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# Concentrations of organochlorine pesticides, polybrominated diphenyl ethers and perfluorinated compounds in the atmosphere of North Greenland<sup>☆</sup>

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## ABSTRACT

Atmospheric concentrations of organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and neutral per- and polyfluoroalkyl substances (PFAS) have been measured at Villum Research Station, Station Nord (North Greenland) in the period 2008–2013. Atmospheric concentrations of OCPs at the same site have been previously reported for the years 2008–2010. The detection frequency and the average concentrations of OCPs have not significantly changed since the previous study. PBDE congeners ( $\sum_{13}$ PBDEs) were measured for the first time in North Greenland at concentrations similar to those observed for other remote sites, confirming that these compounds are ubiquitous in the Northern Hemisphere. The  $\sum_{13}$ PBDEs concentration ranged from not detected (n.d.) to  $6.26 \text{ pg m}^{-3}$ . The BDE congeners found in more than 30% of the samples were BDE-17, BDE-28, BDE-47, BDE-71, BDE-99 and BDE-100. Also for neutral PFAS we present for the first time a multiyear series of measurements for North Greenland. The average sum of the seven measured neutral PFAS ( $\sum_7$ PFAS) ranged from 1.82 to  $32.1 \text{ pg m}^{-3}$ . The most abundant compound was 8:2 FTOH (44% of  $\sum_7$ PFAS), followed by 6:2 FTOH and 10:2 FTOH. Perfluoroalkyl sulfonamides (FOSA) and perfluoroalkyl sulfonamidoethanols (FOSE) were also detected but at much lower concentrations than FTOHs.

Temporal trends were investigated for all measured compounds but no significant trend in concentration was observed. Monthly average concentrations for the six years were calculated for each compound and the seasonal variation was investigated. Some OCPs and FTOHs showed seasonal variations, and in most cases a maximum was found during summer.

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## 1. Introduction

Persistent organic pollutants (POPs) are relatively stable in the environment and are subject to long-range transport to remote regions such as the Arctic, where they may bio-accumulate in the food web (AMAP, 2004) or deposit depending on their bio-availability and physical and chemical properties (Halsall, 2004). The atmosphere plays a key role in the global cycling of volatile and semi-volatile POPs and their delivery to both aquatic and terrestrial food chains. The Arctic environment is under pressure due to a still faster accelerating climate changes (IPCC, 2013) and due to

increased industrial Arctic activities. The measurement of POP concentrations in the Arctic atmosphere is thus a key activity to investigate their long-range atmospheric transport and assess the effect of global control initiatives such as the Stockholm Convention on POPs of the Environmental Program of the United Nations (UNEP) and the Long-range Trans-boundary Air Pollution under the UN's Economic Commission for Europe (ECE). Polyhalogenated organic compounds (or organohalogenated compounds) constitute a large group of chemicals that due to their persistence in the environment, bioaccumulation potential and toxicity have been classified as POPs. The organohalogenated compounds included in the present study are chlorinated pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and polyfluorinated alkyl compounds (PFAS).

OCPs have been used extensively since the late 1950's. After discovering their ubiquitous presence in the environment, their

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tendency to bio-accumulate in the food web and their toxic and hazardous properties for top predators and humans, most OCPs have been banned or restricted in industrialized countries. A number of OCPs – including chlordanes, DDT, hexachlorocyclohexanes (HCHs), and more recently endosulfan – are regulated under the Stockholm Convention on POPs. After reductions in primary emissions of OCPs as part of control strategies, re-emission from previously contaminated soils and oceans has taken over as the main source for atmospheric concentrations of OCPs. Atmospheric concentrations of OCPs in the atmosphere of Greenland have been previously reported for Nuuk (South West Greenland) in a two-years monitoring study (Bossi et al., 2008) and recently for Station Nord (North Greenland) for the years 2008–2010 (Bossi et al., 2013).

Polybrominated diphenyl ethers (PBDEs), as OCPs, belong to the group of semi-volatile organic compounds, which can volatilize in relatively warm source regions and reach the Arctic regions by long-range atmospheric transport. Penta- and Octa-BDE mixtures were banned in the European Union (EU) in 2004. In the same year the production of Penta- and Octa-BDE mixtures was voluntarily phased out in the United States (U.S.). In 2009, the Penta- and Octa-BDE mixtures were included in Annex A of the Stockholm Convention on POPs (production and use of the chemicals listed to be eliminated). Atmospheric measurements of PBDEs in the Arctic have been summarized by de Wit et al. (2010) and Hung et al. (2010). More recent Möller et al. (2011) and Xiao et al. (2012) reported PBDEs measurements in the European and Canadian Arctic, respectively.

Per- and polyfluoroalkyl substances (PFAS) have been found to be ubiquitous in the environment (Giesy and Kannan, 2001). PFAS reach pristine environments, including the Arctic, where they bio-accumulate in the food chain after photochemical oxidation as perfluoroalkane sulfonic acids (PFASAs) and perfluoroalkene carboxyl acids (PFCAs) (Butt et al., 2010). Perfluorooctane sulfonate (PFOS), the major representative of the PFSA group, its salts and perfluorooctane sulfonyl fluoride (PFOS-F) have been recently listed under Annex B of the Stockholm Convention on POPs (production and use of the chemicals listed to be restricted). Recently, PFOA, its ammonium salt and C<sub>11</sub>–C<sub>14</sub> PFCAs have been included in the Candidate List of Substances of Very High Concern for Authorization under the European Chemical Regulation REACH (ECHA, 2013).

The mechanisms considered for explaining the presence of acidic PFAS in remote regions are (i) volatile neutral “precursor” compounds transported with air masses and oxidized to acidic compounds in the atmosphere (Ellis et al., 2004; D'Eon et al., 2006) (ii) direct transport of the acidic PFAS in water by oceanic currents (Prevedouros et al., 2006). The hypothesis of “precursors” compounds is supported by measurements of neutral precursor compounds in the atmosphere in remote region and particularly in the Arctic (Shoeb et al., 2006; Stock et al., 2007; Genualdi et al., 2010; Ahrens et al., 2011; Cai et al., 2012; Xie et al., 2015) and laboratory studies of their photochemical oxidation (Ellis et al., 2004; D'Eon et al., 2006). The “precursors” compounds measured in the atmosphere include fluorotelomer alcohols (FTOH), perfluoroalkyl sulfonamides (FOSA) and perfluoroalkyl sulfonamidoethanols (FOSE).

The main sources of FTOHs in the environment are associated with production, use and disposal of fluorotelomer-based products, while the source of FOSA and FOSE is believed to be the production of perfluorooctyl sulfonyl-based compounds (Prevedouros et al., 2006).

This study presents the results of multiyear measurements (2008–2013) of organohalogen compounds in the atmosphere in North Greenland. The aim of this study is to determine if these compounds are present in the atmosphere of North Greenland, and

to measure their concentrations and their dynamics. We hypothesize that we can explain the measured concentrations by long-range transport or by re-emission following the Clausius–Clapeyron equation. Moreover, seasonal variations and temporal trends have also been investigated.

## 2. Materials and methods

### 2.1. Air sampling

Villum Research Station, Station Nord (81°36' N latitude and 16°40' W longitude; 24 m above sea level) is located in North Greenland (Fig. 1). The high volume sampler (Digitel, Hegnau, Switzerland) used for air sampling is placed in a hut and equipped with a heated sampling head (outside) for sampling total suspended particles. Via a stainless steel tube, sampled air is thereafter led into a PM<sub>10</sub> head that is located inside the hut before finally reaching a particle filter and a cartridge. The impactor surface in the PM<sub>10</sub> head is coated with silicone grease, to avoid the bounce-off of larger particles. The grease is replaced four times a year during maintenance visits. Weekly air samples of about 5000 m<sup>3</sup> have been collected operating at a flow rate of 0.5 m<sup>3</sup> min<sup>-1</sup>. A 15 cm d quartz fiber filter has been used for particle collection, and a polyurethane foam/XAD-2/polyurethane foam cartridge was used for gas phase collection. This type of cartridge was used instead of polyurethane foam alone, as previous studies have shown that the more volatile POPs as e.g. HCB and  $\alpha$ -HCH have a poor sampling efficiency due to breakthrough (Bossi et al., 2008). The polyurethane foam and XAD-2 were cleaned before use with Soxhlet extraction for 8 h using dichloromethane as the solvent. Quartz filters were baked at 450 °C for 24 h. After shipping and before analysis, cartridges and filters were kept at –20 °C. The filter and the PUF sandwich from the same sample were combined for the chemical analyses, as the temperature in the hut (+15 °C) could be up to 65 °C higher than ambient temperature and thus disturb the equilibrium between gas phase and particle bound phase. Sampling dates and average temperatures during sampling are summarized in Tables S14 and S15.

### 2.2. Extraction and analysis of OCPs and PBDEs in air samples

Before extraction, each sample was spiked with a mixture of <sup>13</sup>C-isotope labeled standards of OCs and PBDEs (Cambridge Isotope Laboratories, Tewksbury, MA, USA). The samples were then Soxhlet extracted with n-hexane/acetone (4:1, v/v), and cleaned on silica columns. The extract was evaporated until nearly dryness, and reconstituted in isoctane with <sup>13</sup>C<sub>6</sub>-PCB-53 (Cambridge Isotope Laboratories) added as a recovery standard. Identification and quantification of the target compounds were performed with Gas Chromatography – High Resolution Mass Spectrometry (GC-HRMS) (DFS, Thermo Scientific, Bremen, Germany). The HRMS was operated at a resolution of 10,000 in electron impact ionization mode (EI) at 45 eV. Two *m/z* were monitored for each compound. The criteria for identification were based on the retention time of the analyte compared to that of a certified standard ( $\pm 20\%$ ) and the isotope ratio of the two monitored *m/z* ( $\pm 20\%$  of the theoretical value). The list of the analyzed compounds, the recovery spikes and the monitored *m/z* are summarized in Tables S11 and S12. The details of the analytical method are available in Supplementary Information.

### 2.3. Extraction and analysis of neutral PFAS in air samples

The samples were spiked before extraction with 50 ng each of the following deuterium labeled compounds: 6:2, 8:2 and 10:2

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