural blanks, which all contained quantifiable amounts of SCCPs. These concentrations were generally low (21-48 ng in a 1 ml extract), but high enough to potentially contribute to the levels in the samples. In the first batch (Canadian samples), the blank accounted for 8-90% (Mean: 45%) of the SCCP concentration in the samples. In the second batch (Greenland and Svalbard samples), three blank samples were included, which had a standard deviation of 30%. Their mean value accounted for 18-100% (Mean: 53%) of the SCCP concentrations in the samples. For this reason, all concentrations were blank corrected with the batch-specific blank value (the mean of the three blanks in the second batch). The presence of high and variable blank levels had also been reported for air measurements in the Arctic, as summarized in Chapter 1.2.

For each sample, a recovery rate was determined, based on the addition of  $^{13}\text{C}$ -PCN-27 to the samples. The results are summarized in Table 1. In the first batch, the concentration of  $^{13}\text{C}$ -PCN-27 was outside the calibration range, potentially increasing the uncertainty in the calculation of the concentrations. In the second batch, the spike amount was reduced, thus matching the calibration range. A few individual samples showed a low recovery of approximately 60%, but the majority of samples was close to 100%. This indicated that the sample processing worked satisfactorily, but care should be taken to avoid any losses.

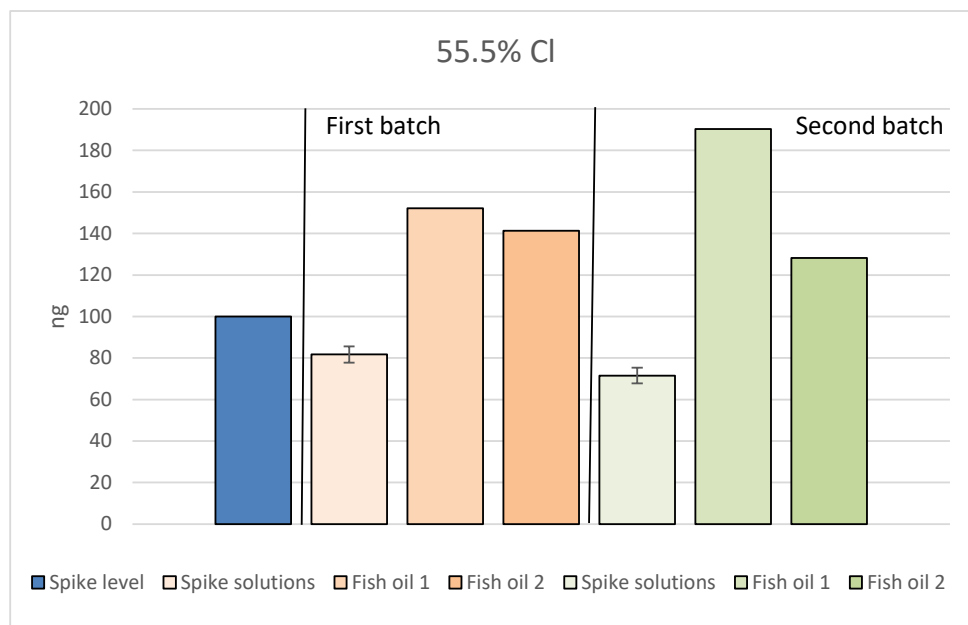
**Table 1.** Recovery rates for  $^{13}\text{C}$ -PCN-27 in the analyses of SCCPs in blubber of ringed seals and control samples (fish oil).

	Ringed seal samples; range (%)	Ringed seal samples; average (%)	Fish oil samples; duplicates (%)
First batch	68-113	96	90; 85
Second batch	59-125	94	90; 98

As described in section 2.5, two samples of fish oil were spiked with 100 ng SCCPs (55.5% CI) for each batch and processed together with the ringed seal samples. The results for these samples showed that the accurate determination of the SCCP concentration was a challenge. The spike solutions were generally quantified to contain slightly lower levels than the theoretical spike concentration (Figure 3). On the other hand, the standard deviation of the three spike solutions was relatively low (4.8 and 5.4% for the first and the second



batch, respectively), indicating that precision is a minor issue in the SCCP determination. The concentration in the spiked fish oil samples exceeded the levels of the spike solutions and the theoretical concentrations. This might suggest that there were still interferences in the SCCP chromatograms although PCBs and some organochlorine pesticides had been removed in a fractionation step. Matrix effects can also play a role, despite the high resolution analysis.

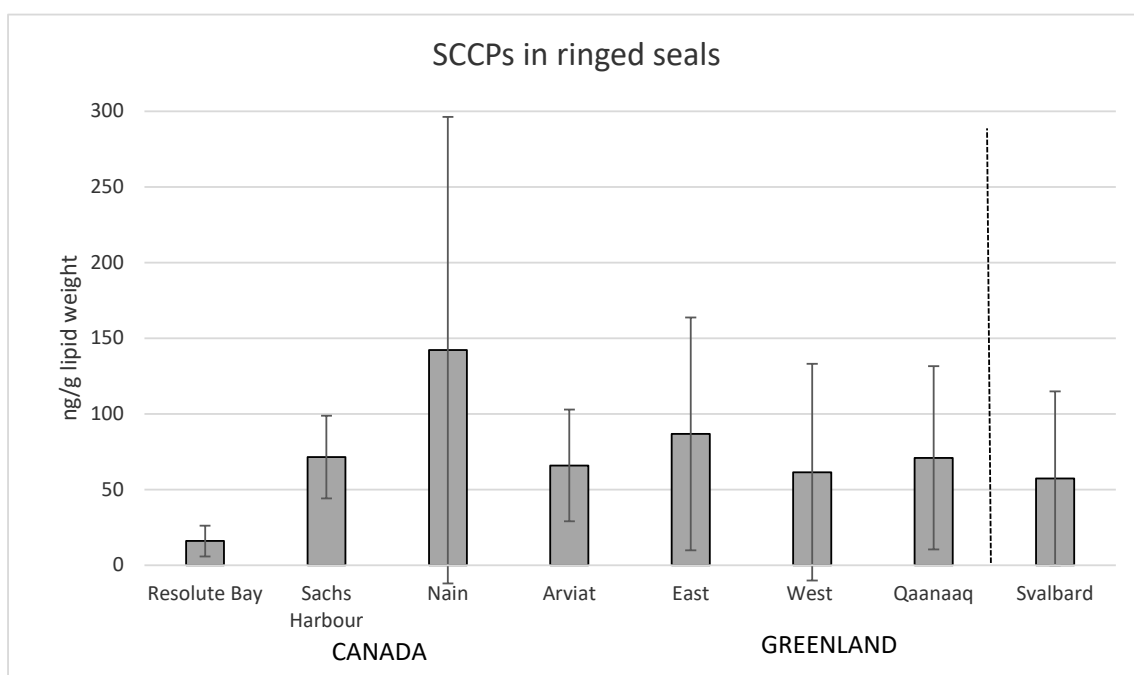


**Figure 3.** SCCPs (ng) in spiked control samples compared to spike solutions (N=3) and the theoretical spike concentration

The concentration of 100 ng/mL, as used in the spike solutions, was close to the LOQ of these analyses. The lowest calibration standard, which defined the LOQ was 100 ng/mL. Due to the low levels expected in the samples, all extracts were concentrated to 100  $\mu$ L. However, it also concentrated the matrix and a potential background contamination. Given the low concentrations in the samples and the increases in measurement uncertainty close to LOQs, sensitivity will remain an issue in the SCCP determination with this analytical technology.

### 3.2 Levels of SCCPs in ringed seals from the Arctic

Figure 4 shows the mean concentrations and standard deviations for  $\Sigma$ SCCPs in the ringed seal samples from different locations (Canada, Greenland, Svalbard). As mentioned in section 3.1, all samples were corrected for the levels in the blanks. Samples from Resolute Bay, Nain, West Greenland, Qaanaaq and Svalbard included one or several individuals with SCCP concentrations below LOQ. Detection frequencies are given in Table 2. Concentrations below LOQ values were replaced with  $LOQ/\sqrt{2}$  in the calculations of means and standard deviations (Figure 4). The results are normalised to ng/g lw to reduce variability among the samples due to differences in lipid content. A Box-Whisker plot of the ww and lw concentrations is shown in chapter 6.



**Figure 4.** Mean SCCP concentrations and standard deviations (ng/g lipid weight) in blubber of ringed seal from locations in Canada (Resolute Bay N=4, Sachs Harbour N=5, Nain N=5, Arviat N=4), Greenland (East Greenland = Ittoqqortoormit N=5, West Greenland = Qeqertarsuaq N=5, Qaanaaq N=5) and Svalbard (N=4).

**Table 2.** Detection frequencies, i.e. percentage of samples above limits of quantification (LOQ)

Location	N	Detection frequency (%)
Resolute Bay (Canada)	4	25
Sachs Harbour (Canada)	5	100
Nain (Canada)	5	80
Arviat (Canada)	4	100
Ittoqqortoormit (East Greenland)	5	100
Qeqertarsuaq (West Greenland)	5	60
Qaanaaq (Northwest Greenland)	5	80
Svalbard	4	75

The mean concentrations ranged between 16 and 142 ng/g lw (14-139 ng/g ww) for the different locations. These are much lower than measured for ringed seals from East and West Greenland in a previous study (Vorkamp et al., 2017). However, the previous method had been based on LRMS and the results were likely affected by interferences from other chlorinated compounds, including MCCPs.

The database currently available for SCCPs in ringed seals from the Arctic is rather diverse, as the studies generally cover a wide time span and determine different parameters (e.g.  $\Sigma$ CPs and  $\Sigma$ SCCPs) (Table 3). It is questionable whether studies from different time periods will be comparable, because of differences in environmental levels, besides the issue of limited comparability due to the challenges in analytical chemistry. No comprehensive time trend has been established for SCCPs in the Arctic, but compilations of air data obtained with comparable methods indicated that there had been an increase from the early 1990s to the most recent measurements in 2010-2015 (Vorkamp et al., 2019). However, data for beluga indicated decreasing concentrations between approximately 1995 and 2005 (Muir et al., 2013). The recent ban of

SCCPs via the Stockholm Convention on POPs could also lead to decreases of environmental concentrations, as observed for other regulated compounds.

Previous analyses of ringed seals from Resolute Bay showed higher concentrations than analysed here (Table 3). In addition to changes in SCCP exposure between the years of sampling, concentrations might also differ between age groups of animals. In this study, the seals from Resolute Bay consisted of two females (< 1 year) and three males (two aged 4 and one < 1 year of age), while the previous study only included adult females (Muir et al., 2013). Besides the data summarized in Table 3, SCCP concentrations were also determined in plasma of ringed seals from Svalbard, with a detection frequency of 100% and a mean concentration (N=10) of 4.96 ng/mL (Harju et al., 2013).

**Table 3.** Previously reported SCCP mean concentrations in ringed seal (blubber) from the Arctic. Updated from Vorkamp et al. (2019)

Location	Year of sampling	N	ΣSCCPs	Reference
Svalbard	1981	7	130 ng/g lw	Jansson et al. (1993)
Ellesmere Island (Nunavut, Canada)	1994	6	530 ng/g ww	Tomy et al. (2000)
West Greenland	1999-2001	6	10.5 ng/g ww	Johansen et al. (2004)
Grise Fjord (Ellesmere Island, Nunavut, Canada)	1998-2004	7; all females	46 ng/g lw	Muir et al. (2013)
Resolute (Canada)	1998-2004	13; all females	138 ng/g lw	Muir et al. (2013)
Pangnirtung (Baffin Is- land, Nunavut, Canada)	1998-2004	12; all females	79 ng/g lw	Muir et al. (2013)
Pangnirtung (Baffin Is- land, Nunavut, Canada)	1998-2004	12; all males	248 ng/g lw	Muir et al. (2013)

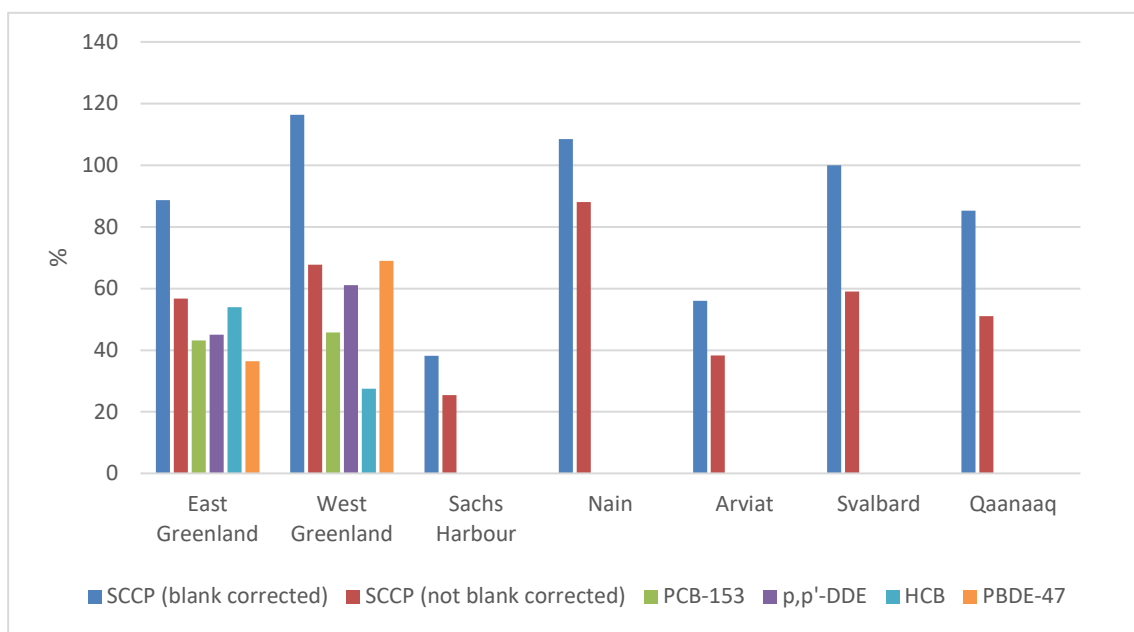
As summarized in chapter 1.2, our review of Arctic air data concluded that ΣSCCPs exceeded the concentrations of many POPs in air, including those of ΣPCB and HCB (Vorkamp et al., 2019). HCB is usually the POP compound with the highest concentrations in Arctic air (Bossi et al., 2016). However, the ΣSCCP concentrations in ringed seals were usually lower than those of other POPs (Table 4). In this study, the ΣSCCP levels in ringed seals from Greenland could be compared to other POP concentrations in the same individuals, determined under the AMAP Core Programme (Rigét et al., 2016). Although the ΣSCCP concentrations were lower than those of most other POPs, the difference seems to be smaller now than in the older studies (Jansson et al., 1993; Tomy et al., 2000; Johansen et al., 2004). This could be indicative of differences in the temporal trends of environmental concentrations of SCCPs and other POPs. Interestingly, the SCCP pattern between ringed seals from East and West Greenland is similar to that of the other POPs, with mean levels in West Greenland being approximately half the mean levels in East Greenland.

**Table 4.** Mean concentrations of  $\Sigma$ SCCP and other POPs in ringed seal (blubber) from this and other studies. Lipid-normalised values are very similar to wet weight concentrations; therefore, values are only given in the reported unit.

Reference	$\Sigma$ SCCPs	$\Sigma_7$ PCBs <sup>a)</sup>	$\Sigma_{10}$ PCBs <sup>b)</sup>	$\Sigma$ PCBs <sup>c)</sup>	PCB-153	p,p'-DDE	$\Sigma$ DDTs	HCB
Jansson et al. (1993)	130 ng/g lw	1500 ng/g lw	n.a.	n.a.	500 ng/g lw	2300 ng/g lw	2900 ng/g lw <sup>d)</sup>	10 ng/g lw
Tomy et al. (2000)	530 ng/g ww	n.a.	n.a.	5410 ng/g ww	n.a.	n.a.	3750 ng/g ww	n.a.
Johansen et al. (2004)	10.5 ng/g ww	n.a.	287 ng/g ww	549 ng/g ww	n.a.	343 ng/g ww	439 ng/g ww <sup>e)</sup>	7.43 ng/g ww
This study – East Greenland	86 ng/g ww	258 ng/g ww	277 ng/g ww	349 ng/g ww	108 ng/g ww	192 ng/g ww	226 ng/g ww	5.63 ng/g ww
This study – West Greenland	60 ng/g ww	103 ng/g ww	116 ng/g ww	151 ng/g ww	35.2 ng/g ww	99 ng/g ww	117 ng/g ww	7.34 ng/g ww

a) PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180; b) PCB-28, PCB-31, PCB-52, PCB-101, PCB-105, PCB-118, PCB-138, PCB-153, PCB-153, PCB-180; c) all congeners included in the study; d) p,p'-DDT, p,p'-DDE, p,p'-DDD; e) p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT, o,p'-DDE, o,p'-DDD. n.a.: not available

Figure 4 indicates large standard deviations for the mean  $\Sigma$ SCCP concentrations, exceeding 100% for results from Nain (Canada), West Greenland and Svalbard. All locations included values below LOQ. In general, a substantial part of this variation was introduced by the blank correction (Figure 5). For the ringed seals from East and West Greenland the variation in the SCCP concentrations prior to blank correction was similar to or only slightly higher than that of other POPs determined in the same animals as part of the AMAP Core Programme (Figure 5). Considering the difficulties with the SCCP determination this result seems surprising, but encouraging. It indicates that blank contamination seems to be a more serious challenge in the SCCP analysis than analytical precision and should be eliminated as a priority.



**Figure 5.** Relative standard deviations (%) of  $\Sigma$ SCCP concentrations before and after blank correction. For ringed seals from East and West Greenland, the relative standard deviations were compared with those of other POP concentrations in the same individuals. Sachs Harbour N=5; Nain N=5; Arviat N=4; East Greenland = Ittoqqortoormit N=5; West Greenland = Qeqertarsuaq N=5; Qaanaaq N=5; Svalbard N=4. Results from Resolute Bay are not included because of too many values below the limit of quantification.

### 3.3 Geographical differences

Applying the same analytical method to determine SCCP levels in ringed seals from different locations in the Arctic should enable spatial comparisons. Except for the lower levels at Resolute Bay, Figure 4 shows rather uniform levels across locations. No significant differences were found between the  $\Sigma$ SCCP concentrations in ringed seals from the various locations. As discussed in chapter 3.2, the blank corrected concentrations showed particularly large variations. However, the same statistical analyses were also applied to the data before blank correction, also resulting in an absence of statistically significant differences between location-specific  $\Sigma$ SCCP concentrations.

As discussed in section 1.2, SCCP levels in freshwater fish were lower in the Canadian Arctic than on Bjørnøya in the Norwegian Arctic (Reth et al., 2006; Basconcillo et al., 2015). However, the studies included different species of freshwater fish, which were collected in 2011 and 2001 for Canada and Bjørnøya, respectively. In addition to the potentially limited comparability of analytical methods, this induces further confounding factors in any comparison across locations.

Spatial trends were also derived from a multi-location study of lake sediment cores from Canada, analysed for SCCPs with the same methodology (Tomy et al., 1999). The sediment samples originated from 50°N-81°N and showed decreasing  $\Sigma$ SCCP concentration with increasing latitude. The presence of SCCPs in remote lakes for the Canadian Arctic was related to long-range atmospheric transport and deposition of SCCPs, whereas some of the more southerly study sites also indicated inputs from local sources. Given the presence of SCCPs in many commercial products until their recent ban through the Stockholm Convention, emission sources related to human activity in the Arctic also seem possible. If the presence of SCCPs in the Arctic is to be related to hemispheric transport patterns or evidence of their long-range transport in a risk assessment or regulatory context, it is important to keep these sources and processes apart.

A latitudinal transect of soil samples from the UK to the Norwegian Arctic showed a steep decline of SCCP concentrations with increasing latitude, with concentrations in all Arctic samples below LOQ (Halse et al., 2015). SCCPs showed no correlation with any soil characterizing parameters, indicating that their distribution was primarily determined by proximity to sources. Based on these results, Halse et al. (2015) concluded that SCCPs were less prone to long-range atmospheric transport, in comparison with other POPs. This conclusion is not entirely supported by the air monitoring data from the Arctic or the deposition of SCCPs in remote Arctic lakes and will need more investigation.

In summary, SCCPs were widely present in ringed seals from the Arctic, with  $\Sigma$ SCCP concentrations generally below those of e.g.  $\Sigma$ PCB and  $\Sigma$ DDT. The analysis did not indicate major geographical differences, but a rather uniform spatial distribution. However, the substantial uncertainty that is introduced into the data due to the presence of and correction for blanks might mask more subtle differences among locations.

## 4 Conclusions and outlook

SCCPs were present in blubber samples of juvenile ringed seals from the Arctic, with location-specific mean concentrations between 16 and 142 ng/g lw. The SCCP concentrations were lower than those of other POPs, such as PCBs and p,p'-DDE. However, studies from the 1990s and 2000s indicate that the SCCP percentage of the total POP burden in ringed seals from the Arctic might have increased. Substantiating this indication would require a more systematic time trend study, which would also be useful for the interpretation of data from former studies and evaluations of efficiency of the SCCP regulation under the Stockholm Convention.

No statistically significant differences were found for  $\Sigma$ SCCP concentrations across the sampling locations. While the concentrations appear highest at Nain and lowest at Resolute Bay, they were generally rather uniform across the locations included in this study. Compared with other POPs, including recently regulated ones, data available on SCCPs in the Arctic are sparse. It would be desirable to extend this initial assessment of a spatial trend to other locations in the Arctic as well as to other media, in order to obtain a better understanding of the presence and distribution of SCCPs in the Arctic environment.

Studying temporal and/or spatial trends in a similar way to other POPs requires robust and sensitive analytical methods for monitoring purposes. Considering the complexity of mixtures of chlorinated paraffins, the GC-Orbitrap HRMS method developed in this project is promising. However, the results of this study have shown that further improvements would be beneficial, in particular regarding accuracy and sensitivity. Furthermore, blanks indicate a risk of sample contamination, which, if possible, should be traced and eliminated in the sample preparation steps. This is particularly important for the correct determination of the relatively low levels in some of the Arctic samples.

Since SCCPs are now globally regulated, MCCPs and LCCPs might be used increasingly as replacement compounds. Their high production volume and molecular similarity to SCCPs make them relevant candidates for future studies in the Arctic. MCCPs with a chlorine content at or above 45 wt% are now under review of the Stockholm Convention.

As discussed for the SCCPs, the knowledge of the environmental fate of all chlorinated paraffins is limited. A relevant topic to study is their long-range transport to the Arctic. This includes the question of signature changes because of differences in physical-chemical properties and resulting exposure to and accumulation in Arctic animals. In this context, it will be important to differentiate long-range transport from local sources, which may also exist for chlorinated paraffins in the Arctic.

## 5 References

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## 6 Appendix

SCCP congener ions used in the quantification method.

SCCP Congener	%Cl	Quant. Ion [M - Cl] <sup>-</sup>	% of All Congener Isotopes	Conf. ions [M - Cl] <sup>-</sup>	% of Quant. Ion
C <sub>10</sub> Cl <sub>5</sub> (C <sub>10</sub> H <sub>17</sub> Cl <sub>5</sub> )	56.32	279.00603 (C <sub>10</sub> H <sub>17</sub> Cl <sub>4</sub> <sup>37</sup> Cl)	35.81	281.00308 277.00898	63.99 62.51
(C <sub>10</sub> H <sub>16</sub> Cl <sub>6</sub> )	60.88	312.96706 (C <sub>10</sub> H <sub>16</sub> Cl <sub>5</sub> <sup>37</sup> Cl)	32.58	314.96411 310.97001	79.99 52.09
(C <sub>10</sub> H <sub>15</sub> Cl <sub>7</sub> )	64.62	346.92809 (C <sub>10</sub> H <sub>15</sub> Cl <sub>6</sub> <sup>37</sup> Cl)	28.80	348.92514 350.92219	95.99 51.19
(C <sub>10</sub> H <sub>14</sub> Cl <sub>8</sub> )	67.91	382.88617 (C <sub>10</sub> H <sub>14</sub> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> )	27.92	380.88912 384.88322	89.3 63.99
(C <sub>10</sub> H <sub>13</sub> Cl <sub>9</sub> )	70.54	416.8472 (C <sub>10</sub> H <sub>13</sub> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> )	27.20	414.85015 418.84425	78.14 74.66
(C <sub>10</sub> H <sub>12</sub> Cl <sub>10</sub> )	72.81	450.80822 (C <sub>10</sub> H <sub>12</sub> Cl <sub>9</sub> <sup>37</sup> Cl <sub>2</sub> )	25.77	452.80527 448.81117	85.32 69.45
(C <sub>11</sub> H <sub>19</sub> Cl <sub>5</sub> )	53.92	293.02168 (C <sub>11</sub> H <sub>19</sub> Cl <sub>4</sub> <sup>37</sup> Cl)	35.42	295.01873 291.02464	63.99 62.51
(C <sub>11</sub> H <sub>18</sub> Cl <sub>6</sub> )	58.52	326.98271 (C <sub>11</sub> H <sub>18</sub> Cl <sub>5</sub> <sup>37</sup> Cl)	32.22	328.97976 324.98566	79.99 52.09
(C <sub>11</sub> H <sub>17</sub> Cl <sub>7</sub> )	62.33	360.94374 (C <sub>11</sub> H <sub>17</sub> Cl <sub>6</sub> <sup>37</sup> Cl)	28.47	362.94079 364.93784	95.99 51.19
(C <sub>11</sub> H <sub>16</sub> Cl <sub>8</sub> )	65.70	396.90182 (C <sub>11</sub> H <sub>16</sub> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> )	27.62	394.90477 398.89887	89.3 63.99
(C <sub>11</sub> H <sub>15</sub> Cl <sub>9</sub> )	68.42	430.86285 (C <sub>11</sub> H <sub>15</sub> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> )	26.90	428.8658 432.8599	78.14 74.66
(C <sub>11</sub> H <sub>14</sub> Cl <sub>10</sub> )	70.77	464.82387 (C <sub>11</sub> H <sub>14</sub> Cl <sub>9</sub> <sup>37</sup> Cl <sub>2</sub> )	25.47	466.82092 462.82682	85.32 69.45
(C <sub>12</sub> H <sub>21</sub> Cl <sub>5</sub> )	51.71	307.03733 (C <sub>12</sub> H <sub>21</sub> Cl <sub>4</sub> <sup>37</sup> Cl)	35.04	309.03438 305.04029	63.99 62.51
(C <sub>12</sub> H <sub>20</sub> Cl <sub>6</sub> )	56.34	340.99836 (C <sub>12</sub> H <sub>20</sub> Cl <sub>5</sub> <sup>37</sup> Cl)	31.87	342.99541 339.00131	79.99 52.09

SCCP Congener	%Cl	Quant. Ion [M - Cl] <sup>-</sup>	% of All Congener Isotopes	Conf. ions [M - Cl] <sup>-</sup>	% of Quant. Ion
(C <sub>12</sub> H <sub>19</sub> Cl <sub>7</sub> )	60.20	374.95939 (C <sub>12</sub> H <sub>19</sub> Cl <sub>6</sub> <sup>37</sup> Cl)	28.17	376.95644 378.95349	95.99 51.19
(C <sub>12</sub> H <sub>18</sub> Cl <sub>8</sub> )	63.64	410.91747 (C <sub>12</sub> H <sub>18</sub> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> )	27.32	408.92042 412.91452	89.3 63.99
(C <sub>12</sub> H <sub>17</sub> Cl <sub>9</sub> )	66.42	444.8785 (C <sub>12</sub> H <sub>17</sub> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> )	26.62	442.88145 446.87555	78.14 74.66
(C <sub>12</sub> H <sub>16</sub> Cl <sub>10</sub> )	68.84	478.83952 (C <sub>12</sub> H <sub>16</sub> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> )	25.20	480.83657 476.84247	85.32 69.45
(C <sub>13</sub> H <sub>23</sub> Cl <sub>5</sub> )	49.67	321.05298 (C <sub>13</sub> H <sub>23</sub> Cl <sub>4</sub> <sup>37</sup> Cl)	34.66	323.05003 319.05594	63.99 62.51
(C <sub>13</sub> H <sub>22</sub> Cl <sub>6</sub> )	54.31	355.01401 (C <sub>13</sub> H <sub>22</sub> Cl <sub>5</sub> <sup>37</sup> Cl)	31.53	357.01106 353.01696	79.99 52.09
(C <sub>13</sub> H <sub>21</sub> Cl <sub>7</sub> )	58.21	388.97504 (C <sub>13</sub> H <sub>21</sub> Cl <sub>6</sub> <sup>37</sup> Cl)	27.86	390.97209 392.96914	95.99 51.19
(C <sub>13</sub> H <sub>20</sub> Cl <sub>8</sub> )	61.70	424.93312 (C <sub>13</sub> H <sub>20</sub> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> )	27.03	422.93607 426.93017	89.3 63.99
(C <sub>13</sub> H <sub>19</sub> Cl <sub>9</sub> )	64.53	458.89415 (C <sub>13</sub> H <sub>19</sub> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> )	26.32	456.8971 460.8912	78.14 74.66
(C <sub>13</sub> H <sub>18</sub> Cl <sub>10</sub> )	67.01	492.85517 (C <sub>13</sub> H <sub>18</sub> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> )	24.93	494.85222 490.85812	85.32 69.45

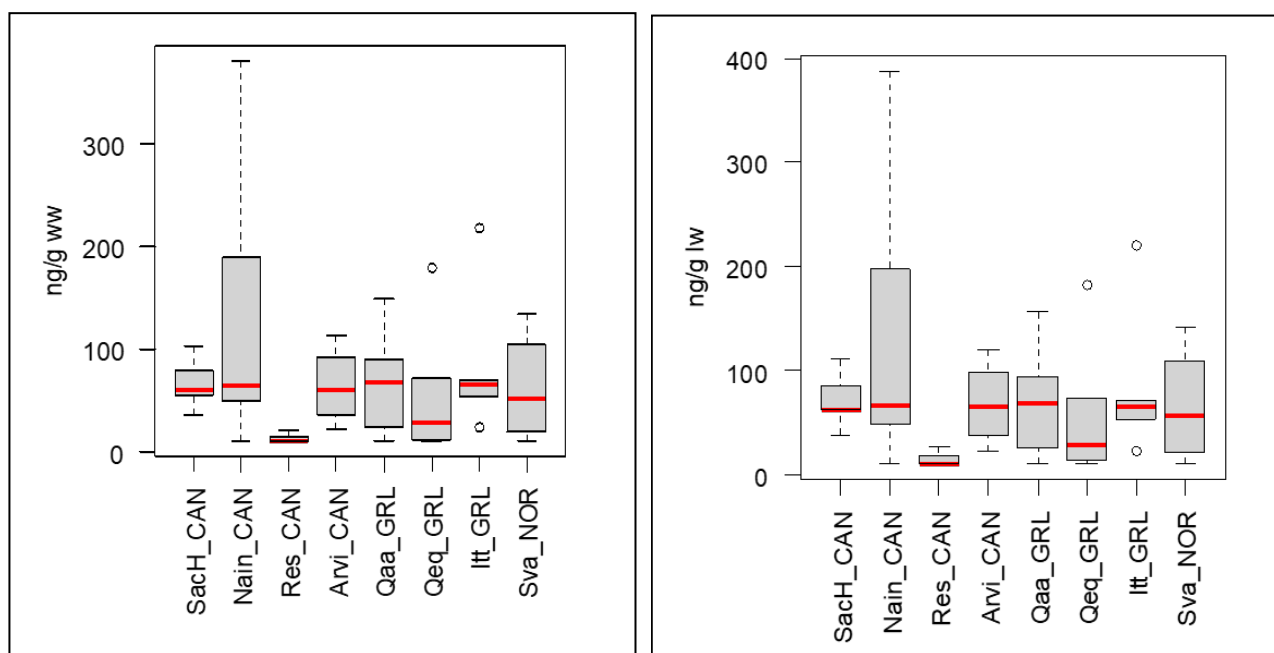
Lipid content of the ringed seal blubber samples

Location	Sample registration number	Sex	Lipid content (%)
Resolute Bay (Canada)	2019-17031	Male	91.6
	2019-17032	Male	90.7
	2019-17033	Male	93.1
	2019-17034	Female	78.0

Location	Sample registration number	Sex	Lipid content (%)
Sachs Harbour (Canada)	2019-17035	Male	93.8
	2019-17036	Male	92.5
	2019-17037	Male	94.1
	2019-17038	Female	89.6
	2019-17039	Female	96.2
Nain (Canada)	2019-17040	Female	95.8
	2019-17041	Female	96.9
	2019-17042	Female	96.5
	2019-17043	Male	98.3
	2019-17044	Female	100
Arviat (Canada)	2019-17045	Female	99.8
	2019-17046	Female	94.6
	2019-17047	Female	94.6
	2019-17048	Female	88.7
East Greenland	2017-15348	Female	99.4
	2017-15349	Male	99.8
	2017-15352	Male	99.3
	2017-15362	Male	99.5
	2017-15363	Male	98.8
West Greenland	2017-15578	Male	92.4
	2017-15579	Male	98.6
	2017-15580	Female	97.6

Location	Sample registration number	Sex	Lipid content (%)
	2017-15581	Male	96.8
	2017-15585	Female	98.2
Qaanaaq	2019-17264	Male	97.4
	2019-17265	Female	95.9
	2019-17266	Male	95.5
	2019-17267	Female	99.2
	2019-17268	Male	94.3
Svalbard	2019-16941	Male	95.1
	2019-16942	Male	94.0
	2019-16943	Female	92.4
	2019-16944	Male	91.0

Box-Whisker-Plots of  $\Sigma$ SCCP concentrations in ringed seals from different locations in the Arctic.



SachH: Sachs Harbour, Canada; Res: Resolute Bay, Canada; Arvi: Arviat, Canada; Qaa: Qaanaaq, Greenland; Qeq: Qeqertarsuaq (=West Greenland); Itt: Ittoqqortoormiit (=East Greenland); Sva: Svalbard

## GEOGRAPHICAL TRENDS OF SHORT-CHAIN CHLORINATED PARAFFINS (SCCPs) IN RINGED SEALS FROM THE ARCTIC

Chlorinated paraffins are high production volume chemicals used in a variety of commercial and industrial applications, e.g. as lubricants, flame retardants and metal working fluids. They are commonly divided into short-, medium and long-chain chlorinated paraffins ( $C_{10}$ – $C_{13}$  (SCCPs),  $C_{14}$ – $C_{17}$  (MCCPs) and  $\geq C_{18}$  (LCCPs), respectively), of which SCCPs are regulated via the Stockholm Convention on Persistent Organic Pollutants (POPs). Due to their complexity, the analytical chemistry is challenging, and different studies often lack comparability. The objective of this project was to study spatial differences in  $\Sigma$ SCCPs in ringed seals from Canada, Greenland and Svalbard. Blubber of juvenile ringed seals ( $N=4$ – $5$  per location) from a total of eight locations (Canada: 4; Greenland: 3; Svalbard: 1) were analysed with gas chromatography with Orbitrap high-resolution mass spectrometry (GC-Orbitrap MS). As blanks showed quantifiable levels of SCCPs, all concentrations were blank corrected. Mean  $\Sigma$ SCCPs ranged between 16 and 142 ng/g lipid weight, without statistically significant differences between locations. Standard deviations exceeded 100% in some cases, but were considerably lower for data without blank correction.  $\Sigma$ SCCP concentrations were generally lower than those of other POPs available for the same individuals from East and West Greenland. However, compared with previous studies from the 1990s to early 2000s, this difference seemed smaller, possibly indicating different temporal developments for SCCPs and other POPs. The applicability of the current analytical method for routine monitoring still poses challenges, in particular regarding sensitivity and blank occurrences.