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Perfluorinated Chemicals in the Arctic Atmosphere

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Twenty high-volume air samples were collected during a
crossing of the North Atlantic and Canadian Archipelago in
July 2005 to investigate air concentrations of fluorotelomer
alcohols (FTOHs) and perfluoalkyl sulfonamido ethanols
(PFASs). These commercial chemicals are widely used as
surface treatments and are believed to be precursors
for perfluorocarboxylic acids (PFCAs) and perfluorooctane
sulfonate (PFOS) that accumulate in humans and biota,
including those from remote arctic regions. The highest
concentrations (sum of gas- and particle-phase) of FTOHs
were for 8:2 FTOH (perfluoroctyl ethanol) (5.8−26 pg/m^3),
followed by 10:2 FTOH (perfluorodecyl ethanol) (1.9−17 pg/
m^3) and 6:2 FTOH (perfluorohexyl ethanol) [BDL (below
detection limit) to 6.0 pg/m^3]. For the PFASs, MeFOSE (*N*-
methyl perfluorooctane sulfonamido ethanol) was
dominant and ranged from 2.6 to 31 pg/m^3; EtFOSE (*N*-
ethyl perfluorooctane sulfonamido ethanol) ranged from
BDL to 8.9 pg/m^3 and MeFOSEA (*N*-methyl perfluorooctane
sulfonamide ethylacrylate) was BDL in all samples. Air
parcel back-trajectories showed that the sampled air was
largely representative of the arctic air mass. Air
concentrations of target compounds were of the same order
of magnitude as reported air concentrations in source
regions. For instance, the mean 8:2 FTOH concentration
was only a factor of about 3 lower than for three urban
samples that were collected in Toronto for comparison. These
findings confirm model results that predict the efficient, long-
range atmospheric transport and widespread distribution
of FTOHs and related compounds in the arctic region. Mean
particulate percentages for FTOHs and PFASs in the
cruise samples (mean temperature, 5 ± 4 °C) were BDL
for 6:2 FTOH, 23% for 8:2 FTOH, 15% for 10:2 FTOH, 32% for
MeFOSE, and 22% for EtFOSE. Further, the partitioning to
particles for MeFOSE and EtFOSE was significantly correlated
with inverse absolute temperature, whereas the FTOHs
did not show this trend. The Toronto samples (mean
temperature, −1 ± 1 °C) showed similar particulate
percentages for MeFOSE and EtFOSE; however, the FTOHs
were substantially less particle-bound. Although the
mechanism for this partitioning is not understood, the
results do indicate the need to better account for particle
phase transport when modeling the atmospheric fate of
these chemicals.

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Introduction

Perfluorooctane sulfonate (PFOS) and perfluorocarboxylic
acids (PFCAs) are widespread and persistent environmental
contaminants that are detected in biological samples includ-
ing those from remote regions such as the Arctic (*1−4*). In
a recent study of contaminants in polar bears, PFOS was
measured in concentrations greater than contaminants such
as organochlorine pesticides (OCPs), polychlorinated bi-
phenyls (PCBs), and polybrominated diphenylethers (PBDEs)
(*5*). PFOS and PFCAs are also abundant in the human
population (*3, 6−9*) and are now being regulated in North
America based on evidence of toxicity effects in animal
models (*10, 11*). In Canada, several perfluorinated chemicals
(PFCs) have been restricted because they are believed to
meet the criteria for POPs (persistent organic pollutants) that
are controlled under the Stockholm Convention, an inter-
national treaty on POPs (*12*). Recently, Canada has adopted
measures for greatly reducing the import of fluorotelomer-
derived products (*13*).

The occurrence of PFOS and PFCAs (mainly PFOA—
perfluorooctanoic acid—the eight carbon chain PFCA that is
dominant in biota) in the arctic environment are a current
research priority. Some investigators argue that the occur-
rence of PFOA and other PFCAs is due to a combination of
direct and indirect sources (*14*). Direct sources of PFCAs
include its use in fluoropolymer manufacture, aqueous fire
fighting foam, and other industrial products, with total global
production estimated to be 4400−8000 t (*14*). These may
undergo subsequent long-range transport through the
atmosphere and oceans. Whereas indirect sources include
volatile and semivolatile commercial precursor compounds
that are released into the environment and then converted
to PFCAs metabolically (*15−19*) and/or via atmospheric
degradation reactions (*20−23*). Most production of perfluo-
rooctyl sulfonyl-based (POSF) products was used to make
neutrals compounds, not anionic PFOS. Accordingly, indirect
sources are believed to dominate for PFOS, i.e., release of
precursors, followed by abiotic and biotic conversion to PFOS.
Precursors for PFOS and PFOA include the perfluoalkyl
sulfonamido ethanols (PFASs) and the fluorotelomer alcohols
(FTOHs).

These precursor compounds (PFASs and FTOHs) are
widely used in commercial products for their ability to impart
stain and water repellency. Because of their ability to volatilize
(*24−28*), these chemicals are abundant in the atmosphere
(*28−31*), exhibiting elevated concentrations in indoor air and
dust (*31*). Human exposure is believed to occur predomi-
nantly in the indoor environment through inhalation of
contaminated air and ingestion of house dust laden with
PFCs (*31*).

To better understand the connection between ambient
concentrations of FTOHs in source regions and its conversion
to PFOA and other PFCAs that occur all over the globe,
Wallington et al. (*23*) have applied a 3D global atmospheric
chemistry and transport model. The model predicts that
FTOHs (namely, 8:2 FTOH) and related degradation products
are ubiquitous in the arctic region at about one-fifth the
concentrations observed in source regions. However, no data
were available to date to validate these results.

In this study, some of Wallington's model predictions (*23*)
are tested against field observations. Air samples were
collected during an ice-breaker crossing of the North Atlantic
Ocean and Canadian Archipelago during July 2005, and
samples were analyzed for FTOHs and PFASs, yielding new
information to further investigate the atmospheric long-range
transport and environmental fate of these compounds.
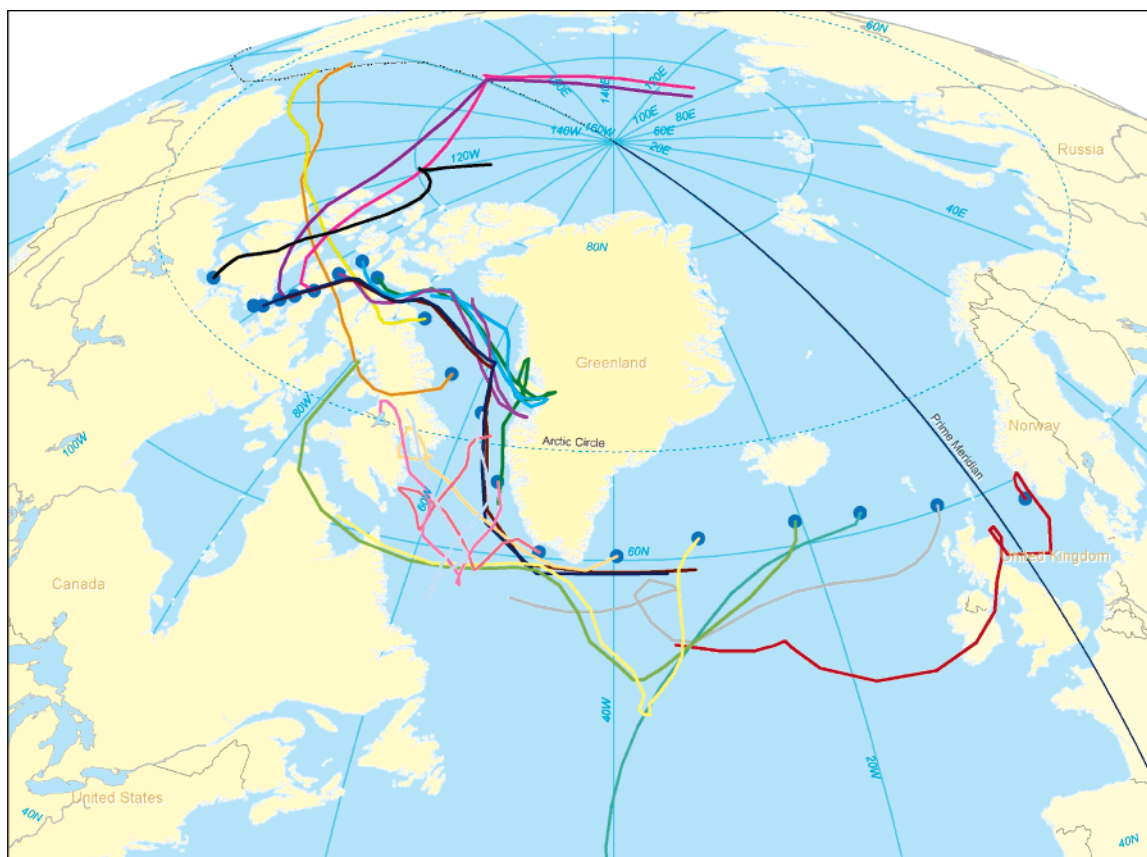
FIGURE 1. Cruise track illustrating sampling sites and "spaghetti plot" of average 6-day air parcel back-trajectories (at 10 m above sea level) for each sample.

Experimental Section

Chemicals. The fluorotelomer alcohols (FTOHs) perfluorohexyl ethanol (6:2 FTOH), perfluoroctyl ethanol (8:2 FTOH), and perfluorodecyl ethanol (10:2 FTOH) were purchased from Oakwood Products Inc. (West Columbia, SC). The perfluoroalkyl sulfonamido ethanols (PFASs) N-methyl perfluorooctane sulfonamido ethanol (MeFOSE), N-ethylperfluorooctane sulfonamido ethanol (EtFOSE), and N-methyl perfluorooctane sulfonamide ethylacrylate (MeFOSEA) had a purity >90% and were obtained from the 3M company. N,N-Dimethylperfluoro-1-octane sulfonamide (N,N-MeFOSA) was used as internal standard for volume correction and methyl-D$_3$-perfluorooctane sulfonamide (D$_3$-MeFOSA) used for recovery check (Wellington Laboratories, Guelph, Canada).

Sample Collection. Twenty high-volume air samples were collected during an expedition of the icebreaker *Oden* on the first leg of a cruise from Gothenburg, Sweden to Barrow, Alaska, via the North Atlantic Ocean and Canadian Archipelago (Figure 1) in July 2005. Air samples were collected daily from July 6 to 27 over a 24-h period with sample volumes of approximately 300 m³ using a modified PS-1 type sampler (Tisch Environmental, Cleves, OH). The sampler was mounted on one of the upper decks near the bow of the ship to minimize sampling of exhaust gases from the stacks that were closer to the ship's stern. The sampling train comprised a glass fiber filter for particle phase collection followed by a polyurethane foam (PUF)/XAD-2 sandwich for trapping gas-phase compounds. The sandwich consisted of 10 g of XAD-2 resin between two PUF plugs [80 mm diameter, 75 mm thick (top), 15 mm thick (bottom)]. The average ambient air temperatures during sampling were in the range from 0 to +15 °C with a mean of 5.2 °C. Surface water temperatures were in the range from −1.5 to 12 °C with a mean of 3.9 °C

(Table 1). Fluoropolymer gaskets were not used on the high-volume sampler to eliminate potential contamination of target compounds. Field blanks ($n = 3$) for PUF/XAD sandwiches were collected by inserting the media in the sampling system and running the pump for ∼1 min. Blanks for GFFs were assessed in the laboratory, also in triplicate, by preparing GFFs, storing them, and then handling them as samples. Samples were shipped cold and stored at −4 °C until extraction. Details are given in Table 1.

For comparison purposes, three air samples were collected using the same equipment at a semiurban site in Toronto in March 2006, when temperatures were from −1.8 to −0.5 °C, slightly lower than temperatures during the cruise (see Table 1 for sample details).

Analysis. Prior to Soxhlet extraction, PUF/XAD sandwiches were spiked with surrogate D3-MeFOSA (10 μL at 50 ng/μL). Extractions were performed with 50/50 petroleum ether/acetone (PE/Ac) for 18−24 h. GFFs were also spiked with D$_3$-MeFOSA prior Soxhlet extracted for 18−24 h using dichloromethane (DCM). All extracts were concentrated by rotary evaporation and then further concentrated to about 0.5 mL under a gentle stream of nitrogen using ethyl acetate as keeper.

PUF/XAD sample extracts were cleaned on a 1-g alumina column (10% deactivation), eluted with 15 mL of 15% DCM in ethyl acetate (F1) followed by another 15 mL of 50% DCM in ethyl acetate (F2). Alumina cleanup was not required for GFF extracts that showed good chromatogram baselines. N,N-MeFOSA was added as an internal standard just prior to the GC/MS analysis to correct for volume differences.

Sample analysis for FTOHs and PFASs was performed by gas chromatography−positive chemical ionization mass spectrometry (GC−PCIMS) using a Hewlett-Packard 6890 GC-5973 mass selective detector MSD in selective ion

TABLE 1. Details for Air Samples Collected across the North Atlantic Ocean, the Canadian Archipelago, and in Toronto, Canada

	date	lat (N)/long. (W)	T_{air}, °C	T_w, °C
	Cruise Samples (2005)			
1	July 6	58°47.5′/3°55.3′ (E)	14.8	11.9
2	July 7	60°16.2′/5°16.8′	11.7	11.0
3	July 8	61°5.2′/13°32.8′	13.0	11.3
4	July 9	61°22.2′/20°43.5′	11.7	11.5
5	July 10	61°5.5′/31°10.9′	9.4	10.1
6	July 11	60°14.2′/39°39.9′	6.7	9.2
7	July 12	60°19.7′/47°32.3′	4.7	2.6
8	July 13	64°14.7′/53°26.7′	4.6	3.0
9	July 14	68°19.0′/58°6.9′	2.2	4.3
10	July15	70°21.8′/64°48.7′	3.6	1.1
11	July 16	73°17.0′/74°55.2′	4.8	3.3
12	July 18	74°41.0′/95°57.6′	0.7	−0.6
13	July19	73°18.0′/96°32.4′	3.3	0.4
14	July 20	71°43.9′/96°28.2′	1.2	−0.7
15	July 21	70°51.3′/98°51.2′	0.3	−1.3
16	July22	70°10.9′/99°12.4′	1.6	−1.5
17	July 24	69°1.9′/101°16.1′	6.1	0.6
18	July25	68°25.8′/111°36.3′	3.2	1.3
19	July 26	70°0.5′/121°23.0′	3.8	1.3
20	July 27	70°24.8′/121°16.1′	3.8	6.5
	Toronto Samples (2006)			
1	March 7	43°41′/79°38′		−2
2	March 16	43°41′/79°38′		0
3	March 21	43°41′/79°38′		−1

TABLE 2. Recovery Results for Target Chemicals after Soxhlet Extraction (GFF ($n = 3$), PUF ($n = 3$) and XAD ($n = 3$)) and Alumina Cleanup ($n = 4$)

	Soxhlet extraction			alumina cleanup		
compd	GFF[a]	PUF[b]	XAD[b]	F1[c]	F2[d]	total %
4:2 FTOH	118 ± 12	75 ± 8	NA	61± 8	22± 6	83
6:2 FTOH	112 ± 7	94 ± 9	88 ±5	66 ± 7	22± 8	87
8:2 FTOH	99 ± 1	96 ± 10	95 ± 3	74 ± 5	23 ± 6	97
10:2 FTOH	101 ± 8	108 ± 9	85 ± 2	78 ± 2	27 ± 5	104
MeFOSE	131± 14	121 ± 18	126 ± 14	42 ± 6	42 ± 6	84
EtFOSE	155 ± 10	166 ± 30	125 ± 6	59 ± 2	36 ± 7	95
MeFOSEA	109 ± 2	107 ± 9	<5	99 ± 2	3 ± 1	102

[a] Extraction with DCM. [b] Extraction with 50/50 petroleum ether/acetone. [c] Fraction 1 eluted in 15 mL of 15% DCM/ethyl acetate. [d] Fraction 2 eluted in 15 mL of 50% DCM/ethyl acetate.

TABLE 3. Gas Phase and Particle Phase Air Concentrations (pg/m^3) for Target Compounds in the Cruise Samples ($n = 20$) and Toronto Samples ($n = 3$)[a]

	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSE	EtFOSE	MeFOSEA
	Cruise, Gas-Phase					
MDL, pg/m^3	1.1	3.5	0.8	1.9	1.0	0.001[b]
min.	BDL	4.16	1.45	BDL	BDL	BDL
max.	5.98	22.7	16.4	23.6	5.17	BDL
arithmetic mean	2.65	11.4	6.27	8.30	1.87	BDL
n	11	20	20	19	19	0
	Cruise, Particle-Phase					
MDL, pg/m^3	0.001[b]	0.001[b]	0.001[b]	1.7	0.001[b]	0.001[b]
min.	BDL	1.07	0.29	BDL	BDL	BDL
max.	BDL	8.37	1.57	15.0	5.5	BDL
arithmetic mean	BDL	3.50	0.80	3.53	1.05	BDL
n	0	20	20	19	5	0
	Toronto, Gas-Phase					
min.	12.4	25.1	12.0	5.38	1.04	BDL
max.	27.2	59.6	36.1	11.8	3.01	BDL
arithmetic mean	17.7	40.2	21.1	8.0	2.33	BDL
	Toronto, Particle-Phase					
min.	0.20	0.30	0.42	2.67	0.40	BDL
max.	0.42	1.31	1.82	6.51	1.68	BDL
arithmetic mean	0.31	0.71	1.09	4.20	0.96	BDL

[a] 6:2 FTOH, perfluorohexyl ethanol; 8:2 FTOH, perfluoroctyl ethanol; 10:2 FTOH, perfluorodecyl ethanol; MeFOSE, methyl perfluorooctane sulfonamide ethanol; EtFOSE, ethyl perfluorooctane sulfonamide ethanol; MeFOSEA, methyl perfluorooctane sulfonamide ethylacrylate. [b] Instrumental detection limit (IDL) was used to calculate MDL.

monitoring (SIM) mode. Methane was used as reagent gas for PCI mode. Analytes were separated on a 30-m DB-wax column with 0.25 mm i.d. and 0.25 μm film thickness. The oven temperature was 60 °C for 10 min, 8 °C/min to 150 °C, and then 10 °C/min to 210 °C. For confirmation, samples were also run on a 60-m DB5 column with 0.25 mm i.d. and 0.25 μm film thickness with helium as the carrier gas. The GC oven temperature was 60 °C for 10 min, 10 °C/min to 240 °C, and then 30 °C/min to 290 °C. All injections (2 μL) were splitless, with the split opened after 0.5 min and the injector at 200 °C. The ion source and quadrupole temperatures were 250 and 106 °C in PCI mode. Further confirmation of MeFOSE and EtFOSE was performed in electron impact ionization (EI) SIM mode using the 60-m DB5 column with ion source and quadrupole temperatures at 230 and 150 °C respectively.

Samples collected in Toronto were treated slightly differently. PUF/XAD extracts were not passed through alumina. This was done to facilitate screening for a wider range of compounds. Otherwise, samples were treated and analyzed the same way as indicated above.

Analytical recoveries for the extraction step and alumina cleanup step were tested separately. This involved spiking three of each sampling media separately (GFF, PUF, and XAD) with 200 μL (8 ng/μL for FTOHs and 4 ng/μL for PFASs) just prior to Soxhlet extraction. Method recoveries/fractionation on alumina was tested by loading 100 or 50 μL of a mixed standard containing 0.8 ng/μL for FTOHs (6:2, 8:2, and 10:2) and 0.4 ng/μL for each PFAS (MeFOSE, EtFOSE, and MeFOSEA) onto the column and analyzing the two fractions.

Results and Discussion

Quality Control/Quality Assurance. Recoveries (±SD) (see Table 2) for the extraction step were in the range 94% ± 9% for 6:2 FTOH to as high as 166% ± 30% for EtFOSE. It is not clear why recoveries for EtFOSE were elevated, but previous researchers have also reported this behavior (*32*). Results for alumina cleanup (Table 2) showed that 6:2, 8:2, 10:2 FTOHs and MeFOSEA eluted mainly in the first fraction, while MeFOSE and EtFOSE were split between both fractions.

Method detection limits (MDL = mean of blanks + 3SD) were calculated from the three field blanks, and results are shown in Table 3. MDLs, expressed as concentrations by dividing by an average air volume of 300 m^3, were in the range 0.8−3.5 pg/m^3 for all target compounds for the PUF/XAD and <1.7 pg/m^3 for the GFFs. When compounds were not detected in blanks, instrumental detection limits (IDLs) were used to calculate MDL. IDL corresponded to the amount of analyte that generated a signal:noise ratio of 3:1. Surrogate recoveries of D_3-MeFOSA that was added to each GFF sample were satisfactory with an average of 105 ± 25%. Data reported in Table 3 were not corrected for blanks or recoveries.

Results obtained on the DB5 column confirmed the analysis on the DB-wax column. For the PUF/XAD samples, ∼75% of results were within ∼15% for all of the targeted compounds. Larger deviations of 30%−40% were observed for samples collected on days 10, 11, 12, 13, and 20 when
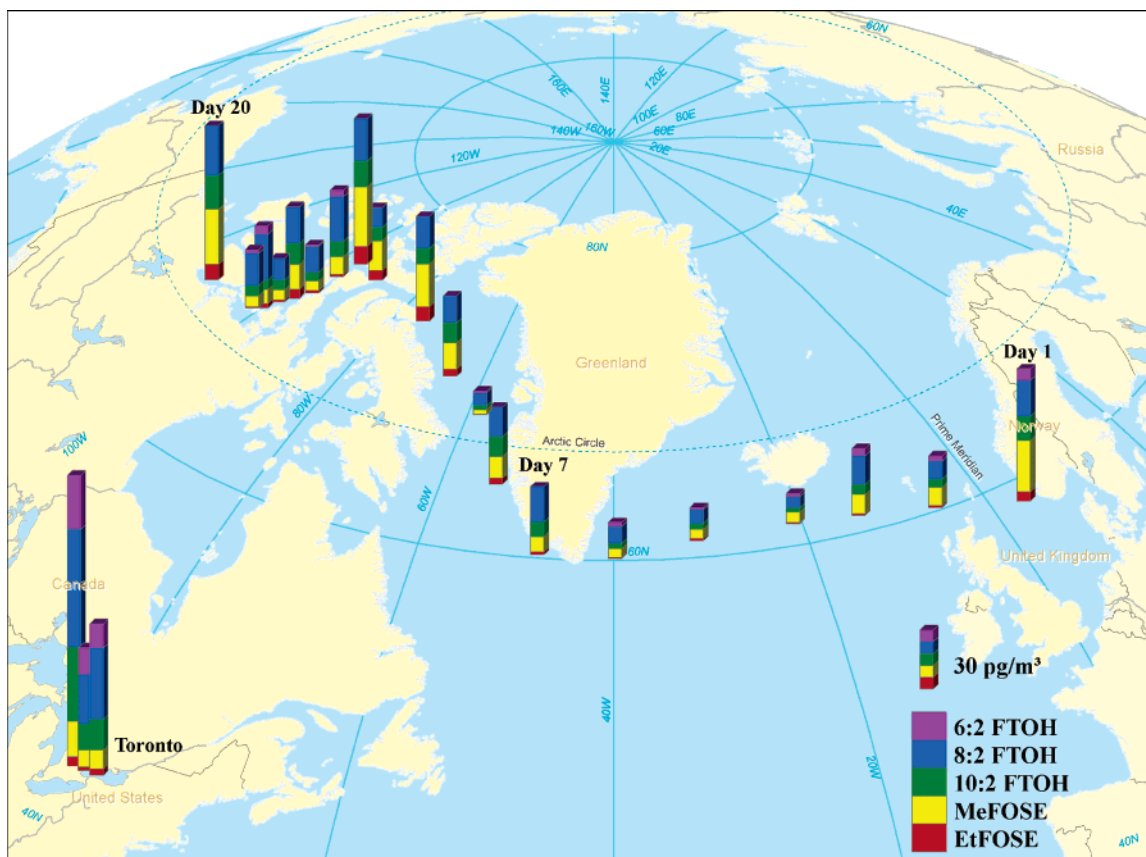
FIGURE 2. Total air concentrations (sum of gas phase and particle phase) for FTOHs and PFASs across the North Atlantic Ocean and Canadian Archipelago (see Figure 1 cruise track) and in Toronto, Canada.

some interference occurred for the DB5 column. Better agreement was obtained for GFF extracts, and results for the two columns were within 10% in ~95% of the samples.

Air Parcel Back-Trajectories. Air parcel back-trajectories were calculated for each sampling point using the Canadian Meteorological Center Trajectory Model (2005). Six-day back-trajectories at 10 m above sea level were calculated every 6 h during each sample and these were averaged to produce one representative trajectory for each sample. Results for all 20 samples were compiled into a "spaghetti plot" (Figure 1) that shows that during the entire cruise track, air collected by the high volume sampler was representative of the arctic air mass. There were no events of strong advection inputs from potential source regions to the south.

FTOHs and PFASs Air Concentrations. Total air concentrations of target compounds at various points along the cruise track and in the Toronto samples are presented in Figure 2 and summarized in Table 3. For the cruise samples, 8:2 FTOH, 10:2 FTOH, and MeFOSE were above the detection limit in all samples, while 6:2 FTOH and EtFOSE were quantifiable in 10/20 and 12/20 samples, respectively. MeFOSEA was not detected in any of the samples analyzed.

The highest concentrations of FTOHs in the cruise samples were for 8:2 FTOH ($5.8-26$ pg/m^3) followed by 10:2 FTOH ($1.9-17$ pg/m^3) and 6:2 FTOH (BDL to 6.0 pg/m^3). 8:2 FTOH represents $50-70\%$ of the total FTOHs. The dominance of 8:2 was expected on the basis of previous measurements in source regions. For instance, air concentrations (pg/m^3) of 8:2 FTOH, in urban locations in North America and Europe, range from 40 to 150 and 33 to 326, respectively (summarized in Table 4). For the Toronto samples, the mean 8:2 FTOH air concentration was (41 ± 18 pg/m^3) ($n = 3$), approximately 3 times higher than the mean concentration of 14.9 pg/m^3 detected in Arctic air. These findings are consistent with

TABLE 4. Air Concentrations (pg/m³, Reported Range and Mean Value (in Parentheses) When Available) of 8:2 FTOH and MeFOSE at Different Locations in North America and Europe

location	8:2 FTOH	MeFOSE	ref
North American Cities, Urban	$40-150^a$	$20-300\ (160)^a$	30
North American cities, rural	$2-10^a$	$10-28\ (19)^a$	30
Toronto, urban (2002/2003)	—	31.7^a	28
Toronto, urban (2006)	$25-60.6\ (41)^a$	$8.8-18.3(12.2)^a$	this work
Manchester, England, urban	< 326	62^a	32
Hazelrigg, England, urban	< 196		32
Hamburg, urban (2005)	$62-270\ (93)$	$3.0-89\ (14)$	36
Waldhof, urban (2005)	$33-110\ (79)$	$0.5-11\ (7.9)$	36
English Channel, marine	180 ± 14	19 ± 3	37

^{a} Sum of particle- and gas-phase concentrations.

Wallington's model (23) that predicts air concentrations of 8:2 FTOH and related reaction products to be approximately 5 times lower in the arctic atmosphere compared to source regions.

MeFOSE air concentrations were next highest and ranged from 2.6 to 31 pg/m^3, while EtFOSE ranged from BDL to 8.9 pg/m^3 and MeFOSEA was BDL in all samples. Concentrations of MeFOSE from other studies (mostly urban and suburban locations) are summarized in Table 4 and range from 3 to 300 pg/m^3 with a mean of 44 pg/m^3. This mean value is
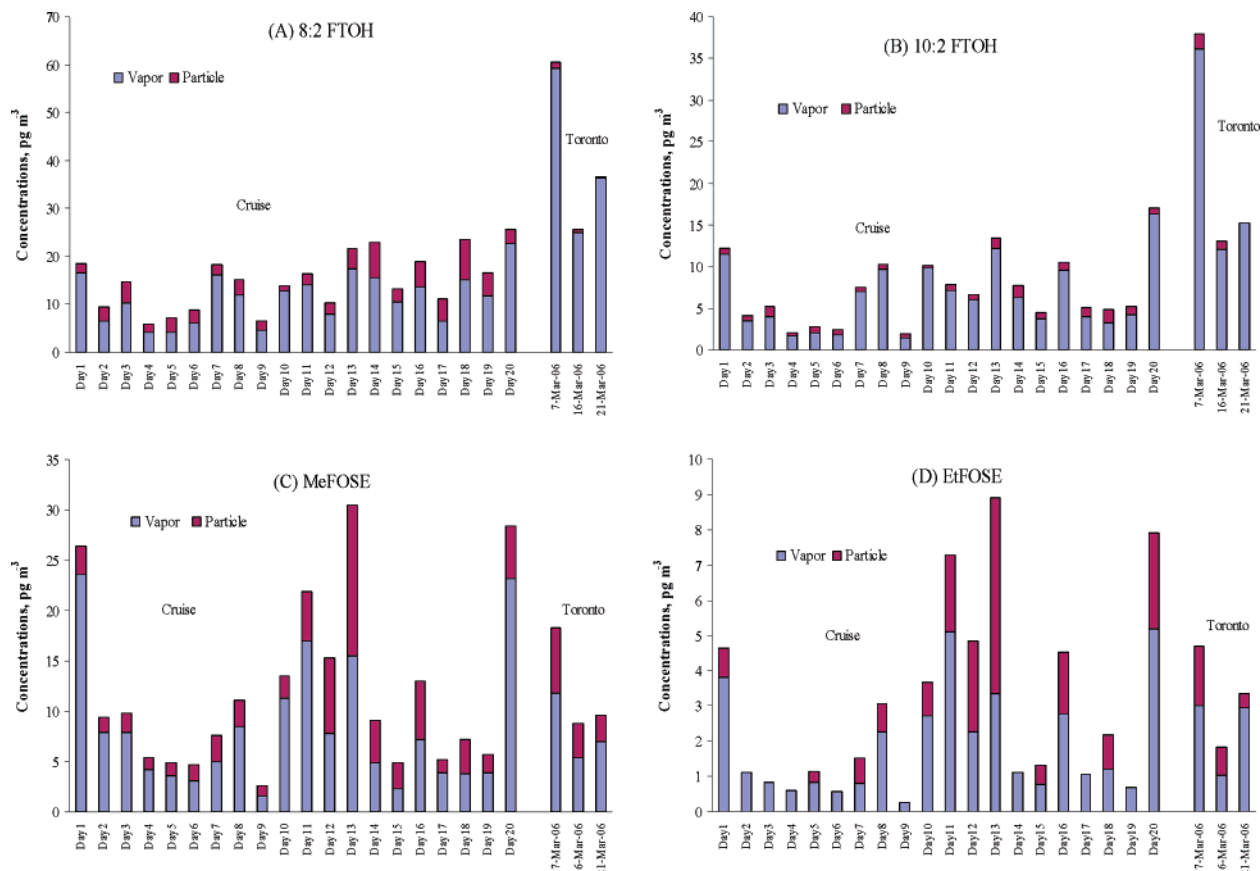
FIGURE 3. Gas- and particle-phase distribution of (A) 8:2 FTOH, (B) 10:2 FTOH, (C) MeFOSE, and (D) EtFOSE from air samples collected on a cruise of the North Atlantic Ocean and Canadian Archipelago and in Toronto, Canada.

approximately 4 times higher than the mean concentration of 11.8 pg/m^3 reported for the cruise samples.

It is interesting to note that the proportions of the two dominant fluorochemicals changed systematically across the cruise track (Figure 2). MeFOSE was dominant in the early samples in the eastern part of the North Atlantic Ocean. Air parcel back-trajectories for these samples were also more representative of the North Atlantic region. The elevated air concentrations for the first sample are consistent with air that passed over potential source regions in northern England and Ireland just prior to arriving at the ship. The samples collected west of Greenland showed a dominance of 8:2 FTOH. Back-trajectories for these samples stemmed from the Canadian Arctic Archipelago and Beaufort Sea. These results suggest a characteristic signature or composition of PFCs for different parts of the arctic region. This will need to be tested further as more data from these regions become available.

Other Fluorinated Compounds. D'eon et al. (*33*) showed that, during the formation of (PFCA) by the atmospheric oxidation of the PFAS *N*-methyl perfluorobutane sulfonamido ethanol (*N*-MeFBSE), a stable intermediate, *N*-methyl perfluorobutane sulfonamide (*N*-MeFBSA), is produced. This intermediate has a lifetime of 20−50 days (*34*), much longer than the 2-day lifetime of the parent compound *N*-MeFBSE (*33*). However, *N*-MeFBSE is not usually investigated in air samples, presumably because it was used to a much lesser extent than the PFASs that were targeted in this study. By analogy, we might expect to see the stable oxidation intermediates of the PFASs (MeFOSE and EtFOSE) that were detected, namely, methyl perfluorooctane sulfonamide (MeFOSA) and ethyl perfluorooctane sulfonamide (EtFOSA). Unfortunately, these compounds were not included during the method development for the cruise samples. Since their

inclusion in our methodology, we found that they are retained on alumina and will not occur in the cruise extracts. The Toronto extracts were therefore not passed through alumina and were analyzed for MeFOSA and EtFOSA. Air concentrations in Toronto were below the detection limit and 1.07 ± 0.46 pg/m^3 for MeFOSA and EtFOSA, respectively. This represents less than 10% of the parent MeFOSE and EtFOSE, suggesting that the oxidation of C8 alkyl chain PFASs may be less important and/or that the intermediates are less stable than expected on the basis of the analogy with MeFBSA. The presence of EtFOSA in air samples could also attributed to its use as an insecticide registered as Sulfluramid. This insecticide is used for control of termites and other indoor pests. EtFOSA has been reported in air from three North American cities, at higher concentrations: Toronto, ∼15 pg/m^3 (*29*); Cleves, OH, ∼40 pg/m^3; and Reno, NV, ∼55 pg/m^3 (*30*).

Particle-Gas Partitioning. PFCs have unique properties and the vapor-pressure-based and K_{OA}-based partitioning relationships developed for conventional POPs (e.g., PCBs, OCPs, and PBDEs) have been shown not to be applicable to them (*28, 35*). PFCs partition more strongly to particles compared to these model predictions. So far no studies have elucidated this partitioning mechanism and the associated temperature dependency.

Results presented in Figure 3 and Table 3 show the particle phase contribution for each of the target chemicals. The percent of particles ranges as follows: BDL for 6:2 FTOH, 23% for 8:2 FTOH, 15% for 10:2 FTOH, 32% for MeFOSE, and finally 22% for EtFOSE. The extent of partitioning to particles is consistent with a decrease in volatility (increase in K_{OA}), which follows the same order with the exception of 8:2 and 10:2 FTOHs, where 8:2 is more associated with particles despite its higher vapor pressure and lower K_{OA} (*28, 35*).

For the Toronto samples the particulate percentages of MeFOSE and EtFOSE were consistent with the cruise samples at 34 ± 6% and 30 ± 16%, respectively. However, the FTOHs showed very little partitioning to particles—5% ± 3% and 2% ± 1% for 10:2 FTOH and 8:2 FTOH, respectively—compared to 15 and 23%, respectively, in the cruise samples. The reasons for the higher particulate percentages in the cruise samples is not clear, but it may be related to differences in particulate matter, a potential contribution of sea spray and/or mist aerosols (14) in the cruise samples that may adsorb to the GFF and contain FTOHs, or differences in atmospheric residence times in the arctic compared to Toronto.

Linear regressions of the ratio of particle-phase to gas-phase contribution versus $1/T$ (1/K) were performed for the cruise samples. FTOHs showed no significant correlation, indicating that their presence on the filter was likely not associated with a temperature effect. However, MeFOSE and EtFOSE showed significant correlations, with $r^2 = 0.53$, $p < 0.01$ for MeFOSE and $r^2 = 0.44$, $p < 0.01$ for EtFOSE. The abundance of FTOHs and PFASs on atmospheric particulate matter indicates the need to better understand the partitioning mechanism, as well as the overall fate of particle-bound fluorinated chemicals.

In summary, this study reports the first measurements of FTOHs and PFASs across the Canadian Arctic Archipelago and North Atlantic region. The findings confirm model results by Wallington et al. (23) that predict the efficient long-range atmospheric transport and widespread distribution of FTOHs and related compounds in the Arctic region. Although FTOHs and PFASs were detected in the particle phase, it is not known what controls this partitioning and how this may vary with particle type, temperature, and the physical chemical properties of these chemicals.

Acknowledgments

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