

Polyfluoroalkyl compounds in the Canadian Arctic atmosphere

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Environmental context. Perfluoroalkyl compounds are of rising environmental concern because of their ubiquitous distribution in remote regions like the Arctic. The present study quantifies these contaminants in the gas and particle phases of the Canadian Arctic atmosphere. The results demonstrate the important role played by gas–particle partitioning in the transport and fate of perfluoroalkyl compounds in the atmosphere.

Abstract. Polyfluoroalkyl compounds (PFCs) were determined in high-volume air samples during a ship cruise onboard the Canadian Coast Guard Ship *Amundsen* crossing the Labrador Sea, Hudson Bay and the Beaufort Sea of the Canadian Arctic. Five PFC classes (i.e. perfluoroalkyl carboxylates (PFCAs), polyfluoroalkyl sulfonates (PFSA), fluorotelomer alcohols (FTOHs), fluorinated sulfonamides (FOSAs), and sulfonamidoethanols (FOSEs)) were analysed separately in the gas phase collected on PUF/XAD-2 sandwiches and in the particle phase on glass-fibre filters (GFFs). The method performance of sampling, extraction and instrumental analysis were compared between two research groups. The FTOHs were the dominant PFCs in the gas phase (20–138 pg m⁻³), followed by the FOSEs (0.4–23 pg m⁻³) and FOSAs (0.5–4.7 pg m⁻³). The PFCAs could only be quantified in the particle phase with low levels (<0.04–0.18 pg m⁻³). In the particle phase, the dominant PFC class was the FOSEs (0.3–8.6 pg m⁻³). The particle-associated fraction followed the general trend of: FOSEs (~25 %) > FOSAs (~9 %) > FTOHs (~1 %). Significant positive correlation between \sum FOSA concentrations in the gas phase and ambient air temperature indicate that cold Arctic surfaces, such as the sea-ice snowpack and surface seawater could be influencing FOSAs in the atmosphere.

Introduction

In recent years, the fate and transport of polyfluoroalkyl compounds (PFCs) in the atmosphere has been recognised as one of the emerging issues in environmental chemistry. Longer chain PFCs are man-made chemicals and have been produced for over 50 years.^[1] Because of their unique chemical and physical properties, they are widely used as processing additives during fluoropolymer production and as surfactants in consumer applications, including stain repellents in textile, furniture and paper products.^[2] Perfluorooctane sulfonate (PFOS) and longer chain perfluoroalkyl carboxylates (PFCAs) are resistant against typical environmental degradation processes and have been found in humans and wildlife in remote regions such as the Arctic.^[3,4]

Three main hypotheses were proposed for the global transport of PFCs. First, PFCAs and polyfluoroalkyl sulfonates (PFSA) can be transported directly in their ionic form by ocean currents.^[5,6] For instance, model scenarios estimated that the majority of perfluorooctanoate (PFOA) is transported by the ocean current to the Arctic (8–23 t year⁻¹).^[7] Second, PFCAs and PFSA can be transported directly in the gas phase or by an aerosol-mediated pathway in the atmosphere.^[8,9] This is supported by the determination of PFCAs and PFSA in the particle phase in urban and remote atmospheres.^[10,11] Furthermore, it is assumed that PFCs can be released into the gas phase in their neutral form by marine aerosols.^[8,12] A recent study

indicates that the aqueous phase can act as a net source for PFOA to the atmosphere.^[9] Third, neutral, volatile precursors, such as fluorotelomer alcohols (FTOHs), fluorinated sulfonamides, and sulfonamidoethanols (FOSAs and FOSEs), could undergo long-range atmospheric transport and be degraded in remote regions to PFCAs and PFSA.^[13,14] Smog chamber experiments have shown that these volatile precursors can degrade by OH-initiated oxidation pathways to PFCAs and PFSA in the atmosphere.^[13–15] The estimated atmospheric lifetimes of FTOHs (~20 days) are sufficient for long-range transport to remote regions^[15] and their presence in remote regions supports this hypothesis.^[11,16] However, the main transport pathway of PFCs to remote regions has not been conclusively characterised to date.

Based on the production volume, historic emissions were estimated to be 6800–45 250 t for perfluorooctylsulfonate fluoride (POSF) (1972–2002).^[17] The majority of the emissions were estimated to have been released to the aqueous environment (~45 000 t) and only a small amount into the air (~235 t).^[17] The emissions for PFCAs ranged between 3200 and 7300 t (1951–2004), from which the indirect emissions (PFCa impurities or precursors) were estimated to be 1–5 % of the total source emissions.^[11] Overall, most studies indicate that the oceanic transport of directly emitted PFCs is the dominant transport pathway to remote regions.^[7,18] However, the presence of PFCAs and PFSA in precipitation,^[19] in water

and fish from high mountain lakes^[20,21] and in ice caps and snow^[22] demonstrate that the atmospheric transport of PFCAs and PFSA and their precursors is an important transport pathway to remote locations like the Arctic. More measurements of the PFCs in the Arctic region are required to better understand the transport pathway.

In this study, PFC concentrations in the Canadian Arctic atmosphere were measured. Air samples were collected during a ship cruise onboard the Canadian Coast Guard Ship *Amundsen* crossing the Labrador Sea and Hudson Bay in summer 2007 and in the Beaufort Sea in spring and summer 2008. The objectives of this research were: (i) to determine concentrations of five PFC classes (i.e. FTOHs, FOSAs, FOSEs, PFCAs, and PFSA) in the Canadian Arctic atmosphere; (ii) to compare the method performance and results between Environment Canada (EC) and the Lancaster Environment Centre (LEC); (iii) to investigate the partitioning behaviour of PFCs in the gas and particle phase; and (iv) to correlate PFC concentrations and particle-associated fractions with ambient air temperature.

Experimental

Sampling campaign

High volume air samples were collected onboard the CCGS *Amundsen* (~15 m above sea level) while crossing the Labrador Sea and Hudson Bay in summer 2007 and the Beaufort Sea in spring and summer 2008. Airborne PFCs were sampled using glass-fibre filters (GFFs) for the particle phase followed by a polyurethane foam PUF/XAD-2 sandwich for the gas phase. Type A/E GFFs were used at EC (102 mm, >1.0- μ m particle retention, Pall Corporation, USA) and type GF/F from LEC (460 \times 570 mm, >0.7- μ m particle retention, Whatman, UK). The (PUF)/XAD-2 sandwich consisted of 15 g of XAD-2 resin (Supelco) between a PUF plug (76-mm diameter and 60 mm thick, Supelco, USA) divided in half (EC) and 25 g of XAD-2 resin (Supelco) between a PUF plug (76-mm diameter and 75 mm thick, Tisch Environment, OH, USA) divided in half (LEC). Air samples were collected by EC in the Labrador Sea ($n=3$), in the Hudson Bay ($n=6$) and in the Beaufort Sea ($n=11$) with a sampling time of ~24 h collecting an air volume of ~385 m³. Furthermore, air samples were collected by LEC in the Beaufort Sea ($n=7$) with a sampling time of ~48 h and a sample volume of ~945 m³. Air samples were collected during an overlapping period at two sampling locations in the Beaufort Sea by EC (sampling locations 10 and 11) and LEC (sampling locations 24 and 27) (see Fig. A1 in the Accessory publication). Field blanks were collected by placing the GFF and PUF/XAD-2 sandwich in the high volume sampler and then removing them after 1 min. Samples were shipped cold and stored at -4 °C until extraction. Details of the sampling locations, dates, air volume and average ambient air temperature are presented in Table A1 and Fig. A1 in the Accessory publication.

Analysis by EC

The target analytes included 22 PFCs (i.e. C₄–C₁₂, C₁₄ PFCAs, C₄, C₆, C₈, C₁₀ PFSAs, 6:2, 8:2, 10:2 FTOH, perfluorooctane sulfonamide (PFOSA), methyl and ethyl FOSA and methyl and ethyl FOSE) plus 16 mass-labelled internal standards (IS) and *N,N*-dimethylperfluoro-1-octanesulfonamide (*N,N*-Me₂FOSA), ¹³C₈ PFOS and ¹³C₈ PFOA as injection standards (InjS) (for details see Tables A2 and A3 in the Accessory publication).

Prior to extraction the PUF/XAD-2 sandwiches and GFFs were spiked with 25- and 5-ng absolute of an IS mixture

containing mass-labelled IS (see Table A2 in the Accessory publication). PUF/XAD-2 sandwiches were Soxhlet extracted with petroleum ether for ~6 h, followed by a ~16-h extraction with methanol. The petroleum ether and methanol extracts were concentrated by rotary evaporation followed by gentle nitrogen blow down to 0.5 and 1 mL respectively. The methanol extract was further purified using the dispersive clean up with ENVI-Carb (100 mg, 1 mL, 100–400 mesh, Supelco, USA) and glacial acetic acid.^[23] After centrifugation, 0.5 mL was transferred into a polypropylene vial. The GFFs were sonicated twice with dichloromethane and then twice with methanol. The dichloromethane and methanol extracts were concentrated by gentle nitrogen blow down to 0.5 and 1 mL respectively. The methanol extract was further purified with ENVI-Carb as described earlier. Prior to injection, 10 ng of *N,N*-Me₂FOSA was added to the petroleum ether and dichloromethane extract respectively and 4 ng of ¹³C₈ PFOS and ¹³C₈ PFOA were added to the methanol extract as InjS.

Analysis was performed using gas chromatography (Agilent 7890A; Agilent Technologies, Palo Alto, CA) – mass spectrometry (Agilent 5975C; Agilent Technologies, Palo Alto, CA) (GC/MS) in selective ion monitoring (SIM) mode using positive chemical ionisation (PCI) for the FTOHs, FOSAs and FOSEs.^[24] Aliquots of 2 μ L were injected on a DB-WAX column (30 m, 0.25-mm inner diameter, 0.25- μ m film, J&W Scientific, Folsom, USA) for quantification and on a DB5MS for confirmation (30 m, 0.25-mm inner diameter, 0.25- μ m film, Agilent Technologies, Palo Alto, CA). The separation and detection of the PFCAs, PFSAs and PFOSA were performed by liquid chromatography (Agilent 1100; Agilent Technologies, Palo Alto, CA) with a triple quadrupole mass spectrometer interfaced with an electrospray ionisation source in negative-ion mode (LC–(–)ESI–MS/MS; API 4000, Applied Biosystems/MDS SCIEX, Foster City, CA). Aliquots of 25 μ L were injected on a Luna C₈(2) 100A column (50 \times 2 mm², 3- μ m particle size; Phenomenex, Torrance, USA) using a gradient of 200 μ L min⁻¹ methanol and water (both with 10 \times 10⁻³ M aqueous ammonium acetate solution (NH₄OAc)). The IS quantification method was used, which is based on the ratio of the peak-areas of the target analyte to the IS.

Analysis by LEC

The target analytes included seven PFCs (i.e. 6:2, 8:2, 10:2 FTOH, methyl and ethyl FOSA and methyl and ethyl FOSE) plus seven mass-labelled IS and *N,N*-Me₂FOSA and ¹³C-hexachlorobenzene (¹³C-HCB) as InjS (for details see Tables A4 and A5 in the Accessory publication).

Extraction of the PUF/XAD-2 sandwiches was performed by sequential cold column extraction with ethyl acetate. Samples were spiked with 5-ng absolute of an IS mixture containing mass-labelled FTOHs, FOSAs and FOSEs and were extracted by three separate immersions for 30 min in ethyl acetate. The three extracts were combined, concentrated by rotary evaporation to ~1 mL and then cleaned by passing through 2 \times 0.7 cm of Envi-Carb. The extracts were concentrated by gentle nitrogen blow down to 0.5 mL and 12.5 ng of *N,N*-Me₂FOSA and ¹³C-HCB was added as InjS. Finally the extract was reduced to a volume of 0.1 mL prior to injection. The GFF samples were not extracted.

Analysis was performed using gas chromatography (Thermo Trace GC Ultra, Thermo Scientific) – mass spectrometry (Thermo DSQ Quadrupole, Mass Spectrometer) (GC/MS) in

SIM mode using PCI for the FTOHs, FOSAs and FOSEs. Aliquots of 2 μL were injected on a SUPELCOWAX column (60 m, 0.25-mm inner diameter, 0.25- μm film, Supelco, Bellefonte, PA). The IS quantification method was used as described for EC.

Quality control

Method detection limits (MDLs) were calculated from the field blanks (average of blanks + 3 \times standard deviation (σ)). Field blank concentrations ($n=4$) were $<5\%$ of the concentrations measured in the samples for the FTOHs, FOSAs, FOSEs and longer chain PFCAs ($\text{C}_{10}\text{--C}_{14}$) (EC). Because of high field blank values for PFOS and shorter chain PFCAs ($0.1\text{--}0.8\text{ pg m}^{-3}$), these compounds were not quantified in the actual sample (EC). Contamination of the samples can arise from different sources during the sample treatment (i.e. sampling, transport, storage, extraction and instrumental analysis). LEC field blank concentrations ($n=3$) were $<8\%$ of FTOH, FOSA and FOSE concentrations. The MDL ranged from $0.1\text{--}1.1\text{ pg m}^{-3}$ for FTOHs, FOSAs and FOSEs in the gas phase and from $0.01\text{--}0.6\text{ pg m}^{-3}$ for FTOHs, FOSAs, FOSEs and $\text{C}_{10}\text{--C}_{14}$ PFCAs in the particle phase (EC). MDLs for FTOHs, FOSAs and FOSEs ranged from $0.1\text{--}2.1\text{ pg m}^{-3}$ in LEC gas phase samples. Method recovery values, calculated from mass-labelled IS spiked prior to extraction and InjS added before injection, ranged from 38–153 % for FTOHs, FOSAs and FOSEs, and from 27–64 % for the PFCAs and PFSA (EC). Recovery values ranged from 25–350 % for FTOHs, FOSAs and FOSEs (LEC). Low recoveries were found for 6 : 2 FTOH as a result of loss by evaporation (e.g. rotary evaporation or nitrogen blow down) whereas high recoveries were observed for the FOSAs and FOSEs because of signal enhancement during GC/MS determination. These results highlight the importance of the label compounds to correct for signal enhancement or suppression. All results were recovery and blank corrected for PFCs. Further details on the surrogates chosen for each native compound have been previously reported.^[6,24]

Results and discussion

PFC concentration comparison between EC and LEC

Both EC and LEC collected high volume air samples using GFFs and PUF/XAD-2 sandwiches and employed a GC/MS system for analysis using PCI and an IS quantification method whereas the sampling period and analytical process were different. In the samples that were collected during two overlapping periods, the concentrations of MeFOSA, MeFOSE and EtFOSE were below the MDL determined by EC and therefore a comparison of the results for these compounds was not possible. In general, the results of EC and LEC are in agreement within a factor of 1–3 ($R=0.93$, Fig. 1 and Table A6 in the Accessory publication). The concentrations differed by a mean factor of 2.0 for 6 : 2 FTOH, 1.5 for 8 : 2 FTOH, 1.3 for 10 : 2 FTOH and 2.2 for EtFOSA. This is a good agreement considering the challenges associated with sampling in a remote area (i.e. Canadian Arctic) with very low PFC concentrations in the atmosphere and separate sampling systems. Besides the different analytical processes, the different sampling times (EC 24 h and LEC 48 h) and sampling volumes (EC $\sim 385\text{ m}^3$ and LEC $\sim 946\text{ m}^3$) may have an influence on the measured concentrations. To our knowledge this is the first intercomparison in which the whole procedure (sample collection to instrumental analysis) was compared for the analysis of PFCs in high volume air samples.

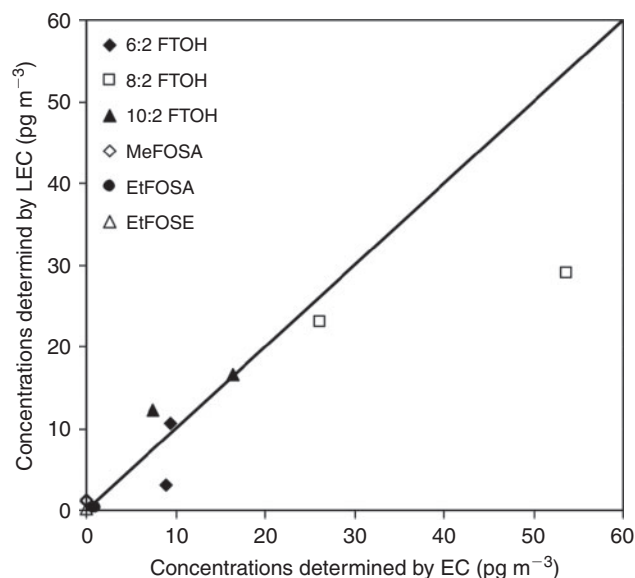


Fig. 1. Comparison of individual polyfluoroalkyl compound (see Table A2 in the Accessory publication for details) concentrations in the gas phase at two overlapping sampling stations investigated by Environment Canada (EC) and Lancaster Environment Centre (LEC) (only sites where the concentrations were above the MDL where included in the comparison).

Instrumental comparability studies showed an average accuracy of 22–44 % for four laboratories^[25] and the values of two laboratories were generally within $\pm 30\%$ of the theoretical values of an unknown standard mixture.^[26] Overall, the results of this field intercomparison study showed similar results as reported for instrumental comparability studies, which did not consider additional factors such as sampling, transport and storage of the samples, sample extraction and the concentration of the extracts. Nevertheless, these results show a future need for an extensive method comparison of PFCs in air.

Air parcel back-trajectories

Back-trajectory analysis was carried out using the HYSPLIT (hybrid single-particle Lagrangian integrated trajectory) model from the NOAA Air Resources Laboratory (see <http://www.Arl.Noaa.gov/ready/hysplit4.html>, accessed 13 July 2011). Six-day air back-trajectories calculated in 6-h steps are shown in Fig. 2a. The results indicate that during the entire cruise track the high volume air samples are representative of the Arctic air mass. The long-range transport of pollutants to the Arctic atmosphere varied seasonally.^[27] For instance, south-to-north transport occurs mainly in springtime and melting ice and re-volatilisation could be a source especially during summer time.^[22,27]

FTOHs, FOSAs and FOSEs in the gas phase

Concentrations of FTOHs, FOSAs and FOSEs in the gas phase of the Canadian Arctic atmosphere are shown in Table 1 and Fig. 2 (for details see Table A7 in the Accessory publication). The ΣPFC concentration in the gas phase ranged between 22 and 162 pg m^{-3} . Generally, the FTOH concentrations were approximately six times higher than $\Sigma\text{FOSA/FOSE}$ concentrations. The dominant FTOH was 8 : 2 FTOH ($15\text{--}83\text{ pg m}^{-3}$), followed by 10 : 2 FTOH ($3.5\text{--}31\text{ pg m}^{-3}$) and 6 : 2 FTOH ($<1.1\text{--}29\text{ pg m}^{-3}$). For the FOSAs/FOSEs, MeFOSE was dominant ($<0.06\text{--}22\text{ pg m}^{-3}$), followed by MeFOSA ($<0.08\text{--}3.6\text{ pg m}^{-3}$), EtFOSE ($<0.06\text{--}1.4\text{ pg m}^{-3}$) and EtFOSA ($<0.04\text{--}1.7\text{ pg m}^{-3}$). Average $\Sigma\text{FOSA/FOSE}$ concentrations

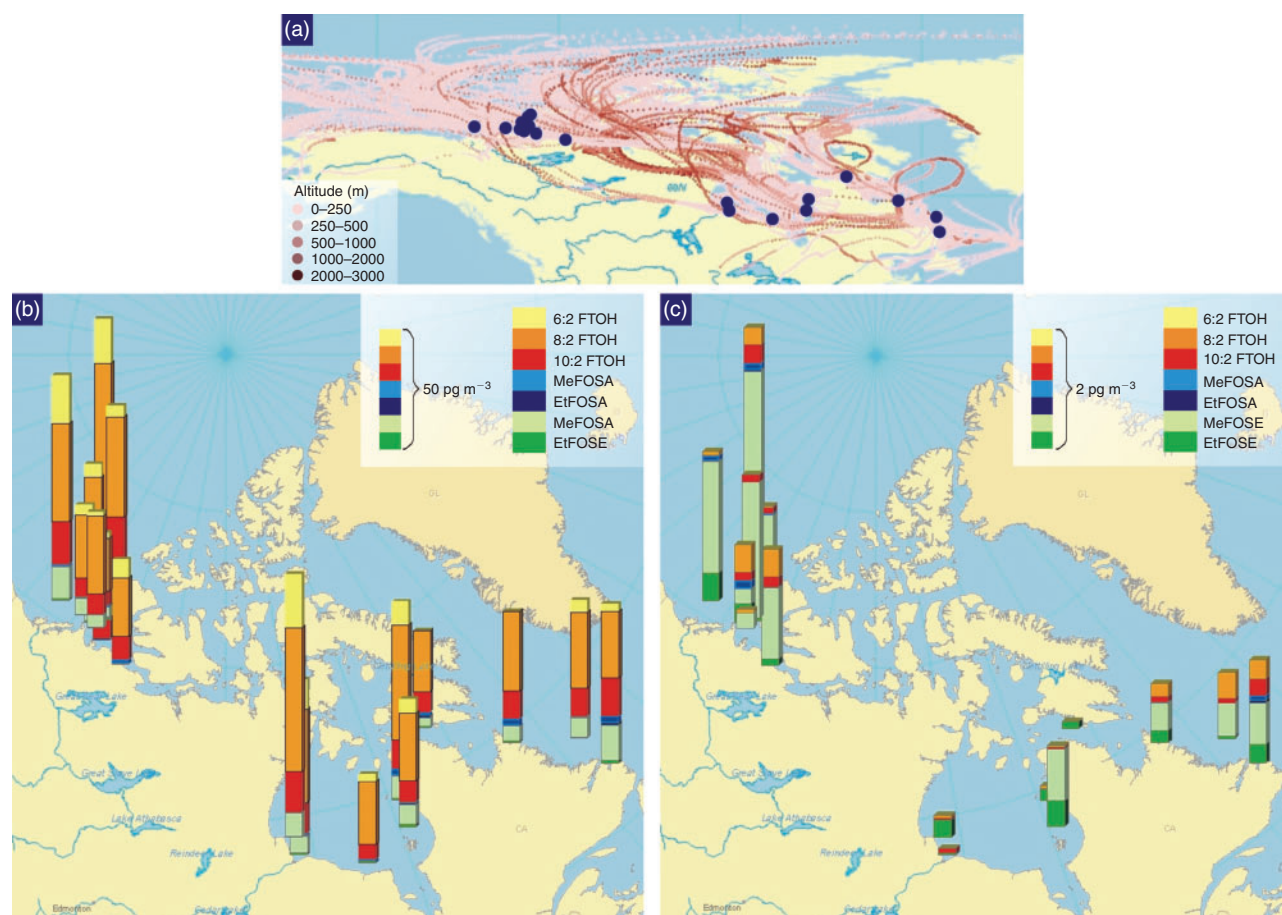


Fig. 2. (a) Six-day back-trajectories at the sampling sites in the Canadian Arctic atmosphere. FTOH (fluorotelomer alcohols), FOSA (fluorinated sulfonamides) and FOSEs (sulfonamidoethanols) concentrations (pg m^{-3}) are shown in (b) gas phase and (c) particle phase (see Table A2 in the Accessory publication for abbreviation details).

Table 1. Polyfluoroalkyl compound concentrations in the Labrador Sea, Hudson Bay and Beaufort Sea in the gas and particle phase determined by Environment Canada (EC) and Lancaster Environment Centre (LEC) (pg m^{-3})

Concentration ranges and average value in parentheses. <x, below the respective method detection limit. For PFC details see Table A2 in the Accessory publication. n.a., not available

PFC	Labrador Sea EC (n = 3)		Hudson Bay EC (n = 6)		Beaufort Sea EC (n = 11)		LEC (n = 7)
	Gaseous	Particulate	Gaseous	Particulate	Gaseous	Particulate	Gaseous
6:2 FTOH	<1.1–6.7 (3.7)	<0.6	<1.1–29 (12)	<0.6	<1.1–26 (9.3)	<0.6	2.0–11 (4.8)
8:2 FTOH	36–43 (40)	0.4–0.9 (0.7)	33–78 (49)	<0.1–0.1 (0.1)	26–83 (44)	<0.1–1.0 (0.4)	15–35 (24)
10:2 FTOH	15–21 (17)	0.2–0.6 (0.3)	8.2–22 (14)	<0.1–0.1 (0.1)	7.5–31 (16)	<0.1–0.6 (0.2)	3.5–17 (10)
\sum FTOHs	59–63 (61)	0.9–1.5 (1.3)	44–129 (75)	<0.1–0.2 (0.1)	39–138 (69)	0.3–1.6 (0.9)	20–56 (37)
MeFOSA	0.5–3.6 (2.4)	<0.1–0.2 (0.1)	0.4–3.2 (1.3)	<0.1	<0.3–2.0 (0.8)	<0.1–0.3 (0.1)	0.3–1.3 (0.8)
EtFOSA	0.5–1.5 (0.9)	<0.04–0.1 (0.1)	<0.2–1.1 (0.5)	<0.04	0.2–1.7 (0.6)	<0.04–0.2 (0.1)	0.1–0.4 (0.3)
\sum FOSAs	1.2–4.7 (3.3)	<0.1–0.3 (0.1)	0.5–3.8 (1.8)	<0.1	0.6–3.4 (1.4)	<0.1–0.3 (0.2)	0.4–1.7 (1.1)
MeFOSE	7.8–19 (12)	1.0–1.4 (1.2)	<0.6–13 (8.3)	<0.4–1.8 (0.53)	<0.6–22 (9.0)	<0.4–7.4 (2.8)	<2.1–4.0 (0.5)
EtFOSE	0.8–1.3 (1.0)	0.1–0.6 (0.4)	0.5–1.4 (0.9)	0.07–0.9 (0.4)	<0.1–1.3 (0.5)	<0.03–3.2 (0.8)	<0.2–0.5 (0.3)
\sum FOSEs	8.7–21 (13)	1.2–2.1 (1.6)	0.8–13 (9.2)	0.3–2.7 (1.0)	0.4–23 (9.5)	0.6–8.6 (3.6)	<2.3–4.6 (1.4)
PFDA	<0.1	<0.01–0.01 (0.01)	<0.1	<0.01	<0.1	<0.01	n.a.
PFUnDA	<0.2	<0.02–0.08 (0.03)	<0.2	<0.02–0.07 (0.02)	<0.2	<0.028	n.a.
PFDODA	<0.2	<0.01–0.06 (0.04)	<0.2	<0.01–0.08 (0.04)	<0.2	<0.01–0.02 (0.01)	n.a.
PFTeDA	<0.1	<0.01–0.01 (0.01)	<0.1	<0.01–0.03 (0.01)	<0.1	<0.01	n.a.
\sum PFCAs	<0.6	<0.04–0.15 (0.09)	<0.6	<0.04–0.18 (0.05)	<0.6	<0.04–0.02 (0.01)	n.a.
\sum PFCs	72–152 (99)	2.4–3.9 (3.0)	48–142 (86)	0.9–3.1 (1.5)	44–163 (80)	1.0–10 (4.6)	22–59 (40)

over the Labrador Sea were higher (17 pg m^{-3}) compared to the Hudson Bay and Beaufort Sea (11 and 7.6 pg m^{-3}), whereas the \sum FTOH concentrations were more consistent at the different sampling locations ($61\text{--}75 \text{ pg m}^{-3}$). In general, these PFC concentration levels were approximately three times lower than in urban areas like Toronto, Canada and Hamburg, Germany.^[16,28]

It is interesting to note that \sum FTOH concentrations in this study were approximately two times higher than measured previously in summer 2005.^[16] FTOHs have an atmospheric half-life of ~ 20 days and can be degraded to PFCAs in the Arctic atmosphere.^[15] This conversion of FTOH to PFCAs is expected to occur especially during summer by reaction with OH radicals. Thus lower FTOH concentrations are expected during summer.^[29] However, both sampling campaigns were carried out during a similar period of the year (i.e. summer 2005^[16] and spring–summer 2007–08 (this study) respectively). The comparison of the ratio of 6 : 2 FTOH to 8 : 2 FTOH to 10 : 2 FTOH on a concentration basis may help to determine whether the sources of FTOHs in the atmosphere changed over time.^[30] The average 6 : 2 FTOH-to-8 : 2 FTOH-to-10 : 2 FTOH ratio of this study was 1.0 : 6.4 : 2.1. This matches well with the ratio observed in the Arctic atmosphere in 2005 (i.e. 1.0 : 5.6 : 2.6),^[16] which suggests that the FTOHs originated from a similar source. The 6 : 2 FTOH-to-8 : 2 FTOH-to-10 : 2 FTOH ratio in urban areas (i.e. 1.0 : 2.3 : 1.2 in Toronto (Canada) and 1.0 : 1.8 : 0.5 in Hamburg (Germany) respectively) has a lower proportion of 8 : 2 FTOH and 10 : 2 FTOH.^[16,28] This can be explained by the shorter half-lives of 6 : 2 FTOH (i.e. 50 days) in comparison to 8 : 2 FTOH and 10 : 2 FTOH (i.e. 80 and 70 days respectively) as calculated from Piekartz et al.^[30] PFCs are supposed to be mainly produced and used in North America, Europe and East Asia.^[1,17] Since the phase-out of POSF-based chemicals, the use of FTOHs has reportedly increased by a factor of two.^[31] The increasing production and consequently increasing emissions to the atmosphere could explain the doubling of the FTOH concentrations between 2005 and 2007–08. However, a difference by a factor of two should not be considered significant and further long-term studies are necessary. Surprisingly, the \sum FOSE concentrations did not change in comparison to the study from 2005, although POSF-based chemicals were phased out in 2002.^[17] However, the products containing POSF-based chemicals are still in use (e.g. carpets)^[17] and the production has shifted partly to other countries.^[32]

FTOHs, FOSAs and FOSEs in the particle phase

All FTOHs, FOSAs and FOSEs, except for 6 : 2 FTOH, were quantified in the particle phase in the Canadian Arctic atmosphere (Table 1, Fig. 2 and Table A8 in the Accessory publication). The \sum FTOH concentrations in the particle phase (i.e. $0.3\text{--}1.6 \text{ pg m}^{-3}$) were lower by a factor of ~ 80 than in the gas phase, whereas the \sum FOSA/FOSE concentrations (i.e. $0.3\text{--}8.8 \text{ pg m}^{-3}$) were lower by an approximate factor of four than in the gas phase. \sum FTOH concentrations were lowest over the Hudson Bay (i.e. $0.3\text{--}0.4 \text{ pg m}^{-3}$), whereas higher concentrations were found over the Beaufort Sea and Labrador Sea (i.e. $0.3\text{--}1.6$ and $0.9\text{--}1.5 \text{ pg m}^{-3}$ respectively). Similarly, average \sum FOSA/FOSE concentrations were lowest over the Hudson Bay (i.e. $0.3\text{--}2.7 \text{ pg m}^{-3}$), whereas highest concentrations were found over the Beaufort Sea (i.e. $0.6\text{--}8.8 \text{ pg m}^{-3}$). It is interesting to note that for the gas phase, the highest FOSA/FOSE concentrations were observed over the Labrador Sea whereas the concentrations in the particle phase were highest over the

Beaufort Sea. This indicates temperature driven partitioning processes (see section ‘Correlation Analyses’ below).

The dominant PFC class was the FOSEs ($0.3\text{--}8.6 \text{ pg m}^{-3}$) with MeFOSE as the dominant compound ($<0.4\text{--}7.4 \text{ pg m}^{-3}$), followed by EtFOSE ($<0.03\text{--}3.2 \text{ pg m}^{-3}$). The FTOH and FOSA concentrations of individual compounds were below 1 pg m^{-3} , whereas the \sum FOSE concentrations were ~ 3 and ~ 20 times higher compared to the \sum FTOH and \sum FOSA concentrations respectively. Comparing our findings with data published from urban areas, the \sum FTOH/FOSA/FOSE concentrations in the particle phase were lower by a factor of 2–3 than in Toronto, Canada^[16] and 7–12 lower than that in Hamburg and Manchester respectively.^[28,33] However, the pattern of the PFC classes in the particle phase were similar and followed the trend FOSEs > FOSAs > FTOHs.

Concentrations of PFCAs

PFCAs and PFSAAs were below MDLs in the gas phase. The longer chain PFCAs, PFDA, PFUnDA, PFDoDA and PFTeDA were quantified in the particle phase, whereas the shorter chain PFCAs ($\text{C}_4\text{--}\text{C}_9$) and PFSAs were not detected (Table 1 and Table A9 in the Accessory publication). PFCAs were only detected sporadically with highest concentrations for PFUnDA and PFDoDA (both 0.08 pg m^{-3}). The concentrations of \sum PFCAs ($<0.04\text{--}0.18 \text{ pg m}^{-3}$) were much lower in comparison of \sum FTOH, \sum FOSA and \sum FOSE concentrations on particles ($<0.1\text{--}1.6$, $<0.1\text{--}0.3$ and $0.3\text{--}8.6 \text{ pg m}^{-3}$ respectively). It is interesting to note that the average \sum PFCA concentrations over the Labrador Sea and Hudson Bay (0.09 and 0.05 pg m^{-3} respectively) were higher than over the Beaufort Sea (0.01 pg m^{-3}), where only PFDoDA could be quantified in two samples. This is consistent with the concentrations of their potential precursor compounds, the FTOHs,^[13] which were highest in the particle phase over the Labrador Sea. Barber et al.^[33] reported PFDA and PFUnDA concentrations of a few pictograms per cubic metre at an urban and a semi-rural area in the UK, which is ~ 100 times higher compared to the levels in this study. Highest concentrations were found for PFOA with up to 828 pg m^{-3} ,^[33] whereas PFOA concentrations in this study were all below the MDL ($<0.8 \text{ pg m}^{-3}$). High air concentrations close to emission sources and low concentrations in remote areas normally indicate a low atmospheric long-range transport potential. The presence of PFCAs in the particle phase could be also attributed to degradation of their potential precursors.^[13]

Gas–particle partitioning

Although the FTOHs, FOSAs and FOSEs were dominantly distributed in the gas phase, individual compounds showed a different partitioning profile (Fig. 3). The particle-associated fraction (ϕ) represents the fraction on particles ($c_{\text{particulate}}$) in relation to the gas phase (c_{gaseous}) in air.

$$\phi = c_{\text{particulate}} / (c_{\text{gaseous}} + c_{\text{particulate}}) \times 100$$

The highest particle-associated fraction was observed for EtFOSEs ($\sim 33\%$). The functional group has the main influence on the partitioning of PFCs. Thus, the particle-associated fractions decrease from the FOSEs ($\sim 25\%$) to the FOSAs ($\sim 9\%$) and FTOHs ($\sim 1\%$). A similar pattern was observed in previous studies from urban and suburban areas in Germany and the UK.^[28,33] In the present study, the particle-associated fraction of ethyl FOSA and FOSE (10 and 33% respectively) was higher

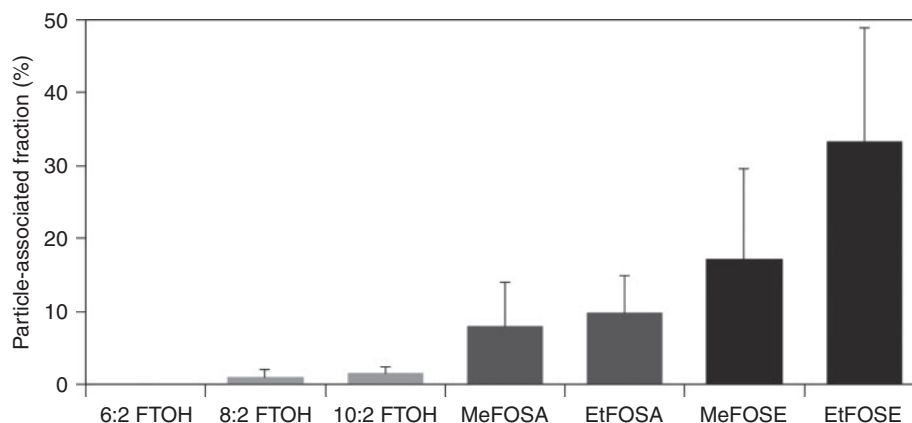


Fig. 3. Particle-associated fraction (ϕ) for individual polyfluoroalkyl compounds in the Canadian Arctic atmosphere. See Table A2 in the Accessory publication for abbreviation details.

compared to the methyl FOSA and FOSE (8 and 17% respectively). Furthermore, the particle-associated fraction for FTOHs increased slightly with increasing chain length (i.e. 6:2 FTOH (0%) < 8:2 FTOH (1.0%) < 10:2 FTOH (1.5%)). This can be attributed to the lower vapour pressure of the longer chain FTOHs (e.g. 144 Pa for 10:2 FTOH) in comparison to the shorter chain FTOHs (e.g. 713 Pa for 6:2 FTOH).^[34]

Longer chain PFCAs (C_{10} – C_{12} and C_{14}) were quantified in the particle phase, whereas no PFCAs could be detected in the gas phase. If half of the MDL was used for the values which were below the MDL, the particle-associated fraction would range from 76–83% for the longer chain PFCAs. However, these results must be considered carefully, because of the low concentration levels in the Arctic region, and Arp et al.^[35] have shown that gas phase PFCAs can adsorb to GFFs and therefore the particle-associated fraction might be overestimated.

Correlation analyses

Individual FTOHs correlated significantly in the gas phase ($P < 0.01$, Pearson Correlation, SPSS version 17.0 for Windows) and also a positive correlation between individual FOSAs/FOSEs were found in the gas and particle phase ($P < 0.01$, Pearson Correlation). Conversely, no correlation was found between the FTOHs and FOSAs/FOSEs ($P > 0.05$, Pearson correlation). This suggests that the FTOHs and FOSAs/FOSEs originated from different sources but individual compounds within these groups might have the same origin.

For the correlation analysis between the temperature and individual concentration levels, only the data from the Beaufort Sea were used to eliminate intercorrelations between the temperature and different sampling locations (Fig. 4). The FTOH, FOSE and FOSA concentrations in the gas phase generally decrease with decreasing temperature. However, this trend was only significant for the \sum FOSA concentrations over the Beaufort Sea ($R = -0.83$, $P < 0.01$, Pearson Correlation, note: PFC concentrations were correlated with inverse temperature). This is an indication that (i) temperature-driven partitioning to atmospheric particulate matter is lowering gas phase concentrations at extremely cold temperatures, or (ii) regional or ‘within-Arctic’ sources such as temperature-driven partitioning between snow–ice surfaces or possibly open seawater may be influencing FOSAs in the atmosphere. The collection of air samples over the

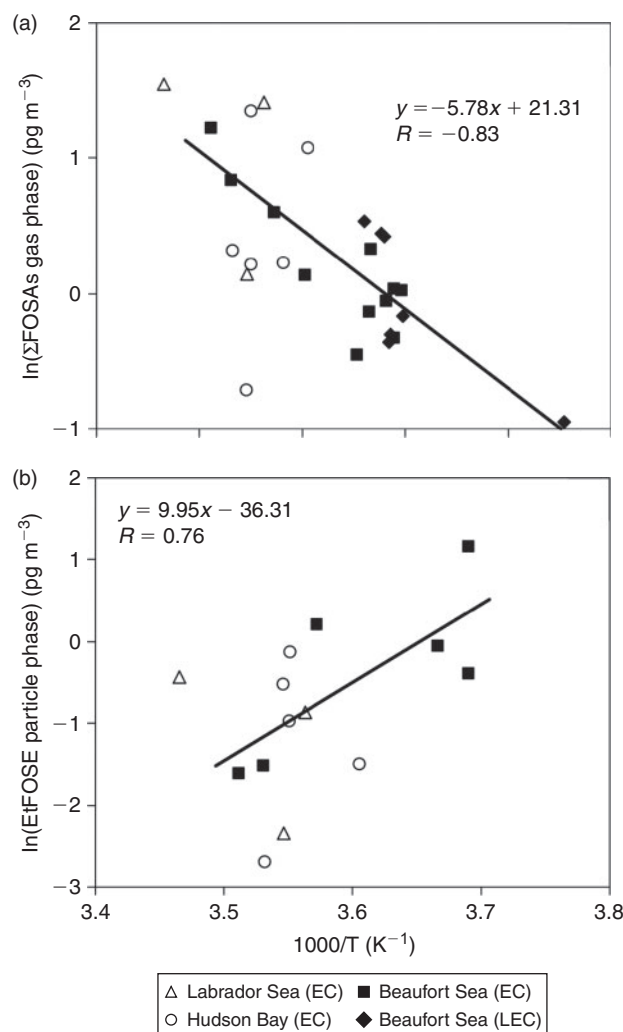


Fig. 4. Correlation between the ambient air temperature and the concentration of (a) \sum FOSAs (fluorinated sulfonamides) in the gas phase and (b) EtFOSE (*N*-ethyl perfluorooctane sulfonamidoethanol) in the particle phase respectively in the Beaufort Sea determined by Environment Canada (EC) and Lancaster Environment Centre (LEC). Note: for the regression analysis the samples from the Labrador Sea (triangles) and Hudson Bay (circle) were not included.

eastern end of the Beaufort Sea was during ice-cover, so the area of open seawater in contact with the overlying atmosphere was negligible, implying that the sea-ice snowpack may be playing a role in controlling ambient concentrations of FOSAs in winter Arctic air. However, the FOSAs can also originate from warm air masses transported over long distances from source regions in the south, although back trajectories showed no influence from the south. Similarly, the concentration of EtFOSE in the particle phase increased with decreasing temperature over the Beaufort Sea ($R = 76$, $P < 0.01$, Pearson correlation). This can be explained by the fact that at colder temperatures, equilibrium phase partitioning of organic compounds is driven towards the particle phase.^[36] The large scatter in the EtFOSE data indicate that, in addition to temperature, other factors (e.g. volatilisation from surfaces or long-range transport from source areas) may also be controlling the air concentrations of this chemical.

Jahnke et al.^[28] showed that the ambient temperature has an influence on the gas–particle partitioning of PFCs. In this study, the particle-bound fraction of FOSAs and FOSEs increased with decreasing ambient air temperature ($R = 0.28–0.65$). It is probable, therefore, that the proportion of these compounds in the particle phase would be higher in winter time compared to the summer time. This effect is generally observed for other condensed phases like water, soil and biota for which the partition coefficient favours the condensed phase at lower temperature.^[36] Thus, fluctuations in ambient air temperature may play an important role for the deposition, degradation, transport and fate of PFCs, even in the Arctic.

Conclusions

The current study presents the spatial distribution of four PFC classes (i.e. FTOHs, FOSAs, FOSEs and PFCAs) in the Canadian Arctic atmosphere. The widespread distribution of PFCs in the Arctic atmosphere shows their potential for long-range atmospheric transport to remote regions. The sampling, extraction and instrumental method performance was compared between EC and LEC and showed a good agreement with each other. In the gas phase, \sum FTOH concentrations were approximately six times higher compared to the \sum FOSA/FOSE concentrations, whereas the FOSEs were the dominant PFC class in the particle phase. The particle-associated fraction followed the general trend PFCAs > FOSEs > FOSAs > FTOHs. Ambient air temperature had a significant influence on the partitioning behaviour of FOSAs and FOSEs. This indicates that the atmospheric behaviour of these compounds is influenced by temperature-driven exchange with surfaces, possibly including extensive areas of sea-ice snow as well as surface seawater. Overall, these results highlight that the gas–particle partitioning of PFCs plays an important role on their global transport and fate in the atmosphere.

Accessory publication

Additional information about the analytes, sampling campaign, intercomparison study and overview of PFC concentrations is available in the Accessory publication (see http://www.publish.csiro.au/?act=view_file&file_id=EN10131_AC.pdf).

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