

# INVESTIGATION OF THE SAMPLING EFFICIENCY OF POLYFLUORINATED CHEMICALS USING SUPER HIGH-VOLUME AIR SAMPLER EQUIPPED WITH XAD-IMPREGNATED PUF DISKS

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## Introduction

Perfluorooctane sulfonate (PFOS) and perfluorocarboxylic acids (PFCAs) are emerging contaminants. These chemicals have been widely detected in human and other biological samples including those from remote regions such as the Arctic. Due to their environmental persistence, bioaccumulation, toxicity, and long-range transport potential, PFOS and PFCAs are increasingly considered as persistent organic pollutants (POPs) candidates. Meanwhile, evidence from studies on their possible precursors has shown that fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamido ethanols (PFASs) can undergo atmospheric degradation to generate PFCAs and PFOS, respectively.

Currently, only very limited concentration and distribution data are available for FTOHs and PFASs in the Arctic atmosphere. There was no such information until Shoeib and her co-workers<sup>1</sup> investigated the air levels of FTOHs and PFASs using high-volume air samples that were collected during a crossing of the North Atlantic and Canadian Archipelago in July 2005. The major reason for this is due to the lack of effective air sampling methodology for collecting these volatile compounds. Recently, a new sampling medium, sorbent (XAD-4 resin)-impregnated polyurethane foam (SIP), has been developed for a passive air sampler and tested for sampling volatile polyfluorinated chemicals (PFCs)<sup>2</sup>. In the present study, SIPs consisting of microsize XAD-2 powder impregnated into polyurethane foam (PUF) disks were prepared for a super high-volume air sampler (SHV: operating flow rate  $\sim 1.3 \text{ m}^3 \text{ min}^{-1}$ ) that would be used for collecting low-level vapour phase PFCs in the Canadian Arctic. Previous studies have shown that PUF by itself has insufficient sorbing capacity for trapping volatile PFCs such as FTOHs. The use of SIPs is to rectify the problem of breakthrough. This paper investigates the sampling efficiency of PFCs with XAD-2-impregnated PUF Disks.

## Materials and Methods

To improve sampling capacity and prevent breakthrough of gas-phase PFCs with SHV under low temperature conditions, large-size PUF disks were impregnated with microsize XAD-2 powder. Briefly, the pre-cleaned XAD-2 resin (Supelpak 2, Supelco, Bellefonte, PA) was rinsed with acetone, completely air-dried in fume hood, and then ground to approximately  $0.7 \mu\text{m}$  size powder. After re-cleaning with dichloromethane and hexane by Soxhlet extraction for over 48 h and re-drying, the microsize XAD-2 powder was used to prepare an XAD slurry with a

concentration of about 6 g L<sup>-1</sup> in hexane by sonication. The SIPs were prepared by repeatedly dipping a PUF disk into the XAD slurry and removing solvent from the disk, followed by pre-drying the sorbent-impregnated disk on a hot plate and complete drying in a desiccator. The average impregnated quantity of XAD-2 is approximately 3.5 g. Then, the SIP disks were installed into a sampling head for SHV air sampling (see Figure 1). In total, three air sampling tests were conducted at a field site, Downsview (residential and industrial area), in north Toronto. The tests were undertaken by the comparison with a regular PS-1 high-volume air sampler (HV: flow rate: ~0.25 m<sup>3</sup> min<sup>-1</sup>) using conventional PUF/XAD-2/PUF sandwiches (PUF plug: 75 mm x 37 mm; XAD-2: 10 g)<sup>3</sup>. Gaseous compounds were collected with SIPs and PUF/XAD-2/PUF sandwiches for SHV and HV, respectively. Particulates were trapped on glass fiber filters (GFFs) for both types of samplers (GFF for SHV: 22.2 cm diameter; GFF for SHV: 10.2 cm). Sampling details are shown in Table 1. Samples and blanks were stored at -20°C and in the dark until extraction.

Gas-phase samples (e.g., SIPs and PUF/XAD-2/PUF sandwiches) and particle-phase (GFF) samples were Soxhlet extracted separately with dichloromethane (400 mL) for 24 h. After removal of XAD particles (if applicable), the extracts were reduced in volume by rotary evaporation and exchanged into isooctane (1 mL). The final extracts were analysed by gas chromatography/mass spectrometry (6890GC/5793MS) after adding *N,N*-dimethylperfluoro-1-octane sulfonamide (*N,N*-Me<sub>2</sub>-FOSA) as internal standard. Positive chemical ionization (PCI) mode was used. Helium and methane were used as carrier and reagent gases. A DB-WAX capillary column (30 m length × 0.25 mm i.d., 0.25 μm film thickness) was employed. The temperature program started at 60 °C for 2 min, 2 °C min<sup>-1</sup> to 70 °C, 8 °C min<sup>-1</sup> to 150 °C, then 10 °C min<sup>-1</sup> to 210 °C. The target compounds in this study include (1) FTOHs: perfluorotetyl ethanol (4:2 FTOH), perfluorohexyl ethanol (6:2 FTOH), perfluorooctyl ethanol (8:2 FTOH), and perfluorodecyl ethanol (10:2FTOH); (2) PFASs: *N*-methyl perfluorooctane sulfonamido ethanol (MeFOSE), *N*-ethylperfluorooctane sulfonamido ethanol (EtFOSE), and *N*-methyl perfluorooctane sulfonamide ethylacrylate (MeFOSEA); (3) perfluorooctane sulfonamides (PFOSAs): *N*-methyl perfluoro-1-octane sulfonamide (MeFOSA), and *N*-ethyl perfluoro-1-octane sulfonamide (EtFOSA). The blanks were investigated for all the target compounds in GFFs and microsize XAD-2 powder used for SHV sampling. All compounds were below detection limits in blank GFFs and no detection of 4:2 FTOH, 6:2 FTOH, MeFOSA, EtFOSA, and EtFOSE in blank XAD. The blanks observed for 8:2 FTOH, 10:2 FTOH, and MeFOSE in the sorbent were less than 3% of those measured in 1-week samples. No blank correction was applied to the results.

## Results and Discussion

For most target compounds, the results demonstrated that using SIPs significantly improved their sampling efficiency. On the other hand, 4:2 FTOH and MeFOSEA were not detected in any samples collected. This was not unexpected as these chemicals have very high volatilities. Therefore, these two compounds are not included in the discussion below.

Table 1. Information on air sampling with SHV and HV samplers

SHV sampling	Period	Air volume (m3)	Sampling media
1	1 week (Mar 15 - 22, 07)	12150	Top: SIP, bottom: PUF
2	1 week (Mar 22 - 29, 07)	12210	Top: SIP, bottom: SIP
3	2 week (Mar 29-Apr 12, 07)	24580	Top: SIP, bottom: SIP
HV sampling	Period	Air volume (m3)	Sampling media
1	1 week (Mar 15 - 22, 07)	2110	PUF/XAD/PUF
2	1 week (Mar 22 - 29, 07)	2050	PUF/XAD/PUF
3	2 week (Mar 29-Apr 12, 07)	4130	PUF/XAD/PUF

The compounds investigated were predominantly in the gas-phase, especially for FTOHs and PFOSAs. For example, the measured quantities of PFCs in top SIPs and GFFs in SHV showed that FTOHs and PFOSAs have an average particulate percentage of less than 2% (range: 0-3%). The average particulate percentages for MeFOSE and EtFOSE were 10% and 11% (range: 8-12%). Similar particle/gas distribution patterns were also observed in HV samples. These findings indicate that it is necessary to measure particle-phase concentrations of perfluorooctane sulfonamido ethanols to evaluate their total air concentrations.

Breakthrough of each compound during different sampling periods was evaluated based on the gas-phase concentrations derived from the top and bottom sampling media that were installed in the SHV (see Table 2). For FTOH, considerable breakthrough (~60%) was found for 6:2 FTOH, reflecting the fact that this compound has high volatility. Approximately 10% and 30% breakthrough were observed for 8:2 FTOH during 1-week and 2-week sampling. This suggests that long sampling time (i.e., high air sample volume) may cause significant loss of trapped 8:2 FTOH from SIP in urban areas, where ambient air concentration is high, as equilibrium is approached. For 10:2 FTOH, less than 3% breakthrough was observed for a 2-week period. No breakthrough was found for MeFOSE, EtFOSE, MeFOSA, and EtFOSA. In addition, our test using non-sorbent-impregnated PUF as bottom sampling medium (Table 2) showed no recovery of FTOHs, demonstrating that using XAD is critical for capturing volatile fluorinated chemicals.

The comparison of air (gas- and particle-phase) data from SHV and HV samplers was conducted. The average gas-phase concentrations derived from SHV (top SIPs) are about 67-83% those derived from HV for detected fluorinated chemicals, except for 6:2 FTOH (ca. 20%) (Table 3). Although the cause of the differences is still under investigation, the low recovery of 6:2 FTOH by SHV is likely due to its high volatility and the fact that the air volumes collected by SHV (e.g., 24580 m<sup>3</sup> per 2-weeks) was much higher than those drawn by HV (e.g., 4130 m<sup>3</sup> per 2-weeks). In terms of particle-phase sampling, no 6:2 FTOH was detected in GFF samples collected by both types of samplers. For the other compounds, similar average concentrations in GFFs derived from SHV and HV were observed, indicating the comparability of particle-phase data.

Table 2. Gas-phase concentrations (pg m<sup>-3</sup>) derived from SHV sampler operating continuously for 1 to 2 weeks

	SHV-Top			SHV-Bottom			Breakthrough (%)
	SIP			PUF (non-impregnated)	SIP		
	Mar 15- Mar 22	Mar 22- Mar 29	Mar 29- Apr 12	Mar 15-Mar 22	Mar 22- Mar 29	Mar 29- Apr 12	
<b>6:2 FTOH</b>	<b>3.1</b>	<b>3.1</b>	<b>3.2</b>	<b>BDL</b>	<b>4.0</b>	<b>4.5</b>	<b>58</b>
<b>8:2 FTOH</b>	<b>21</b>	<b>29</b>	<b>26</b>	<b>BDL</b>	<b>2.8</b>	<b>12</b>	<b>20</b>
<b>10:2 FTOH</b>	<b>9.7</b>	<b>13</b>	<b>13</b>	<b>BDL</b>	<b>0.40</b>	<b>0.31</b>	<b>3</b>
<b>EtFOSA</b>	<b>0.58</b>	<b>0.65</b>	<b>0.39</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>&lt; 2</b>
<b>MeFOSA</b>	<b>0.63</b>	<b>0.61</b>	<b>0.43</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>&lt; 4</b>
<b>MeFOSE</b>	<b>3.0</b>	<b>4.1</b>	<b>1.9</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>&lt; 6</b>
<b>EtFOSE</b>	<b>0.91</b>	<b>1.7</b>	<b>0.85</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>&lt; 4</b>

Table 3. Comparison of gas-phase concentrations (pg m<sup>-3</sup>) derived from SHV and HV samplers

	SHV-Top SIP			HV-PUF/XAD/PUF			SHV-Conc/HV-Conc (%)			Ave (%)
	Mar 15- Mar 22	Mar 22- Mar 29	Mar 29- Apr 12	Mar 15- Mar 22	Mar 22- Mar 29	Mar 29- Apr 12	Mar 15- Mar 22	Mar 22- Mar 29	Mar 29- Apr 12	
6:2 FTOH	3.1	3.1	3.2	9.3	16	31	33	19	10	21
8:2 FTOH	21	29	26	24	52	43	86	55	60	67
10:2FTOH	9.7	13	13	11	27	14	84	48	95	76
EtFOSA	0.58	0.65	0.39	0.55	1.1	0.53	105	58	74	79
MeFOSA	0.63	0.61	0.43	0.61	1.2	0.68	103	53	64	73
MeFOSE	3.0	4.1	1.9	2.3	6.6	3.4	130	62	57	83
EtFOSE	0.90	1.7	0.85	0.79	3.1	1.2	113	55	71	80

In summary, this study provides the first measurement for active air sampling of volatile fluorinated chemicals using SIPs as the gas-phase sampling medium. Results indicate predominant existence of these compounds in the gas-phase, particularly for FTOHs and PFOSAs. No substantial breakthrough was observed for most investigated fluorinated chemicals, indicating substantial improvement of sampling capacity after the impregnation of PUF with microsize XAD-2 powder. Under arctic conditions, we expect breakthrough of PFCs to be much lower given that the sorptive capacity of SIP disks increases greatly at cold temperatures. These findings show promise for the use of SIP disks in arctic monitoring programs employing SHV air samplers.

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### Reference

- (1) Shoeib M., Harner T. and Vlahos P. *Environ. Sci. Technol.* 2006; 40: 7577.
- (2) Shoeib M., Harner T., Lee, S. C., Lane, D. and Zhu J. *Anal. Chem.* 2008 ; 80: 675.
- (3) Yao Y., Harner T., Ma J., Tuduri L. and Blanchard P. *Environ. Sci. Technol.* 2007; 41: 688.



Figure 1. Photo of the SHV air sampler equipped with XAD-2-impregnated PUF disks