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Sorbent-Impregnated Polyurethane Foam Disk for Passive Air Sampling of Volatile Fluorinated Chemicals

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A passive air sampler comprising a polyurethane foam (PUF) disk impregnated with XAD-4 powder has been developed. This sorbent-impregnated PUF (SIP) disk builds on previous work using PUF disk passive air samplers that have been effective in spatial air mapping studies of nonpolar hydrophobic chemicals, without the need of electricity or expensive air sampling equipment. In this study, PUF disks and SIP disks are calibrated for sampling volatile polyfluorinated chemicals—specifically, the fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamides (PFASs). Results demonstrate the low sorptive capacity of the PUF disk samplers, particularly for the FTOHs, with PUF disks reaching equilibrium within 1 day, after collecting ~0.4 and 1.2 m³ of air for 8:2 FTOH and 10:2 FTOH, respectively. This limits their use for these target compounds when time-weighted, linear-phase sampling is desired. The presence of just 0.4 g of XAD powder in the SIP disks greatly increases the sorptive capacity (by ~2 orders of magnitude for the FTOHs) and provides linear-phase sampling for a period of several weeks. PUF–air partition coefficients, $K_{\text{PUF-A}}$, calculated for the FTOHs and PFASs are considerably lower than values predicted using previously established correlations against the octanol–air partition coefficient, K_{OA} , demonstrating the unique partitioning behavior of the polyfluorinated chemicals. Using results from these calibration tests, air concentrations of FTOHs were derived from PUF disk samples that were deployed in 52 homes in Ottawa, Canada, during 2002/2003. These represent the first comprehensive measurements of FTOHs in indoor air in North America. Range and (geometric mean) air concentrations (pg m⁻³) were 261–28 900 (2070) for 8:2 FTOH and 104–9210 (890) for 10:2 FTOH. These air concentrations are orders of magnitude higher than observed for outdoor air, establishing indoor environments as important for human exposure and also as potential sources to the larger environment.

Perfluorinated chemicals (PFCs) are widespread environmental contaminants.^{1–5} Regulatory efforts are underway to limit their use due to concerns over the persistence, accumulation, and toxicity of some members of this class.^{6–8} Of all the PFCs, perfluorooctanesulfonate (PFOS) and perfluorocarboxylic acids (PFCAs) are most widely detected in human and other biological samples including those from pristine areas such as the Arctic.^{1–4,9,10} The delivery of these chemicals to remote locations is attributed to two processes: (1) transport by ocean currents and (2) air transport and transformation of volatile precursor compounds. Controlled studies have confirmed the plausibility of the atmospheric pathway by demonstrating the atmospheric degradation of fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamido ethanols to PFCAs and PFOS, respectively.^{11–14} This fate pathway is also demonstrated by results from a recent snow study in the Arctic region.¹⁵

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Recent ship-based surveys of FTOHs and perfluoroalkyl sulfonamides (PFASs) confirm model predictions¹² of their widespread atmospheric distribution.^{16,17} Additional information on the global distribution of PFAS was obtained from samples collected during December 2004 to March 2005 at more than 40 sites operated under the Global Atmospheric Passive Sampling (GAPS) network.¹⁸ This type of spatially resolved information, which is only made possible by the low-cost and simplicity of passive air samplers, is invaluable for assessing regional and global transport of chemicals. However, results for FTOHs were below detection in the GAPS samples, likely due to a low sorption capacity of polyurethane foam (PUF) disks for FTOHs.¹⁹

In an effort to expand the applicability of PUF disks to more volatile chemicals such as the FTOHs, a PUF disk impregnated with XAD-4 powder (or SIP disk—sorbent-impregnated PUF disk) was developed. XAD is a styrene–divinylbenzene copolymer with relatively high sorptive capacity for organic and polar chemicals, compared to PUF.^{20–22} Galarneau et al. successfully used XAD-impregnated glass fiber filters as an alternative to PUF plugs to collect gas-phase semivolatile organics in high-volume air samplers.²³ This study describes the coating and calibration of SIP disk samplers for passive air sampling of FTOHs and PFASs.

EXPERIMENTAL SECTION

Chemicals. Fluorotelomer alcohols, perfluorohexylethanol, perfluorooctylethanol, and perfluorodecylethanol (6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, 98% purity), respectively, were purchased from Oakwood Products Inc. (West Columbia, SC). Perfluoroalkyl sulfonamides, *N*-methylperfluorooctane sulfonamidoethanol (MeFOSE), *N*-ethylperfluorooctane sulfonamidoethanol (EtFOSE), and *N*-methylperfluorooctane sulfonamide ethylacrylate (MeFOSEA) were obtained from the 3M Co. *N,N*-dimethylperfluoro-1-octane sulfonamide (*N,N*-Me₂FOSA, 98% purity) was used as internal standard for volume correction, and methyl-D₃-perfluorooctane sulfonamide (D₃-MeFOSA, 98% purity), 2-*N*-(deuteriomethylperfluoro-1-octanesulfonamido)tetradeuterioethanol (D₇-N-MeFOSE, 98% purity), and 2-perfluorooctyl-[1,1-²H₂,1,2-¹³C₂]ethanol (¹³C 8:2 FTOH, 98% purity) were used as surrogates for checking recoveries (Wellington Laboratories, Guelph, ON, Canada).

Preparation of SIP Disks. Prior to coating, PUF disks (14 cm diameter × 1.35 cm thick; surface area, 365 cm²; mass, 4.40 g; volume, 207 cm³; density, 0.0213 g cm⁻³; Tisch Environmental) were precleaned by first washing in water and then extracting by Soxhlet—first using acetone for 24-h and then for a further 24-h using petroleum ether. The PUF disks were dried in a vacuum

desiccator for ~18 h and stored in solvent-rinsed glass jars until used.

Amberlite XAD-4 (Supelco, Bellefonte, PA) was cleaned by successive sonications (30 min) with methanol, dichloromethane, and hexane and then ground to a powder in a Retsch planetary ball mill to an average particle size of 0.75 μm according to the method described by Gundel and Lane.²⁴ The XAD powder was further cleaned in a porous thimble by successive 24-h Soxhlet extractions using methanol, dichloromethane, and hexane and then dried in a vacuum desiccator. XAD-4 was used due to its larger surface area of 725 m² g⁻¹ and mean pore diameter of 40 Å compared to 300 m² g⁻¹ and 90 Å for XAD-2.

SIP disks were prepared according to a method adapted from Gundel and Hering²⁵ and, more recently, Galarneau et al.²³ for coating glass fiber filters. An XAD-4/hexane slurry (6.4 g L⁻¹) of 1700 mL was prepared in a large glass beaker. This was sonicated for 30 min and then stirred using a magnetic stir bar to suspend XAD powder during the coating step. Using tongs to hold the PUF disk, each disk was dipped into the slurry and held for 30 s. The disk was lifted from the slurry, and excess solution was allowed to drain back into the beaker. With each successive dipping (3 times), the solvent was allowed to drain from different sides of the disk to help ensure a uniform coating. The disks were laid on precleaned, heated aluminum foil (30–40 °C for ~5 min) after the last dipping. Ten SIP disks were prepared from each batch of slurry. SIP disks were dried in a vacuum desiccator for 2–3 days. The aforementioned procedure led to PUF disks that were uniformly impregnated with XAD-4 powder (Figure 1), with an average XAD-4 mass of 435 mg (standard deviation of 68 mg or ~15%, *n* = 75).

Uptake Study. SIP and PUF disks were calibrated by deploying them in a large, recently carpeted library of an office building (constructed ca. 1970). Twelve PUF disks and eight SIP disks were deployed individually in “indoor” chambers (Tisch Environmental, Village of Cleves, OH) situated on top of book shelves (~2.5-m height). The chambers are similar to ones used in other studies,²⁶ protected PUF and SIP disks from deposition of coarse particles. PUF disks were deployed for 120 days from December 2005 to April 2006. Duplicate PUF disks were harvested on days 14, 47, and 84 to verify reproducibility. SIP disks were deployed over the period from July to November 2006. PUF and SIP disks were collected at different intervals to investigate their uptake profile. Details on the deployment of PUF disks are provided elsewhere.¹⁹

Low-volume active air samples were collected throughout the time course of the uptake study using a BGI-400-4 personal air sampler (from BGI Inc., Waltham, MA). The sampling rate was adjusted to ~3 m³ day⁻¹ (~2 L min⁻¹) to be in the same range as previously estimated sampling rates of PUF disk samplers.²⁶ A PUF-XAD sandwich contained in the ORBO-1000 glass sampling

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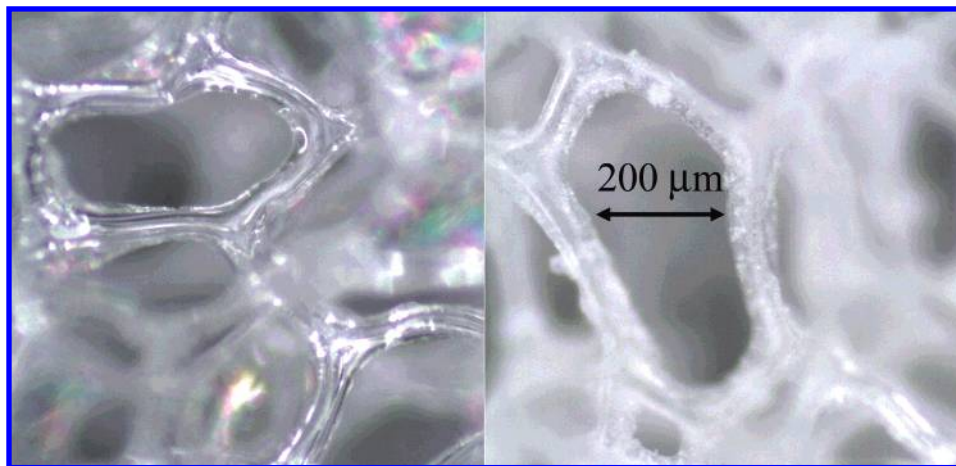


Figure 1. Optical microscopy magnifications (50 \times) showing a single cavity of an uncoated PUF disk (left) and an XAD-4 impregnated PUF disk (SIP) (right).

head (Supelco, Bellefonte, PA) was used as the sampling medium (first PUF, 22 mm o.d. \times 38 mm; followed by 1.6 g of XAD-2; and a second PUF, 22 mm o.d. \times 38 mm). Five active samples were collected for periods of \sim 14 days each, with air sample volumes of \sim 60 m³.

For two of the samples, a quartz fiber filter (QFF) was included at the top of the sampling head to assess sorption of target compounds to the particle phase. Breakthrough of target compounds was also evaluated during two of the samples by adding a second cartridge containing 6 g of XAD-2 downstream of the first PUF-XAD cartridge. Breakthrough tests were also assessed for high-volume air samples (PS-1). In these cases, 12 g of XAD was used in the PUF-XAD-PUF cartridge.

Sample Analysis. Prior to Soxhlet extraction, samples (SIPs, the combined PUF-XAD cartridges from active air samples and XAD from breakthrough test samples) were fortified with the following surrogates to check recoveries: ¹³C 8:2 FTOH, D₃-MeFOSA, and D₇-N-MeFOSE (10 μ L of 10 ng μ L⁻¹ each). PUF, SIP, and PUF-XAD were extracted by Soxhlet using 50/50 petroleum ether/acetone. QFFs were extracted with dichloromethane. Extractions were carried out for \sim 24 h. All extracts were concentrated by rotary evaporation and then further concentrated to \sim 0.5 mL under a gentle stream of nitrogen using ethyl acetate as keeper. For SIP disks, a centrifugation step (4000 rpm for 10 min) was required to separate particles (very small amounts of abraded foam and/or XAD powder). *N,N*-Me₂FOSA was added as an internal standard to correct for volume differences just prior to transferring the samples to the vials in preparation for analysis by gas chromatography/mass spectrometry (GC/MS).

Quantification of FTOHs and PFASs in samples was performed by gas chromatography–positive chemical ionization (PCI) mass spectrometry using a Hewlett-Packard 6890 GC-5973 mass-selective detector in the selective ion monitoring mode. Methane was used as reagent gas for PCI mode. Details on ions (*m/z*) monitored are provided in the Supporting Information, Table S1. Analytes were separated on a 30-m DB-wax column with a 0.25-mm i.d. and a 0.25- μ m film thickness. The oven temperature was 60 $^{\circ}$ C, 10 min, 8 $^{\circ}$ C min⁻¹ to 150 $^{\circ}$ C, and then 10 $^{\circ}$ C min⁻¹ to 210 $^{\circ}$ C. For confirmation, samples were also run on a 60-m DB5 column with 0.25-mm i.d. and 0.25- μ m film thickness with helium as the carrier gas. The GC oven temperature was 60 $^{\circ}$ C, 10 min,

10 $^{\circ}$ C min⁻¹ to 240 $^{\circ}$ C, and then 30 $^{\circ}$ C min⁻¹ to 290 $^{\circ}$ C. All injections (2 μ L) were splitless, with split opened after 0.5 min, and the injector at 200 $^{\circ}$ C. The ion source and quadrupole temperatures were 250 and 106 $^{\circ}$ C in PCI mode. Quantification was based on peak areas. Analyte concentrations were calculated using a five-point calibration using a linear fit.

RESULTS AND DISCUSSION

Quality Assurance/Quality Control. Surrogate recoveries determined for all passive and active samples were 87 ± 15 , 126 ± 50 , and $86 \pm 21\%$ for ¹³C 8:2 FTOH, D₇-N-MeFOSE, and D₃-MeFOSA, respectively. Samples were recovery-corrected as follows: ¹³C 8:2 FTOH was used for 6:2, 8:2, and 10:2 FTOHs, D₃-MeFOSA was used for methyl perfluorosulfonamide (MeFOSA) and ethyl perfluorosulfonamide (EtFOSA) and D₇-N-MeFOSE was used for methyl perfluorosulfonamidoethanol (MeFOSE) and ethyl perfluorosulfonamidoethanol (EtFOSE), respectively. Blank values were assigned to the time zero for the uptake study. Duplicate PUF disks, taken to assess the PUF uptake profile, showed less than 15% variability (Figures 2a and 3a) in most cases; however, there were some instances where variability was higher, up to \sim 40%. This is consistent with the findings of Gouin et al.²⁷ that showed a coefficient of variance of 30% for numerous duplicate PUF disk samples.

Breakthrough. The sampling efficiency of the PUF and XAD for trapping gas-phase target compounds was tested in a series of separate breakthrough experiments using both low-volume and high-volume samplers. For high-volume air samples ($n = 3$, air volume \sim 300 m³), a PUF-XAD-PUF sandwich was used. The top PUF was separated from the XAD and bottom PUF and analyzed individually to assess breakthrough in the first (top) PUF. Substantial breakthrough through the top PUF was observed for 6:2, 8:2, and 10:2 FTOHs with $>95\%$ of the total FTOHs detected in the XAD, indicating that the PUF plug itself is not adequate as sampling media for FTOHs. Breakthrough values for other compounds were as follows: \sim 40% for MeFOSA and EtFOSA and $<8\%$ for MeFOSE and EtFOSE. For low-volume air samples ($n = 2$, air volume 60 m³), a second XAD-2 column was connected downstream of the PUF-XAD-PUF sampling train. The 6:2 FTOH

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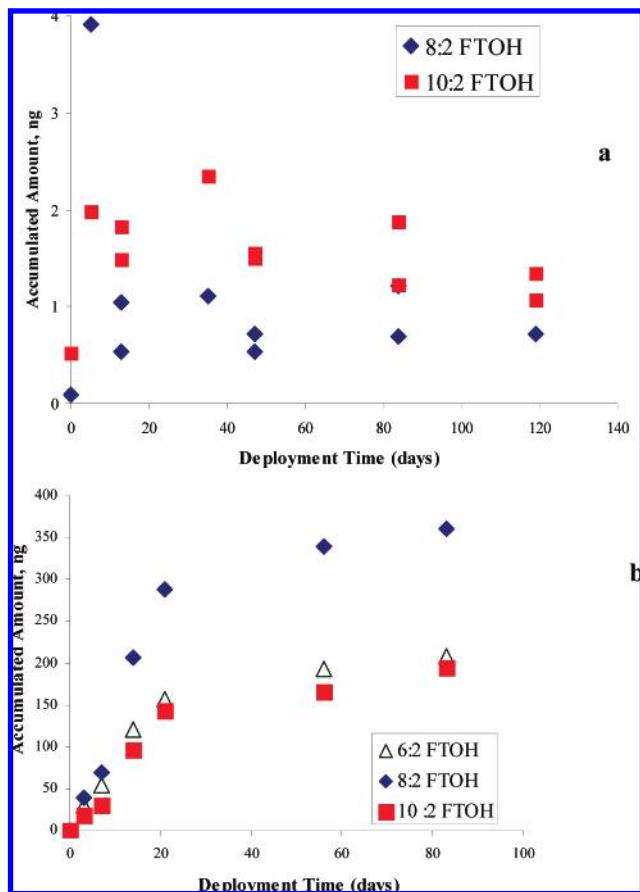


Figure 2. Sampling profiles for FTOHs presented as the amount (ng) accumulated after each time interval for PUF disks (a) and SIP disks (b). Note that 6:2 FTOH in PUF disks was below detection in all samples.

was the only target analyte detected in the downstream trap with ~30% breakthrough.

Theory of Passive Air Samplers. The accumulation of chemical by a passive air sampler is equivalent to the rate of uptake minus the rate of loss²⁸ and can be described by

$$V_{\text{PSM}} (dC_{\text{PSM}}/dt) = k_A A_{\text{PSM}} (C_A - C_{\text{PSM}}/K_{\text{PSM-A}}) \quad (1)$$

where V_{PSM} is the volume of the passive sampling medium (PSM) (cm^3), C_{PSM} and C_A are concentrations (ng m^{-3}) in the PSM and air respectively, A_{PSM} is the planar area of the passive sampler (cm^2), k_A is the air-side mass-transfer coefficient (cm s^{-1}), and $K_{\text{PSM-A}}$ is the PSM-air partition coefficient. Initially, when the term $C_{\text{PSM}}/K_{\text{PSM-A}}$ is small (because C_{PSM} is minimal) uptake is linear and a function of k_A , A_{PSM} , and C_A . Ideally, these are the conditions under which the passive sampler will function when deployed in the field when a time-weighted sampling is desired. As chemical builds up in the PSM, the term $C_{\text{PSM}}/K_{\text{PSM-A}}$ becomes more important; uptake is reduced and becomes curvilinear. Finally, when C_{PSM} establishes its equilibrium (equal fugacity) value such that $C_{\text{PSM}}/K_{\text{PSM-A}} = C_A$, there is no net uptake and C_{PSM} reaches a plateau.

The two parameters that govern the uptake profile (k_A and $K_{\text{PSM-A}}$) can be determined experimentally from an exposure/

Table 1. Total Air Concentrations (pg m^{-3} , Gas + Particle Phase) for Target Compounds Collected with Low-Volume Samplers ($n = 5$)

compound	mean, pg m^{-3}	range, pg m^{-3}	% on particles ($n = 2$)
6:2FTOH	1680	2330–982	nd ^a
8:2FTOH	3350	4790–2060	nd
10:2FTOH	1700	2160–1270	nd
EtFOSA	86	96–67	nd to 3
MeFOSA	BDL	BDL	BDL
MeFOSE	273	395–161	25 ; 41
EtFOSE	188	276–100	26 ; 58
MeFOSEA	BDL	BDL	BDL

^a nd, not detected.

uptake study. This is done by exposing the sampler to a constant air concentration and monitoring the accumulation of target analytes in the PSM over time. From a plot of C_{PSM} versus time, k_A is derived from the linear portion and $K_{\text{PSM-A}}$ from the plateau phase, with knowledge of the ambient C_A . The sampling rate (R , $\text{m}^3 \text{day}^{-1}$) can be determined by dividing the slope by C_A .

Further details for calibration of PUF disk-type passive air samplers are given by Shoeib and Harner²⁸ and Harner et al.²⁹

Ambient Air Concentrations of Target Chemicals, C_A , in the Library. Air concentrations of target compounds in the library, determined from low-volume air samples ($n = 5$), are summarized in Table 1. Target compounds include fluorotelomer alcohols: 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, and perfluoroalkyl sulfonamides: MeFOSA, EtFOSA, MeFOSE, and EtFOSE. Over the PUF and SIP deployment period, FTOHs were the dominant target analytes in the library atmosphere, representing more than 90% of the total. The 8:2 FTOH had the highest average air concentrations (pg m^{-3}) at 3350, followed by 10:2 FTOH at 1700 and 6:2 FTOH at 1680. Concentrations of FTOHs in this indoor environment were approximately 10–100 times higher than reported for outdoor ambient air in North America,^{16,30–33} Germany,³⁴ and Northwest Europe.³⁵ An indoor study that collected high-volume samples in Norwegian homes reported air concentrations (pg m^{-3}) of 2990, 3424, and 3559 for 6:2, 8:2, and 10:2 FTOH, respectively.³⁵

Of the remaining target compounds, MeFOSE shows the highest air concentration (pg m^{-3}) of the perfluoroalkyl sulfonamides at 273 followed by EtFOSE at 188 and EtFOSA at 86. The values for MeFOSE and EtFOSE are toward the low end of the range of values previously reported in the indoor air samples from an indoor air survey in Ottawa in 2002/03³¹ but still ~1 order of magnitude higher than typical outdoor ambient levels that have been reported in the literature.^{16,30–33} EtFOSA, which is used as

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Table 2. Calibration Results for PUF and SIP Disks

	C_{Air} (pg m ⁻³)	C_{PSM} (pg disk ¹)	C_{PSM} (pg m ⁻³ disk)	$K_{\text{PSM-A}}$	$\log K_{\text{PSM-A}}$	k_A (m d ⁻¹)	R (m ³ d ⁻¹)
PUF Disks							
6:2 FTOH	1680	—	—	—	—	—	—
8:2 FTOH	3350	1100	5.25×10^6	1570	3.196	—	—
10:2 FTOH	1700	1600	7.64×10^6	4484	3.652	—	—
N-EtFOSA	86	2000	9.55×10^6	110994	5.05	—	—
N-MeFOSE	273	12000	5.73×10^7	209790	5.32	4.06×10^1	1.5
N-EtFOSE	188	8000	5.73×10^8	203095	5.31	3.79×10^1	1.4
SIP Disks							
6:2 FTOH	1680	200000	9.55×10^8	568182	5.754	—	4.6
8:2 FTOH	3350	375000	1.79×10^9	535059	5.728	1.24×10^2	4.6
10:2 FTOH	1700	200000	9.55×10^8	560508	5.749	1.22×10^2	4.6
N-EtFOSA	86	150000 ^a	7.16×10^8	> 8324524	> 6.920	7.04×10^1	2.6
N-MeFOSE	273	210000 ^a	1.00×10^9	> 3671329	> 6.565	4.06×10^1	1.5
N-EtFOSE	188	120000 ^a	5.73×10^9	> 3046422	> 6.484	3.79×10^1	1.4

^a SIP disks did not reach equilibrium over the 83-day course of the experiment; values were taken at the end of the deployment time to calculate the lower limit of $K_{\text{SIP-A}}$.

an insecticide, registered as Sulfluramid, for the control of termites and other indoor pests, has been reported in outdoor ambient air from North American cities at the following concentrations (pg m⁻³): Toronto, 15³⁰ and 1¹⁶; Cleves, OH, 40; Reno, NV, 55³² and European cities Hamburg and Waldhof, Germany, at 3.1 and 2.6, respectively,³⁴ and Hazelrigg and Manchester, UK, at 5.8 and 6.7, respectively.³⁵ MeFOSE and MeFOSEA were below detection in all of the library air samples.

PFASs were detected in both the gas and particle phases (Table 1) of the low-volume air samples. The particle phase represented >25% of the total concentration for MeFOSE and EtFOSE and less than 3% for EtFOSA. Other studies have also reported particle association for the PFASs, particularly MeFOSE and EtFOSE.^{16,33–34} The 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were not detected in the particle phase. However, measurements in the Arctic region did detect some minimal particle association for the FTOHs,¹⁶ and ocean-derived mist/aerosols were discussed as a potential source.

It is noteworthy that concentrations of target compounds in the library atmosphere decreased gradually over the period of the study (December 2005 to October 2006). This may be attributed to a gradual reduction in emission from the recently installed carpets or changes in building ventilation over this period. As a result of the gradual decline of C_A during the course of the calibration, it was necessary to correct the uptake curve using a moving average C_A .

Calibration Results for PUF Disks and Sorbent-Impregnated PUF (SIP) Disks. Fluorotelomer Alcohols. The rapid equilibration of 8:2 and 10:2 FTOHs in the PUF disks is shown in Figure 2a (6:2 FTOH was below detection). With the exception of one apparent outlier on day 5, the amount of FTOH in the PUF disk remained relatively constant over the deployment period with a slight drop-off toward the end of the study, consistent with the low-volume air sample results that showed a similar decline.

The effective air volume for a chemical that has come to equilibrium in a PUF disk (V_{AIR} , m³) can be determined from the ambient air concentration, C_A , and the amount accumulated on the PUF disk. V_{AIR} represents the volume of air that the PUF disk has sampled in its approach to equilibrium. Or alternatively, $K_{\text{PSM-A}}$ is the equivalent volume of air that contains the same mass

of analyte as 1 unit volume of passive sampling medium under equilibrium conditions, i.e., $K_{\text{PSM-A}} = V_{\text{AIR}}/V_{\text{PSM}} = C_{\text{PSM}}/C_{\text{AIR}}$.²⁹

This allows air concentrations for FTOHs to be derived from PUF disk data by dividing the mass of FTOHs accumulated on the PUF disk by the V_{AIR} value. From Figure 2a, the average amount of 8:2 and 10:2 FTOH collected on the PUF at equilibrium was 1.1 and 1.6 ng, respectively. Dividing the amount accumulated by the average air concentrations in library air (Table 1) produces effective air volumes of ~0.4 and ~1.2 m³ for 8:2 and 10:2 FTOH, respectively. These low volumes of air sampled are consistent with breakthrough results that showed very low sorptive capacity for the PUF disks.

The ratio of C_{PUF} and C_A is the PUF-air partition coefficient, $K_{\text{PUF-A}}$. Previous studies for nonpolar hydrophobic chemicals have shown that $\log K_{\text{PUF-A}}$ is well correlated to $\log K_{\text{OA}}$ and can be calculated as: $\log K_{\text{PUF-A}} = 0.6366 \log K_{\text{OA}} - 3.1774$.²⁸ However, this relationship does not hold for the FTOHs. For instance, the $\log K_{\text{OA}}$ at 25 °C of 5.56 reported for 8:2 FTOH³⁶ corresponds to a predicted $\log K_{\text{PUF-A}}$ value of 4.7. The measured value of $\log K_{\text{PUF-A}}$ from this study of 3.2 (Table 2) is more than 1 order of magnitude lower than the predicted value, again indicating the lower than expected sorptive capacity of PUF disks for the FTOHs. These results emphasize the need to develop new partitioning relationships for FTOHs and other fluorinated chemicals.

The addition of only 0.4 g of XAD-4 powder to PUF disks results in a greatly increased sorptive capacity (Figure 2b) of SIP disks for FTOHs. The uptake profile now exhibits a linear portion lasting ~3 weeks. This is beneficial in circumstances where it is preferable to have a time-weighted, integrated air sample. Because sampling media blank values tend to increase with the sorptive capacity, it is important to design the sampler to achieve a balance of adequate sorptive capacity for target compounds for the planned duration of deployment. In other words, a SIP disk with more than 0.4 g of XAD-4 would not necessarily be beneficial for our purposes. However, in some cases where longer deployment times are required, for instance, when volatile compounds are targeted, it may be necessary to increase the loading of XAD-4 in order to

(36) Goss, K.-U.; Bronner, G.; Harner, T.; Hertel, M.; Schmidt, T. C. *Environ. Sci. Technol.* **2006**, *40*, 3572–3577.

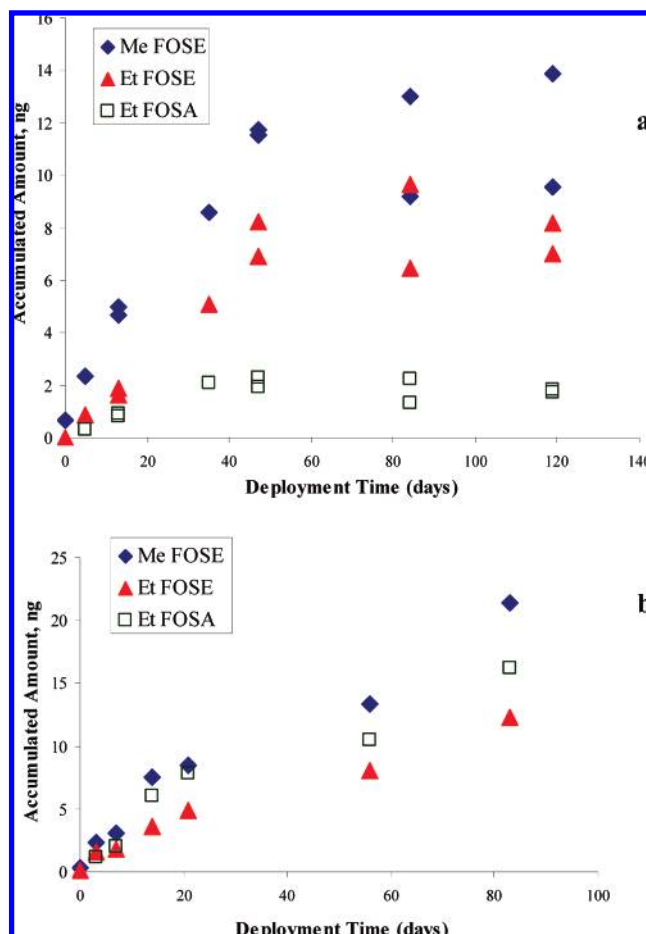


Figure 3. Sampling profiles for PFASs presented as the amount (ng) accumulated at each time interval for PUF disks (a) and SIP disks (b).

ensure time-weighted, linear, sampling for the duration of deployment.

Linear uptake rates R ($\text{m}^3 \text{ day}^{-1}$) for FTOHs in the SIPs were calculated for the first 21 days of deployment and are given in Table 2. $K_{\text{SIP-A}}$ values based on equilibrium (plateau phase) are also presented in Table 2. With these two parameters, effective air volumes for SIP disks samplers can be calculated under a range of deployment periods.

Perfluoroalkyl Sulfonamides. Figure 3 shows the uptake profile for the PFASs (EtFOSA, MeFOSE, and EtFOSE) for PUF disks (a) and SIP disks (b). PFASs exhibit linear sampling in PUF disks for several weeks prior to reaching equilibrium whereas, for SIPs, their profiles are linear for the entire duration of the study.

PUF disk sampling rates ($\text{m}^3 \text{ day}^{-1}$) for MeFOSE and EtFOSE calculated over the linear uptake range (that extends for ~ 47 days) and using air concentration data from Table 1, were 1.4 and 1.5 ($R^2 = 0.99$), respectively. These are lower but within a factor of ~ 2 of values previously established for PUF disks deployed during the Ottawa study, using collocated passive and low-volume samplers.³¹ The lower values in the library study may be due to more variable air concentrations. As discussed previously, the air concentrations in the library declined gradually during the uptake study. It is also possible that the low air flow in the library where the samplers were positioned above book shelves and near the

ceiling may have resulted in reduced mass-transfer rates. For SIP disks, the lower sampling rates for the PFASs (~ 1.4 – $2.6 \text{ m}^3 \text{ day}^{-1}$ for MeFOSE/EtFOSE to EtFOSA, respectively) compared to the FTOHs ($\sim 4.6 \text{ m}^3 \text{ day}^{-1}$) may be partly explained by particle association of the PFASs. The calculated sampling rates are based on total air concentrations whereas passive samplers have been shown to sample mainly gas phase, although fine/ultrafine particles are also collected.²⁶ Alternatively, it is also possible that the discrepancy is real and due to some sampling advantage of the FTOHs. This is an area for further study.

$K_{\text{PUF-A}}$ values determined from C_{PUF} (in the plateau phase) and C_{AIR} are given in Table 2. Consistent with the results for FTOHs, the $K_{\text{PUF-A}}$ values are much lower than predicted using the $K_{\text{PUF-A}} - K_{\text{OA}}$ relationship developed for nonpolar hydrophobic chemicals.²⁸ For instance, based on $\log K_{\text{OA}}$ values (20°C) reported for MeFOSE and EtFOSE (7.7 and 7.8, respectively),³³ the predicted $\log K_{\text{PUF-A}}$ values are 6.0 and 6.1, whereas the measured values are ~ 5.3 for both chemicals (Table 2), ~ 1 order of magnitude smaller.

Because SIP disks did not establish equilibrium over the 83-day course of the experiment, it was not possible to quantify the SIP–air partition coefficient, $K_{\text{SIP-A}}$. Instead the result was reported as the lower bound, i.e., greater than some $K_{\text{SIP-A}}$ value. The amount accumulated in SIP disk at the end of the 83-day period was used to calculate this lower limit.

Linear uptake rates for PFASs in the SIP disks were calculated for the entire deployment period and are given in Table 2. The derived sampling rates of ~ 1.4 – $2.6 \text{ m}^3 \text{ day}^{-1}$ are similar to the values derived for PUF disks (Table 2). This is expected because uptake by PUF disks is air-side controlled and hence proportional to the planar surface area of the PUF disk, which is not different for the SIP disks.²⁸

SIP Disk Sampling Profile. As discussed previously, $K_{\text{PSM-A}}$ or, in this case, $K_{\text{SIP-A}}$ is the equivalent volume of air that contains the same mass of analyte as 1 unit volume of SIP under equilibrium conditions, i.e., $K_{\text{SIP-A}} = V_{\text{AIR}}/V_{\text{SIP}} = C_{\text{SIP}}/C_{\text{AIR}}$. Thus, by analogy and replacing terms in eq 1, the equivalent air sample volume is,²⁹

$$V_{\text{AIR}} = K_{\text{SIP-A}} V_{\text{SIP}} (1 - \exp[-(A_{\text{SIP}})/(V_{\text{SIP}})(k_A/K_{\text{SIP-A}})] t) \quad (2)$$

Figure 4 is a plot of V_{AIR} versus time, constructed using k_A and $K_{\text{SIP-A}}$ values from Table 2 for the FTOHs and MeFOSE. For the FTOHs, which experience curvilinear sampling after the first several weeks, it is particularly important to derive the effective air volume using eq 2 for long deployment times when estimating air concentrations, to account for reduced sampling rates (and hence, the lower air sample volume) as equilibrium is approached.

For MeFOSE and other PFASs that have a large $K_{\text{SIP-A}}$ value, eq 2 is less critical and the linear sampling rate, R ($\text{m}^3 \text{ day}^{-1}$) can be used to estimate the sample air volume. It is important to note that $K_{\text{SIP-A}}$ values listed in Table 2 will vary depending on the type of PUF disk used and amount of XAD-4 coated onto them. Because XAD-4 dominates the sorptive capacity of the SIP, $K_{\text{SIP-A}}$ can be expected to be roughly proportional to the amount of XAD-4 coated onto the PUF disk. For more accurate determina-

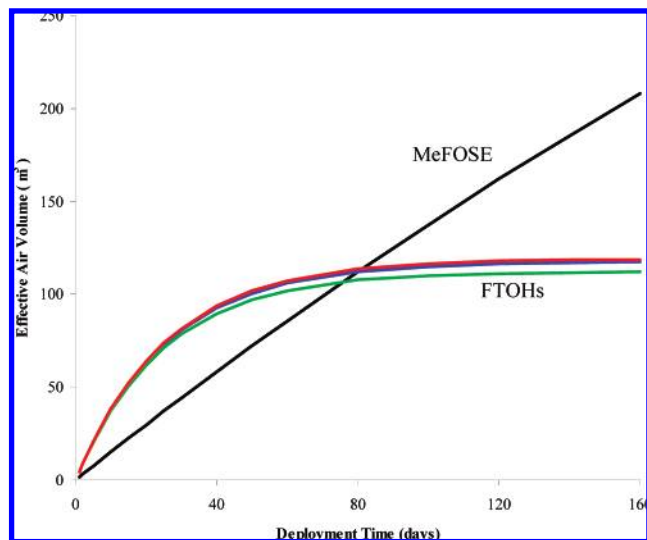


Figure 4. Uptake profile for MeFOSE and 6:2, 8:2, and 10:2 FTOHs for SIP disks derived using eq 2 and uptake parameters listed in Table 2.

tions of air concentrations using SIP disks, it may be desirable to use depuration compounds (DCs).^{27,29} These are isotopically labeled compounds that can be added to the SIP disks prior to exposure. Because sampling by SIP disks is air-side controlled, the mass-transfer coefficient and hence sampling rate can be derived from the loss of the DCs during deployment. Ideally, several DCs should be used that represent all classes of target chemicals.

One topic that merits further exploration is the mechanism of sorption of target compounds to the PUF versus SIP disks. The theory of PUF disk samplers is based on the assumption of absorption into the polymeric material, uniformly throughout the PUF and kinetics that are driven by air-side control.²⁸ The sorption capacity of SIP disks, however, is defined by the sum of the

absorption to PUF and adsorption to XAD powder. The contribution of the XAD powder becomes increasingly important for chemicals such as the FTOHs, with low K_{OA} values, that do not absorb appreciably onto PUF, as this study highlights. This dual capacity of SIP disks may impact the shape of the uptake profile (particularly near the equilibrium point) and should be investigated in future, targeted studies. It would also be useful to define the point at which kinetics switches from air-side controlled to sorbent-side controlled. Previous work suggests that kinetics will become sorbent-side controlled for chemical with very low K_{OA} (or K_{PSM-A}) values.²⁸ This too will need to be investigated through controlled chamber studies.

Derived Indoor Air Concentrations of FTOHs from the Ottawa Campaign. In 2002–2003, an indoor sampling campaign was carried out in the city of Ottawa, Canada, using PUF disk passive samplers deployed in more than 50 homes. Details on the campaign are given elsewhere.³¹ Using the equivalent air volume estimates of 0.4 and 1.2 m³ for 8:2 FTOH and 10:2 FTOH derived from this calibration study, we are now able to derive air concentrations for FTOHs from amounts accumulated on the PUF disks. Results from 52 homes are presented in Figure 5. Air concentrations (pg m⁻³) of 8:2 FTOH range from 261 to 28 900 pg m⁻³ with geometric mean of 2070; 10:2 FTOH concentrations are slightly lower and range from 104 to 9210 pg m⁻³ with geometric mean of 890 pg m⁻³. The geometric mean values for 8:2 and 10:2 FTOH are within a factor of 2 of the average concentrations observed in the library during the calibration study. Again, these indoor air concentrations are 1–2 order of magnitude higher than outdoor^{16,30,32,34} making homes a likely important source to the atmosphere. It is also noteworthy that 8:2 FTOH and 10:2 FTOH were positively correlated ($R^2 = 0.94$, $p < 0.001$), indicating that they originate from the same source.

The combined burden of 8:2 and 10:2 FTOH in indoor air is similar to the burden associated with sulfonamido ethanols (sum of MeFOSE and EtFOSE) that were previously reported.³¹ Further,

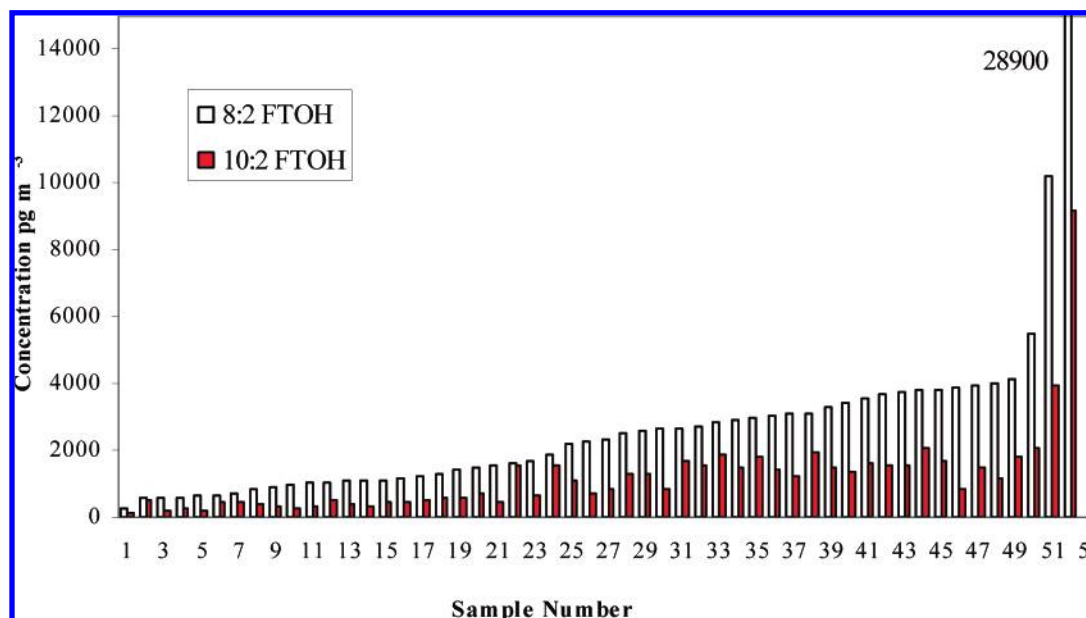


Figure 5. Derived indoor air concentrations of 8:2 FTOH and 10:2 FTOH from PUF disk air samples deployed in 52 homes during 2002–2003.

$\Sigma(8:2 + 10:2 \text{ FTOH})$ and $\Sigma(\text{MeFOSE} + \text{EtFOSE})$ were not correlated ($p = 0.8$), indicating different indoor sources of these chemical classes.

In summary, new information is presented for a novel passive air sampling device that builds on previous studies and experience using PUF disk air samplers. The greatly increased capacity of the SIP disk, compared to the PUF disk, makes it useful for more volatile compounds when time-integrated sampling is desired. More work is planned to further develop and test SIP disks for application to a broader range of chemicals during field deployments and for potential application of DCs to confirm site specific sampling rates for SIP disks.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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