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Trends of perfluorochemicals in Greenland ringed seals and polar bears: Indications of shifts to decreasing trends

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HIGHLIGHTS

- Perfluorinated alkylated substances (PFASs) in Greenland polar bears and ringed seals.
- Several PFASs peaked around year 2006.
- The peak occurred later in Greenland compared to similar species from Canadian Arctic and European seal species.

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ABSTRACT

Time-series of perfluorinated alkylated substances (PFASs) in East Greenland polar bears and East and West Greenland ringed seals were updated in order to deduce whether a response to the major reduction in perfluoroalkyl production in the early 2000s had occurred. Previous studies had documented an exponential increase of perfluorooctane sulphonate (PFOS) in liver tissue from both species. In the present study, PFOS was still the far most dominant compound constituting 92% (West Greenland ringed seals), 88% (East Greenland ringed seals) and 85% (East Greenland polar bears). The PFOS concentrations increased up to 2006 with doubling times of approximately 6 years for the ringed seal populations and 14 years in case of polar bears. Since then a rapid decrease has occurred with clearing half-lives of approximately 1, 2 and 4 years, respectively. In polar bears perfluorohexane sulphonate (PFHxS) and perfluorooctane sulphonamide (PFOSA) also showed decreasing trends in recent years as do perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnA). For the West Greenland ringed seal population perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), PFDA and PFUnA peaked in the mid 2000s, whereas PFNA, PFDA and PFUnA in the East Greenland population have been stable or increasing in recent years. The peak of PFASs in Greenland ringed seals and polar bears occurred at a later time than in Canadian seals and polar bears and considerably later than observed in seal species from more southern latitudes. We suggest that this could be explained by the distance to emission hot-spots and differences in long-range transport to the Arctic.

1. Introduction

Perfluorinated alkylated substances (PFASs) are used as surfactants or raw materials in surfactant production and can be formed in the environment from polyfluorinated precursors (Buck et al., 2011). They are commonly divided into two main groups: perfluorinated carboxylic acids (PFCAs) and perfluorinated sulphonic acids (PFSAs). Once emitted to the environment, they are resistant to hydrolysis, photolysis, biodegradation, or metabolism because of the energy of the carbon–fluorine bond (Banks et al., 1994). Therefore PFASs are very persistent in the environment and they are transported world-wide including transport to the Arctic region (Butt et al., 2010). The pathways of PFASs to the Arctic have been subject of great scientific interest and two main transport ways have been proposed: One pathway is that of airborne precursors, such as fluorotelomer alcohols (FTOHs), fluorinated sulphonamides (FOSAs), and sulphonamido ethanols (FOSEs) followed by atmospheric oxidative transformations to PFSAs and PFCAs and subsequent wet and dry deposition (Ellis et al., 2004; Schenker et al., 2008). Young and Mabury (2010) recently reviewed the atmospheric formation of perfluorinated acids. The other pathway is as direct long-range oceanic transport (Schenker et al., 2008). The relative contribution of each pathway to PFAS levels in the Arctic is not fully understood (Butt et al., 2010). In biota PFCAs and PFSAs bind to blood proteins and therefore bioaccumulate mainly in liver, kidneys and bile secretions in contrast to the lipophilic legacy persistent organic pollutants (POPs) (Jones et al., 2003).

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Perfluorooctane sulphonate (PFOS) is usually found in much higher concentrations compared to other fluorinated compounds in Arctic wildlife (Butt et al., 2010).

The largest producer of perfluorooctane sulphonyl fluoride (PFOSF), the 3M US company, announced to phaseout its PFOSF-based chemicals including PFOS in 2000 (3M, 2000). PFOS was banned in the EU in June 2008, and in 2009 PFOSF and PFOS were included in the Stockholm Convention on POPs. However, the production of PFOSF in China has increased by roughly a factor of 10 since the 3M product phase out and it is the only country documented to currently produce PFOS but no emission inventory is available (Lim et al., 2011). These changes in production pattern likely influence global emission patterns and may be reflected in the accumulation in Arctic biota.

Kannan et al. (2001) and Giesy and Kannan (2001) were among the first to describe PFOS in pinniped species and polar bears from the Arctic (Alaska and Norway). During the 2000s several reports were published on PFASs in ringed seals and polar bears in the Arctic (e.g. ringed seal: Martin et al., 2004; Bossi et al., 2005a; polar bears: Kannan et al., 2005; Bossi et al., 2005b; Smithwick et al., 2005; Butt et al., 2007, 2008). The first temporal trend studies of PFASs in liver tissue of ringed seals in the Arctic and polar bears were published in mid-2000s, generally providing evidence of increasing concentrations: Bossi et al. (2005a) reported on exponential increases of PFOS and other PFAS concentrations in ringed seals from the western and eastern coast of Greenland covering a period from the 1980s up to 2003. An exponential increase of PFOS was also reported by Smithwick et al. (2006) in polar bears from several locations in the North American Arctic covering a period from 1972 to 2002. Similarly Dietz et al. (2008) reported on exponentially increasing trends of several PFASs in polar bears from East Greenland. However, some decreases have been shown in the Canadian Arctic as well: Temporal trends of PFASs in two populations of ringed seals in the Canadian Arctic covering a period up to 2005 showed increasing trends of C_9–C_{15} PFCAs during the whole period, while PFOS and PFOSA showed maximum concentrations in 1998 and 2000, respectively, and a statistically significant decrease to 2005 (Butt et al., 2007). Also in Northern sea otters (*Enhydra lutris kenyoni*) from Alaska a decrease in concentration of PFOS was found in the period from 2001 to 2007 (Hart et al., 2009). These inconsistent temporal trends of PFOS in Arctic marine mammals were highlighted in two recent reviews (Butt et al., 2010; Sturm and Ahrens, 2010). From more southern latitudes decreasing trends in recent years were reported for several species, for example in harbour seals (*Phoca vitulina*) from the German Bight (Ahrens et al., 2009). In grey seals (*Halichoerus grypus*) from the Baltic Sea statistically decreasing trends or a leveling off with maximum levels in the late 1990s were found for several PFASs (Kratzer et al., 2011).

The aim of this study was to update the Greenlandic PFASs time-series of polar bears from East Greenland and ringed seals from West Greenland and East Greenland in order to deduce changes in recent years as potential responses to changes in the global production pattern and to identify when these potential shifts occurred.

2. Material and methods

2.1. Sample collection and age determination

Ringed seal samples were collected from Ittoqqortoormiit (Scoresby Sound) (70°28′ N 21°95′E) in Central East Greenland during the period 1984–2010 and from Qeqertarsuaq (68°59′ N 53°18′ E) in Central West Greenland from 1982 to 2010. Polar bear samples were collected from Ittoqqortoormiit in the period from 1984 to 2011. The sampling was done in cooperation with local Inuit subsistence hunters. Samples were transported and stored at −20 °C until chemical analysis. In the laboratory, liver samples were lightly thawed before the chemical analysis was performed. The individual age estimation of the ringed seals and bears was done by counting the cementum Growth Layer Groups (GLG) of the canine or lower right incisor (I_3), respectively, after decalcification, thin sectioning (14 μm) and staining with Toluidine Blue as described by Hensel and Sorensen (1980) and Dietz et al. (1991). Smithwick et al. (2005) documented that the ΣPFAS in polar bear increased significantly with age which may also be the case for ringed seals. Hence, we have chosen individuals of ringed seals and polar bears below six years in this study in order to minimize age influence on our temporal trends.

2.2. Extraction and analysis

Liver samples were analysed for concentrations of PFOS, PFOSA, perfluorohexane sulphonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluroundecanoic acid (PFUnA). The extraction method was based on ion pairing as described by Bossi et al. (2005a). $^{13}C_2$-PFDA and $^{13}C_4$-PFOS were used as surrogate standards. Instrumental analysis was performed by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS-MS) with electrospray ionization (ESI). The extracts (20 μL injection volume) were chromatographed on a C18 Betasil column (2.1 × 50 mm, Thermo Hypesil-Keystone, Bellafonte, PA, USA) using an Agilent 1100 Series HPLC (Agilent Technologies, Palo Alto, CA, USA). The HPLC was interfaced to a triple quadrupole API 2000 (Sciex, Concorde, Ontario, Canada) equipped with a TurboIon Spray source operating in negative ion mode. Instrument set-up, quality assurance and calibration procedures as well as the standards and reagents used are described in detail by Bossi et al. (2005a).

2.3. Quality assurance

The samples were extracted and analysed in batches together with a procedural blank. The target compounds were not detected in any of the blank samples. The detection limit of the analytical method (MDL) was defined as those concentrations of the analytes needed to produce a signal-to-noise ratio (S/N) of 3:1. The MDLs for the entire time-series were 0.2 (PFOS), 0.5 (PFOSA), 0.8 (PFHxS), 1.2 (PFOA), 1.4 (PFNA), 0.8 (PFDA) and 0.7 (PFUnA) ng g^{-1} ww. Recoveries were above 90% for the target analytes (Bossi et al., 2005a). Samples and quantification standards are spiked with ^{13}C-labelled compounds before extraction and the target analytes are quantified by linear standard regression using the ratio analyte/labelled compound. Concentrations of the analytes in samples have not been corrected for recovery as calibration standards followed the same extraction procedure as samples. For each batch a sample was randomly selected and extracted in triplicate and the repeatability of the analytical method was evaluated based on 8 repetitions of triplicates (Bossi et al., 2005a).

2.4. Data treatment

Estimation of annual mean and standard deviation for those compounds with less than 80% of the values below MDL (left-censored data) was done by Regression on Order Statistics (ROS) using the library NADA of the statistical R packages (R Development Core Team (2012); Helsel 2005). No estimation of annual mean and standard deviation was done in case of more than 80% of the values below MDL. Pearson's correlation was applied to tests of correlations among PFAS concentrations. Linear mixed effect (LME) models were applied to test differences in PFAS concentrations