

## Air Concentrations of Fluorinated Chemicals from a Trans-Atlantic cruise from Sweden to Alaska.

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### Introduction

Perfluorooctane sulfonate (PFOS) and perfluorocarboxylic acids (PFCAs) have recently emerged as priority environmental pollutants due to their widespread detection in biological samples including those collected from remote regions such as the Arctic<sup>1,2</sup>. The occurrence of PFOS and PFCAs in remote regions is likely the result of atmospheric transport of more volatile compounds (precursors) such as fluorinated telomers (FTOH) and perfluoroalkyl sulfonamides (PFASs) as supported by recent smog chamber studies<sup>3,4</sup>. Uptake and biotransformation of precursors may also explain high level of PFOS and PFCAs in biological samples<sup>5,6</sup>. In this study, results for FTOHs and PFASs are reported from samples collected during a 21 day crossing of the Atlantic and Arctic Oceans in July of 2005 (Gotheberg, Sweden to Barrow, Alaska) by the Swedish Ice Breaker Oden.

### Material and Methods

Twenty air samples across the cruise transect (Figure 1) over the period July 6-27, 2005, were collected using a conventional high volume air sampler (PS-1, Tisch Environmental, Cleves, OH, sampling rate ~0.21 m<sup>3</sup>/min.). The sampling train composed of a glass fiber filter followed by a polyurethane foam (PUF)/ XAD-2 sandwich. The sandwich consisted of 10g XAD-2 resin between two PUF plugs (80 mm diameter, 75 mm thick (top), 15mm thick (bottom)). Samples were collected over ~24 hours resulting in 300 m<sup>3</sup> air and average temperatures during sampling were near 0 °C. Teflon gaskets were not used on the hi-vol sampler to eliminate potential contamination. Field blanks were collected by inserting the media to the sampling system and turning the pump on for ~1min. Samples were shipped cold and stored at -4 °C until extraction. For comparison purposes, three air samples were collected at a semi-urban site in Toronto in March 2006 using the same set-up and over similar temperatures, near 0 °C.

PUF/XAD sandwiches were Soxhlet extracted together with 50/50 petroleum ether /acetone (PE/Ac) for 18-24 hours. GFFs were also 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.

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

Analysis of 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 monitoring (SIM) mode. Confirmation of Me FOSE and Et FOSE was performed in electron impact ionization (EI) SIM mode. Methane was used as reagent gas for PCI mode. Analytes were separated on a 60 m DB5 column with 0.25 mm i.d. and 0.25 μm film thickness, and helium was used as the carrier gas. The GC oven temperature was 60 °C, 10 min, 10 °C/min to 240 °C, then 30 °C/min to 290 °C. Splitless injections were 2 μL with split opened after 0.5 min, and the injector was at 200 °C. The ion source and quadrupole were 250 and 106 °C and 230°C and 150 °C for PCI and EI respectively.

### Results and Discussion

**Quality Control/Quality Assurance.** Extraction recoveries for target compounds (FTOHs and PFASs) were validated by spiking three of each sampling media separately (GFF, PUF and XAD) just prior to Soxhlet extraction. Recoveries ( $\pm$ SD) (see Table 1) were in the range  $94\% \pm 9\%$  for 6:2FTOH to as high as  $166\% \pm 30\%$  for ET FOSE. The high recoveries for MeFOSE (and EtFOSE) are not explained however other researchers have noted this behaviour<sup>7</sup>.

The elution of target chemicals from the alumina column were also tested by loading  $\sim 10$  L of a mixed standard containing  $50$  ng/L of each component onto the column. Results are listed in Table 1. Method detection limits (MDL = average blanks + 3 standard deviation) were calculated from the three field blanks and results are shown in Table 2. Data reported in table 2 were not corrected for blanks or recoveries. Results for four samples are not reported at this time (samples collected on days 10, 11, 12 and 13) due to poor chromatography / interferences.

### Air Concentrations of Fluorinated Compounds

Table 2 and Figures 1 and 2 summarize gas-phase air concentrations of target compounds at various points along the cruise track. The highest concentration (geometric mean, pg/m<sup>3</sup>) was observed for 8:2 FTOH (17.1) followed by MeFOSE (12.6). 8:2 FTOH was above the detection limit in all samples reported. Lowest concentrations for all target chemicals occurred during the crossing of the north Atlantic Ocean (samples 2-6). The highest concentrations of MeFOSE and EtFOSE were for samples 1 and 20 in the North and Beaufort Seas respectively. High concentrations of FTOH (especially 8:2) and MeFOSE were observed during samples 7 and 8, collected in the Labrador Basin – possibly reflecting the background concentration in advective flow off the North American continent. These compounds were also elevated during the southernmost part of the transect through the Canadian Archipelago (samples 15-19).

The dominance of 8:2 is consistent with the results of a global atmospheric chemistry model for the northern hemisphere including the Arctic<sup>8</sup>. The model predicts that 8:2 is ubiquitous in the atmosphere of the northern hemisphere as a result of atmospheric lifetimes on the order of 10-20 days. Further, air concentrations of 8:2 and related compounds are expected to be only a factor of  $\sim 5$  lower than for source areas. This is consistent with the results of this study. Reported air concentrations of FTOHs in the North America range from 22 to 403 pg/m<sup>3</sup><sup>9</sup>. The wintertime (March 2006) mean air concentration of 8:2 FTOH taken at a semi urban location in Toronto, Canada, determined in our laboratory, was  $63.2 \pm 48$  pg/m<sup>3</sup> (n=3), around 4 times higher than the mean concentration of 17.1 pg/m<sup>3</sup> detected in Arctic air.

Several target compounds were detected on the GFFs however, results are not available for reporting at this time.

### References

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## Fluorinated compounds - sources, environmental levels and transformation

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Table 1. Method recoveries ( $\pm$ SD) for target compounds on various sampling media (GFF, n=3; PUF, n=3; and XAD, n=3) and fractionation results for alumina cleanup (n=4).

Compounds	Soxhlet Extraction			Alumina Cleanup		
	GFF	PUF	XAD	Fraction 1 %	Fraction 2 %	Total %
FTOH 6:2	112 +/- 7	94 +/- 9	88 +/- 5	66 +/- 7	22 +/- 8	87
FTOH 8:2	99 +/- 1	96 +/- 10	95 +/- 3	74 +/- 5	23 +/- 6	97
FTOH 10:2	101 +/- 8	108 +/- 9	85 +/- 2	78 +/- 2	27 +/- 5	104
Me FOSE	131 +/- 14	121 +/- 18	126 +/- 5	42 +/- 6	42 +/- 6	84
Et FOSE	155 +/- 10	166 +/- 30	125 +/- 6	59 +/- 2	36 +/- 7	95
Me FOSEA	109 +/- 2	107 +/- 9	< 5	99 +/- 2	3 +/- 1	102

Extraction solvents were: DCM for GFF and 50/50 PE/Ac for PUF and XAD.

Alumina: fraction 1, 15ml of 15% DCM/ ethyl acetate; fraction 2, 15ml of 50% DCM/ ethyl acetate.

Table 2. Results summary for target chemicals.

Compounds	FTOH 6:2	FTOH 8:2	FTOH 10:2	MeFOSE	EtFOSE	MeFOSEA
MDL, pg/m <sup>3</sup>	2.2	4.8	1.7	4.7	1.8	0.5
Air Concentrations, pg/m <sup>3</sup>						
Mim.	BDL	6.16	2.12	BDL	BDL	BDL
Max	11.7	73.3	38.8	51.3	28.5	BDL
Arithmetic mean	4.56	22.1	8.43	16.5	6.86	BDL
Geometric mean	3.68	17.1	6.02	12.6	4.23	BDL
n of samples	10	16	16	15	11	0

FTOH 6:2 perfluorohexyl ethanol, FTOH 8:2 perfluorooctyl ethanol, FTOH 10:2 perfluorodecyl ethanol, MeFOSE methyl perfluorooctanesulfonamidoethanol, EtFOSE ethyl perfluorooctanesulfonamidoethanol, MeFOSEA methyl perfluorooctanesulfonamidethylacrylate.

Figure 1. Cruise track and sampling sites for July 2006.



Sample#	Date	Lat. (N) / Long. (W)
1	July 6	58° 47.5' / -3° -55.3'
2	July 7	60° 16.2' / 5° 16.8'
3	July 8	61° 5.2' / 13° 32.8'
4	July 9	61° 22.2' / 20° 43.5'
5	July 10	61° 5.5' / 31° 10.9'
6	July 11	60° 14.2' / 39° 39.9'
7	July 12	60° 19.7' / 47° 32.3'
8	July 13	66° 22.1' / 47° 41.1'
9	July 14	68° 19.0' / 58° 6.9'
10	July 15	70° 21.8' / 64° 48.7'
11	July 16	73° 17.0' / 74° 55.2'
12	July 17	74° 22.7' / 89° 53.8'
13	July 18	74° 41.0' / 95° 57.6'
14	July 19	73° 18.0' / 96° 32.4'
15	July 20	71° 43.9' / 96° 28.2'
16	July 21	70° 51.3' / 98° 1.2'
17	July 24	70° 10.9' / 99° 12.4'
18	July 25	69° 22.1' / 100° 10.9'
19	July 26	68° 25.8' / 111° 36.3'
20	July 27	70° 0.5' / 121° 23.0'

\* at start of sample

Figure 2. Gas phase air concentration of target compounds

