UNCOMMON PFC-PROFILE IN ARTIC ICE SAMPLES FROM RUSSIA

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Introduction

Per- and polyfluorinated compounds (PFCs) have recently emerged as important pollutants. During the last decade, they have gained attention due to their toxicity and global distribution. PFCs compile a broad group of chemicals with a wide range of uses in consumer and industrial products[1,2]. PFCs are found in the environment in populated and industrialised areas[3-5]. However, similar to other persistent organic pollutants, but via different processes due to their different properties, long range transport processes may lead to pollution of areas with little to none human activities. The presence of PFCs in remote areas, like Artic environment has been demonstrated from North of Canada to Norway[6,7]. However, no information is available yet on the environmental presence of PFCs in the Polar Region of Russia. The Polar Regions are very restricted areas and difficult to access. To better understand the environmental processes that govern their distribution and fate, especially in these fragile environments, research is needed.

The objective of our work is to study the presence of PFCs in the ice from the North Russian Federation within the North Pole Region in order to shed some light on inputs of PFCs, potentially from long range transportation.

Material and Methods

Water from ice cores were sampled at Baydaratskaya Bay (Russian Federation), during May 2007. Ice-core slices (of approximately 500 mL of water) from different depths (varying from surface to 300 cm) were allowed to melt and placed in plastic bottles and kept at temperature below 4ºC until their analysis.

The target compounds of this study are displayed in table 1. The analytical methodology for the determination of the PFCs concentration in the samples consisted on a SPE (solid phase extraction) step with a Weak Anion Exchange (WAX) followed by their detection with a triple quadrupole LC/MS system. Samples, consisting of 500 mL of unfiltered water, were passed through an Oasis WAX cartridge previously activated with methanol and 0.1% NH_4OH in methanol. The cartridge was sequentially eluted with a sodium acetate buffer, methanol and 0.1% NH4OH in methanol[8]. The first elution was discarded, the PFCs were collected in the other fractions, which were concentrated to a volume of 0.5 mL and diluted 1:1 with ultra-pure water before their injection on an Agilent 1200 HPLC coupled with an Agilent 6410 ESI-MS/MS system. The PFCs were chromatographically separated on a Symmetry C18 (50 mm x 2.1 mm i.d., 5 µm particle size, kept at 20°C), which was preceded by a Symmetry C18 precolumn (20 mm x 3.9 mm i.d., 5 µm particle size). The eluents consisted of 2mM ammonium acetate in water and methanol. The flow was 300 $\mu L \cdot min^{-1}$. The injection volume was 20 µL. The capillary voltage was set at 1000 V, the nebuliser at 25 PSI, the gas flow at 6 $L \cdot min^{-1}$ and the gas temperature was set at 325°C. The samples were quantified using the MRMs (multiple reaction monitoring) detailed in table 1.

Quality Assurance. A selection of mass labelled internal standards ($^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_4$-PFOS, $^{13}C_2$-PFDcA, $^{13}C_2$-PFUnA, $^{13}C_2$-PFDoA) was used to validate the extraction method, and was added to the sample 8 hrs before extraction at 20 $pg \cdot uL^{-1}$. A procedural blank was run in parallel to the samples. The blank contained no PFC except for a small amount of PFUnA. The average recovery of the mass labelled internal standards was 72%.

Table 1. Target compounds analyzed and MS/MS parameters used.

Acronym	Name	MRM transition (cone voltage)
PFBA	perfluorobutanoic acid	213→169 (60)
PFHxA	perfluorohexanoic acid	313→269 (80)
PFHpA	perfluoroheptanoic acid	363→319 (80)
PFOA	perfluorooctanoic acid	413→469 (80)
PFNA	perfluorononanoic acid	463→419 (100)
PFDA	perfluorodecanoic acid	513→569 (100)
PFUnA	perfluoroundecanoic acid	563→519 (100)
PFDoA	perfluorododecanoic acid	613→669 (100)
PFBS	perfluorobutane sulfonate	299→80 (150)
PFHxS	perfluorohexane sulfonate	399→80 (150)
PFOS	perfluorooctane sulfonate	499→80 (200)
PFOSA	perfluorinated sulfonamide	498→78 (200)

Results and Discussion

PFCs were found in all the ice samples, where perfluorocarboxylic acids were present in higher concentrations than the perfluorosulfonates. Unexpectedly, the most abundant compound was PFOSA, showing the highest levels in the majority of the samples, followed by PFOA. Average values for each PFC are displayed in table 2. PFOSA, PFOA, PFNA and PFDA were found in all the samples, meanwhile PFHxS, was not found in any sample. Concentrations are in the $pg \cdot L^{-1}$ range, similar to those found in ice caps from the Canadian Artic[9]. PFOA and PFDA concentrations in the Russian Artic are similar to the higher concentrations found in the Canada Artic, meanwhile PFNA, PFUnA and PFOS concentration in ice from the Russian Artic are within the medium values of the Canadian ones.

Table 2. Average concentration and standard deviation (in brackets) of PFCs in Russian Arctic ice ($pg \cdot L^{-1}$).

	Average (± S.D.)
PFBA	24.6 (±62.7)
PFHxA	25.5 (±35.7)
PFHpA	36.4 (±67.0)
PFOA	130.7 (±77.2)
PFNA	37.4 (±39.2)
PFDA	22.4 (±13.5)
PFUnA	13.3 (±3.4)
PFDoA	3.6 (±5.0)
PFBS	13.2 (-)
PFHxS	<LOD
PFOS	5.3 (-)
PFOSA	824.1 (±592.1)

There could be several reasons causing the contamination of PFCs, including long range transport by water current or by air, as well as local human activity. The latter is not likely, as in this remote area there is neither population, nor industrial activity. Long range transport by ocean transportation also seems unlikely to bring PFCs to this area. The currents are weak and the process would take decades. Ocean transportation would be expected from a correlation between PFOS and perfluorocarboxylic acids. Since PFOS was only found in 1 sample, and in a small amount, no correlation could be done in this study. We believe that PFCs fluxes to Baydaratskaya Bay happen via atmosphere. Strong winds, predominantly from the South, could bring precursors from the North part of the Ural Mountains, were industries are located, to the Bay. This process takes days to weeks and in the meantime, atmospheric transformation of precursors to the compounds, detected in our samples, could take place.

Concerning the perfluorinated carboxylic acids (PFCAs), fluorotelomer alcohols (FTOHs) are the likely precursors. Studies showed that FTOHs, volatile compounds with low water solubility, have atmospheric lifetimes long enough to be transported to remote areas. FTOHs are susceptible to trophospheric oxidation producing PFCAs[10-13]. These PFCAs, relatively non-volatile and persistent, can be scavenged by wet or dry deposition[11]. The long-range transport and degradation of FTOHs could explain not only the presence of long-chain PFCAs in the Artic, but also the PFCAs profile observed. The most used fluorotelomer alcohol, the 8:2 FTOH is known to produce PFOA and PFNA[11]. A correlation of PFOA and PFNA concentrations has been observed, suggesting their common precursor, the 8:2 FTOH, and therefore supporting the hypothesis of atmospheric origin of the PFCs in the Russian Artic.

Concerning the perfluorinated sulfonates and sulfonamides, unexpected high PFOSA levels, and a low presence of the perfluorosulfonates were found. High PFOSA levels have been observed in few studies dealing with marine mammals[14, 15], in contrast to the general trend of PFOS predominance. Fluorosulfamidoalcohols (FSAA), are degraded to PFOSA and afterwards to PFOS[14,16]. FSAA are volatile PFCs, and therefore susceptible to long-range transport and atmospheric degradation, as previously described for FTOHs, but with different atmospheric lifetimes and degradation rates. A partial degradation of FSAA to PFOSA, and therefore not to PFOS, could be an explanation for the levels of PFOSA found. Concentrations of PFCs in Artic regions are higher in spring and summer, showing evidence of seasonality[9]. The Russian Artic ice analysed in this work, collected in spring, come from water that was frozen the previous autumn, just after the expected maximum peak of contamination. The period of time, between PFCs transport and deposition in the water and its freezing, could not be enough for the complete degradation of FSAA, which could explain the high presence of PFOSA, but not PFOS in the samples.

The low levels of PFOS, compared to PFOA and other PFCAs, could be explained as a consequence of the reduction in PFOS production and use. As a consequence of PFOS substitution by PFBS in certain uses[17]the higher abundance of PFBS compared to PFOS support this hypothesis. A decrease in PFOS concentration in the Artic have been recently reported in air[6], water[9] and seals[18], suggesting the atmosphere as the main transport route of PFCs to the Artic, and not the ocean as has been previously suggested[19]. Nonetheless further research is needed in order to elucidate the environmental processes, fate and behaviour of PFCs in the Artic Regions. Next step will focus on expanding the study area and including other environmental compartments.

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