Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands

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Perfluorinated acids were detected in livers of fish, birds and marine mammals from Greenland and the Faroe Islands.

Abstract

Extensive screening analyses of perfluorooctane sulfonate (PFOS) and related perfluorinated compounds in biota samples from all over the world have identified PFOS as a global pollutant and have shown its bioaccumulation into higher trophic levels in the food chain. Perfluorinated compounds have been found in remote areas as the Arctic. In this study a preliminary screening of PFOS and related compounds has been performed in liver samples of fish, birds and marine mammals from Greenland and the Faroe Islands. PFOS was the predominant fluorochemical in the biota analyzed, followed by perfluorooctane sulfonamide (PFOSA). PFOS was found at concentrations above LOQ (10 ng/g wet weight) in 13 out of 16 samples from Greenland and in all samples from the Faroe Islands. The results from Greenland showed a biomagnification of PFOS along the marine food chain (shorthorn sculpin < ringed seal < polar bear). The greatest concentration of PFOS was found in liver of polar bear from east Greenland (mean: 1285 ng/g wet weight, n = 2). The geographical distribution of perfluorinated compounds in Greenland was similar to that of persistent organohalogenated compounds (OHCs), with the highest concentrations in east Greenland, indicating a similar geographical distribution to that of OHCs, with higher concentrations in east Greenland than in west Greenland.

Keywords: PFOS; Perfluorinated compounds; Marine environment; Greenland; The Faroe Islands

1. Introduction

Perfluorooctanesulfonate (PFOS) is the stable end product of the degradation of various sulfonated fluorochemicals. Sulfonyl-based fluorinated compounds have been produced and used for over 40 years as surfactants and polymers in textiles, upholstery, carpeting and in particular fire-fighting foams. In 2000, the production of sulfonyl-based fluorochemicals was estimated to be 2.9 million kg (Kannan et al., 2002a). Because of the high-energy carbon-fluorine bond, PFOS and related fluorochemicals are stable in the environment and resist hydrolysis, photolysis and biodegradation (Kissa, 2001). They are nonvolatile, have high molecular weights and can repel both water and oils (Kissan et al., 2001b). A major manufacturer of these compounds announced a phase-out of their production from December 2000, due to concerns about their environmental persistence and their potential biological effects (Taniyasu et al., 2003). The toxicity of perfluorinated...
compounds has not been well characterized, but recent studies have shown a potential effect on metabolism (peroxisome proliferators) and intercellular communication (Hu et al., 2002; Berthiaume and Wallace, 2002). Laboratory tests have also raised speculation about the hepatic toxicity of PFOS (Hoff et al., 2003).

In 2001 it was discovered that fluorochemicals such as PFOS were accumulating in biota throughout the world (Kannan et al., 2001a). Although the predominant use of these compounds is in populated and industrial areas, several studies have demonstrated that they are widespread in the environment, even in remote areas as the Arctic (Kannan et al., 2001a; Martin et al., 2004).

Perfluorinated compounds have distribution patterns similar to those of persistent organohalogenated compounds (OHCs) with regard to global biospheric distribution, bioaccumulation and biomagnification. Unlike OHCs, which accumulate in lipid-rich tissues, perfluorinated compounds bind to blood proteins and accumulate in liver and gall bladder (OECD, 2002). The global distribution of PFOS and related fluorochemicals in fish, birds, marine and terrestrial mammals has been demonstrated by several studies from both North America, Europe and Asia (Giesy and Kannan, 2001; Kannan et al., 2001a; Kannan et al., 2002a–c; Hoff et al., 2003; Taniyasu et al., 2003). Concentrations of PFOS in remote areas were generally several times less than those from industrialized and urbanized regions. The Arctic is one of the remote areas primarily exposed to long range transport of organic chemicals of anthropogenic origin. PFOS has been detected in liver and blood of marine mammals from coastal regions of Alaska, Spitzbergen and the Canadian Arctic (Kannan et al., 2001a; Giesy and Kannan, 2001; Martin et al., 2004). Detection of PFOS and related fluorinated compounds in remote areas is somehow unexpected because of the low volatility of these compounds, making their long range atmospheric transport quite improbable (Hurley et al., 2004). Some researchers have hypothesized that the global distribution of PFOS may occur via airborne neutral compounds that yield the free acid upon degradation (Martin et al., 2002).

The present investigation reports the results from a screening of PFOS and other perfluorinated acids in biota (fish, birds and mammals) from Greenland and the Faroe Islands. Samples were selected to provide a first clue to the levels of perfluorinated acids in the upper part of Greenland/Faroes marine ecosystem.

2. Materials and methods

2.1. Sample collection

Hepatic tissue was sampled from the Greenland Inuit subsistence hunt of polar bear (Ursus maritimus), minke whale (Balaenoptera acutorostrata), ringed seal (Phoca hispida), black guillemot (Cepphus grylle) and shorthorn sculpin (Myoxocephalus scorpius), and from pilot whales (Globicephala melas) and fulmars (Fulmarus glacialis) from the Faroe Islands. Specifically, samples of polar bears were collected by the Inuit hunters between 1999 and 2002 from Ittoqqortoormiit (70°30’N/22°W) in central east Greenland (Fig. 1). Samples of minke whale were obtained in 1998 from central west Greenland (between 60° and 70°N) and east Greenland (65°38’N/37°45’W) during licensed whaling operations. Ringed seal samples were collected in 2002 at Ittoqqortoormiit in east Greenland and Qeqertarsuag (68°59’N/53°18’W) in central west Greenland and in 1998 at Avanersuaq (77°29’N/66°75’W) in northwest Greenland. Seals from Ittoqqortoormiit and Qeqertarsuag were all males, while the seals from Avanersuaq were all females. Samples of black guillemot and shorthorn sculpin were obtained from Ittoqqortoormiit and Qeqertarsuag between 2000 and 2001. All samples were kept at outdoor temperature (−5 to −20 °C) until frozen storage (−20 °C). Five individual samples were pooled before the chemical analyses. The pooling of individuals was done as homogeneously as possible with regard to age and sex in order to obtain representative samples from the respective sampling locations.
If possible, the same age group and sex was chosen for the different sampling locations to be able to evaluate possible geographical differences.

Samples of long-finned pilot whale liver were taken from 28 individuals during a traditional hunt event in Miðvágur, the Faroe Islands (Fig. 2) on July 2001. Due to the limited number of adult males in this hunt, however, the samples were fortified with adult male samples taken in the hunt in Bøur a few days after the Miðvágur hunt. Samples were taken within approximately 4 h after death from altogether 11 juveniles, 16 adult females and 3 adult males. Samples were kept frozen (−20 °C) from a few hours after the sampling until the further sample preparation. Fulmars were taken during two different sampling events on the island Nólsoy and at Viðareiði (Fig. 2). The birds were frozen shortly after the hunt, and kept frozen (−20 °C) until dissection. The pooled samples were prepared by cutting equal masses of liver from each individual belonging to the pools of either females or males. The samples were homogenized prior to analysis.

2.2. Analysis

The following compounds were analyzed: perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (PFOSA), perfluoroctanoic acid (PFOA), and perfluorohexanesulfonate (PFHxS). Teflon or glass containers were avoided through the whole extraction procedure. Liver tissue was homogenized and 5 g were weighed. Deionized water (25 ml) was added and the sample was thoroughly mixed for 15 s with a vortex mixer. The homogenate (1 ml) was transferred to a polypropylene centrifuge tube and 1 ml of a 0.5 M tetrabutylammonium hydrogen sulphate (TBA) solution (pH 10), 2 ml of sodium carbonate/sodium bicarbonate buffer and 5 ml methyl-tert-butyl-ether (MTBE) were added to each sample. The samples were shaken for 20 min and then centrifuged for 25 min at 3500 rpm. The MTBE layer (4 ml) was transferred to a polypropylene tube and the solvent was evaporated to dryness. The extract was reconstituted in 500 μl methanol and vortex mixed for 15 s.

Sample extracts were analyzed by liquid chromatography- tandem mass spectrometry (LC-MS-MS) with electrospray ionization (ESI). The methanol extracts (10 μl injection volume) were chromatographed on a C8 Luna 5 μm, 150×2.00 mm analytical column (Phenomenex, Torrance, CA, USA) using a PE Series 200 HPLC (Perkin Elmer, Norwalk, CT, USA). The mobile phase A was 2 mM ammonium acetate and the mobile phase B was methanol. The gradient was operated at a flow rate of 0.3 ml/min starting from 45% A to 95% B in 4.5 min and then held for 7.5 min. The total run time was 16 min with an equilibration time of 10 min between injections. 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. The source temperature was maintained at 375 °C and the spray voltage at −4500 V. The analyses were performed with a multiple reaction monitoring (MRM) method that monitored one to two mass transitions (parent ion→product ion) for each analyte. The values of the voltages applied to the sampling cone, focusing lenses, collision cell and quadrupoles were optimized in MRM mode by direct infusion of a solution containing the analytes. The precursors and product ions for each analyte, together with the applied collision energy are summarized in Table 1. The most abundant ion was used for quantitation purposes and the second abundant ion, when present with sufficient intensity, was used for confirmation purposes.

Blank samples were prepared using bovine liver previously checked for the target analytes. Blank samples did not contain any of the target analytes at concentrations above the detection limit. Quantification of the target analytes in samples was performed using a five point external calibration curve consisting of five
blank samples spiked with the analytes in the concentration range 10–1000 ng/g wet weight and extracted following the same procedure as samples. QC samples (100 ng/g wet weight) were prepared in duplicate and extracted using the same procedure as calibration standards and samples.

The detection limit and the limit of quantification of the analytical method (Table 1) have been determined as three and five times the standard deviation of eight samples spiked at a concentration of 25 ng/g wet weight. Mean recoveries ($n=5$) of PFOS, PFOSA, PFOA and PFHxS in spiked liver matrix (concentration: 50 ng/g, wet weight) were 91, 58, 105, and 77%, respectively. Concentrations of the analytes in samples have not been corrected for recovery as calibration standards followed the same extraction procedure as samples.

### 3. Results and discussion

Samples from Greenland consisted of five pooled individuals and two samples for each sampling location were analyzed for each species (Table 2). Samples from the Faroe Islands consisted of three or more pooled individuals (Table 3). Since the aim of this study was to perform a preliminary screening of perfluorochemicals in Greenland and the Faroe Islands, pooled samples were chosen. The variations in concentrations of perfluorochemicals due to age and gender were not considered in the present study. However, several authors (Giesy and Kannan, 2002; Kannan et al., 2001a,b, 2002a–c) have concluded that the variations in concentrations of perfluorochemicals found between sexes and among different age groups are not statistically significant.

#### 3.1. Samples from Greenland

The concentrations of perfluorinated acids measured in animals from Greenland are summarized in Table 2. In agreement with the published work on monitoring of perfluorinated acids in biota, PFOS was the predominant fluorochemical in the biota analyzed, followed by PFOSA. PFOS was found at concentrations above LOQ (10 ng/g wet weight) in 13 out of 16 samples. The greatest concentration of PFOS was found in liver of polar bear from east Greenland (mean of two samples:

<table>
<thead>
<tr>
<th>Species</th>
<th>Pooled individuals ($n$)</th>
<th>Sampling year</th>
<th>Location</th>
<th>Sex</th>
<th>Age/length range</th>
<th>PFOS</th>
<th>PFOSA</th>
<th>PFOA</th>
<th>PFHxS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar bear (Ursus maritimus)</strong></td>
<td>5</td>
<td>1999–2001</td>
<td>Ittoqqortoormiit</td>
<td>M + F</td>
<td>3–15 years</td>
<td>1245</td>
<td>nd</td>
<td>&lt;12</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2000–2002</td>
<td>Ittoqqortoormiit</td>
<td>M + F</td>
<td>5.5–28 years</td>
<td>1325</td>
<td>5</td>
<td>&lt;12</td>
<td>&lt;7</td>
</tr>
<tr>
<td><strong>Minke whale (Balaenoptera acutorostrata)</strong></td>
<td>5</td>
<td>1998</td>
<td>4 from central west Greenland; 1 from central east Greenland</td>
<td>M</td>
<td>Adult</td>
<td>&lt;10</td>
<td>29</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Ringed seal (Phoca hispida)</strong></td>
<td>5</td>
<td>2002</td>
<td>Ittoqqortoormiit</td>
<td>M</td>
<td>4.5–5.5 years</td>
<td>67</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2002</td>
<td>Ittoqqortoormiit</td>
<td>M</td>
<td>3.5–7.5 years</td>
<td>52</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2002</td>
<td>Qeqertarsuaq</td>
<td>M</td>
<td>0.5–1.5 years</td>
<td>&lt;10</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2002</td>
<td>Qeqertarsuaq</td>
<td>M</td>
<td>0.5–3.5 years</td>
<td>10</td>
<td>&lt;4</td>
<td>&lt;12</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1998</td>
<td>Avanersuaq</td>
<td>F</td>
<td>6–12 years</td>
<td>27</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1998</td>
<td>Avanersuaq</td>
<td>F</td>
<td>10–29 years</td>
<td>27</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Black guillemot (Cepphus grylle)</strong></td>
<td>5</td>
<td>2000</td>
<td>Qeqertarsuq</td>
<td>F</td>
<td>Adult</td>
<td>13</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2000</td>
<td>Qeqertarsuq</td>
<td>F</td>
<td>Adult</td>
<td>14</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2000</td>
<td>Ittoqqortoormiit</td>
<td>F</td>
<td>Adult</td>
<td>13</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Shorthorn sculpin (Myoxocephalus scorpius)</strong></td>
<td>5</td>
<td>2002</td>
<td>Qeqertarsuq</td>
<td>F</td>
<td>30–36 cm</td>
<td>&lt;4</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd, not detected.
1285 ng/g wet weight). These levels are about four times higher than the mean level (350 ± 33 ng/g) reported in Alaskan polar bear liver by Kannan et al. (2001a), and lower than the levels found in bears from the southern Hudson Bay reported by Martin et al. (2004) (3100 ± 878 ng/g wet weight). The Hudson Bay subpopulation is at significantly lower latitude compared to the Greenland subpopulation, and the increased levels in the former may be due to proximity to regional sources.

This overall trend of PFOS levels being higher in east Greenland than west Greenland (Fig. 3) is similar to the geographic trend for polychlorinated biphenyls (PCBs) and other organohalogen compounds in polar bears (Norstrom et al., 1998) and other marine organisms (de March et al., 1998; de Wit et al., 2004). In addition, the east Greenland levels are somewhat lower than found in a recent study on east Greenland polar bears (Smithwick, personal communication), where an average concentration of 2470 ± 246 ng/g (wet weight) was obtained from as many as 29 individuals (12 males and 17 females) with ages ranging from 2 to 20 years in both sexes.

The PFOS concentrations in polar bears from east Greenland are comparable to those found in liver of fish eating mammals (mink and otter) from industrialized and urbanized regions (Kannan et al., 2002b).

The concentration of PFOS in hepatic tissue from ringed seals (52–67 ng/g wet weight) from east Greenland was higher than the concentration measured in ringed seals (< LOQ, 10.1 ng/g wet weight) from

<table>
<thead>
<tr>
<th>Species</th>
<th>Pooled individuals (n)</th>
<th>Sampling year</th>
<th>Location</th>
<th>Age/sex</th>
<th>Average length/weight (min–max)</th>
<th>PFOS</th>
<th>PFOSA</th>
<th>PFOA</th>
<th>PFHxS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long finned pilot whale (<em>Globicephala melas</em>)</td>
<td>11</td>
<td>2001</td>
<td>Miðvágur</td>
<td>Juveniles/M+F</td>
<td>298 cm (186–445)</td>
<td>28</td>
<td>43</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Fulmar (<em>Fulmarus glacialis</em>)</td>
<td>16</td>
<td>2001</td>
<td>Miðvágur</td>
<td>Adult/F</td>
<td>453 cm (400–498)</td>
<td>39</td>
<td>62</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2001</td>
<td>Bøur</td>
<td>Adult/M</td>
<td>561 cm (540–578)</td>
<td>65</td>
<td>47</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1998–1999</td>
<td>Nólsoy and Viðareiði</td>
<td>F</td>
<td>676 g (471–754)</td>
<td>29</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1998–1999</td>
<td>Nólsoy and Viðareiði</td>
<td>M</td>
<td>828 g (731–948)</td>
<td>24</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd, not detected.

Table 3
Concentrations of perfluorinated surfactants in liver (ng/g, wet weight) of birds and mammals from Faroe Islands

Fig. 3. Concentrations (analysis of two samples) of PFOS in biota from Greenland and the Faroe Islands.
Qeqertarsuq (central west Greenland) and still higher than ringed seals in Avanersuaq (northwest Greenland), where both samples had a concentration of 27 ng/g wet weight. The higher concentrations on the east coast compared to the west coast of Greenland have also been documented for other organohalogens (e.g. PCBs and DDTs,) in ringed seals (Cleemann et al., 2000a; Riget et al., 2004). The east Greenland concentrations were about 10 times lower than the mean concentration found in liver of ringed seals (460 ng/g wet weight) from the Baltic Sea (Kannan et al., 2002a).

The average concentrations of PFOS in bird liver from black guillemot were similar when comparing east and west Greenland. In case of other organohalogens (PCBs, DDTs, chlordanes, PBDEs) Vorkamp et al. (2004) found somewhat higher concentrations in black guillemot liver and egg samples from east Greenland than from west Greenland.

The concentration of PFOS in liver of shorthorn sculpin was higher in samples from east Greenland compared to west Greenland. A similar spatial trend for organohalogens (DDTs, PCBs) in sculpins was reported earlier (Cleemann et al., 2000b; Riget et al., 2004) and explained by the long-range transport from western Europe and Asia. A similar tendency seems to apply for the distribution of PFOS. However, this tendency needs to be confirmed by a more detailed study including the analysis of individual samples, where the significance of age and gender can be investigated.

The results from Greenland showed increasing concentrations of PFOS: shorthorn sculpin <ringed seal <polar bear, indicating biomagnification of PFOS along the marine food chain. The concentrations of the other fluorochemicals were below LOQ or not detected for all samples, with the exception of a shorthorn sculpin sample (9 ng/g wet weight PFOSA).

3.2. Samples from the Faroe Islands

The samples from the Faroe Islands included only two species, pilot wale and fulmar (Table 3). The concentration of PFOS in juvenile pilot whale (28 ng/g wet weight) was similar to the concentration measured in adult females (39 ng/g wet weight), but lower than the concentration measured in adult males (65 ng/g wet weight). However, Kannan et al. (2001a) did not find a positive correlation between liver concentrations of PFOS and age, presumably due to accumulation patterns different from those observed for other organochlorine compounds (e.g. PCBs and DDTs). Due to the surfactant-like properties, perfluorinated acids undergo entero-hepatic circulation (Giesy and Kannan, 2002). Similarly to butyltin, the compounds bind to proteins and are therefore retained in blood and liver rather than accumulated in lipid reservoirs.

PFOSA was found in all samples of pilot whale at concentrations similar to or higher than those of PFOS. Similar concentrations were found in minke whale samples from west Greenland, where PFOS was detected but not quantified, and the concentration of PFOSA was 29 ng/g wet weight. These data are in accordance with Kannan et al. (2002a,b), who found concentrations of PFOSA 1—5-fold greater than those of PFOS in liver of cetaceans from Mediterranean Sea. In general, PFOSA was distributed sporadically in certain species and locations and was usually found in 10—15% of the samples analyzed. Kannan et al. (2002a) also pointed out that PFOSA was an intermediate in the production of several perfluorinated compounds and also a metabolic product in mammals of n-ethyl perfluorooctanesulfonamide (sulfluramid), an insecticide used for the control of cockroaches, termites and ants (Vitayavirasuk and Bowen, 1999). The presence of PFOSA at high concentrations in certain samples and locations in the present study may indicate different sources of exposure of PFOS and PFOSA (Kannan et al., 2002a).

4. Conclusions

The results of this preliminary investigation indicate that perfluorochemicals, particularly PFOS, are important contaminants in marine environment of Greenland and the Faroe Islands. The concentrations of PFOS followed a biomagnification order along the marine food chain, with the highest concentrations observed in liver of polar bears. With the exception of black guillemot, the geographic distribution of PFOS in Greenland was similar to that of persistent halogenated compounds with higher concentrations in east Greenland. The exposure routes through which perfluorinated compounds can reach areas far from their sources are still to be explained. More data are needed about the spatial distribution of these compounds in the Arctic regions in order to trace their sources. Moreover, the hypothesis that more volatile compounds may be the atmospheric precursors of perfluorinated acids has to be verified by monitoring these precursors in remote areas.

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sample collection in east Greenland, where Jonas Bronlund organized the polar bear sampling. In addition we would like to thank Eric W. Born (Greenland Institute of Natural Resources) for providing minke whale samples. Gert Asmund collected the sculpins in west Greenland and Per Møller collected the black guillemot from west Greenland in 2001. Birgit Groth and Inga Jensen are acknowledged for technical assistance in sample preparation and the chemical analyses.

References


