

Indoor Air & Dust Concentrations of Fluorotelomer Alcohols

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Introduction

Perfluorooctane sulfonate (PFOS) and perfluorocarboxylic acids (PFCAs) are globally distributed contaminants that are detected in human and other biological samples. Recent studies have elucidated the biotic and abiotic transformation pathways of fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamido ethanols (PFAS) to PFCAs and PFOS respectively (1, 2). PFAS and FTOH are known to occur in commercial products used in indoor environments. Indoor environments may in turn act as a key source of these chemicals to the outside environment. Further, elevated concentrations of these chemicals in indoor air and dust may be important pathway of human exposure (3).

This study presents the first coupled indoor air and dust concentrations of FTOHs, from a survey of 60 homes in Ottawa, Canada collecting during 2002/03. Results are compared to levels of PFAS reported for the same study (3). The results for FTOH were made possible by calibration of the polyurethane foam (PUF) disk samplers for FTOHs. The calibration showed that PUF disks equilibrate quickly with ambient air FTOHs (in a matter of several hours), allowing air concentrations to be derived from the puf-air partition coefficient, in a similar approach as used for rapidly equilibrating thin-film samplers (4).

Materials and Methods

Calibration of PUF disk samplers for FTOHs

Ten PUF disks passive samplers were deployed in a large, recently carpeted library of an office building (constructed ca. 1970) over 119 days to assess their uptake of FTOHs over time. PUF disks purchased from Tisch Environmental (Village of Cleaves, OH) were collected at different intervals and duplicates taken on days 13, 47, 84 and 119 to check reproducibility. Five active air samples were collected over the course of the study using a low-volume air sampler (BGI-400-4 Personal Air Sampling Pumps, BGI Incorporated, Waltham, MA). The glass sampler head (ORBO-1000, i.d. 22 mm, from Supelco) comprised a PUF/XAD sandwich – top PUF plug (22 mm o.d. x 76 mm) followed by 1.6g of XAD-2, and bottom PUF plug (22 mm o.d. x 38 mm). The active sampler was run for 14 day increments, equivalent to ~60m³ of air. Details on passive sampler preparation and collection of indoor air and dust samples are given elsewhere (3).

Sample extraction and analysis

Prior to extraction, sampling media were spiked with the following surrogates: 8:2 ¹³C FTOH, D₃-MeFOSA and D₇ MeFOSE (10ul of 10 ng/ul each). PUF disks PAS and PUF/XAD sandwich were extracted with 50/50 petroleum ether/acetone. 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. N,N-MeFOSA was added as an internal standard to correct for volume differences. Quantitation of FTOHs in samples 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.

Results and Discussion

Quality assurance/Quality control

Surrogate recoveries for PUF disks used for the uptake study and low volume active samples were: 87% ±15%, 126%±50% and 86%±21% for ¹³C FTOH 8:2, D₇-N MeFOSE and D₃- N MeFOSA respectively. Data were corrected as follows: ¹³C FTOH 8:2 was used for 6:2, 8:2 and 10:2 FTOHs; D₃- N MeFOSA was used for Me FOSA and Et FOSA; D₇-N MeFOSE was used for MeFOSE and EtFOSE data. Blank values were assigned to the time zero for the uptake curve. 10:2 and 8:2 were detected in PUF blanks (n=3) at average of 15 to 23% of

the level detected in the samples respectively and less than 5 % for PFASs. Duplicate PUF disk samples showed less than 15% variability in 80% of the samples.

Calibration of PUF disks for FTOHs:

Table 1 presents average concentrations (pg/m^3) derived from low volume active air samples during the library calibration study for several fluorinated compounds: 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, ethyl perfluorosulfonamide (EtFOSA), Methyl perfluorosulfonamido ethanol (MeFOSE) and ethyl perfluorosulfonamido ethanol (EtFOSE). The fluorotelomer alcohols represented more than 90% of total fluorinated compounds detected in the library. 8:2 FTOH (mean, $3345 \text{ pg}/\text{m}^3$) was the most abundant, followed by 10:2 FTOH and 6:2 FTOH (1703 and $1680 \text{ pg}/\text{m}^3$, respectively). Levels of FTOHs were 20-100 times higher than outdoor ambient air in North America (3, 5). MeFOSE show the highest level of sulfonamides with total average concentration (pg/m^3) of 273 followed by EtFOSE at 188 and EtFOSA at 86.

Results for the PUF disks study showed that FTOHs had equilibrated rapidly and concentrations in the PUF disk remained constant over the entire study period, demonstrating the relatively low sorptive capacity of PUF for FTOHs. Based on mean air concentrations derived from the active samples (Table 1) and the constant concentration in the PUF disks, PUF-air partition coefficients were calculated and converted to equivalent air volumes following the approach described by Harner et al. (4). Equivalent air volumes were $\sim 0.4 \text{ m}^3$ (8:2 FTOH) and $\sim 1.0 \text{ m}^3$ (10:2 FTOH). Levels of 6:2 FTOH in the PUF disk were below detection, a reflection of the low sorption capacity of PUF disks for volatile chemicals.

Uptake profiles for PFASs in the library calibration study were linear with the exception of EtFOSA that began to plateau after ~ 30 days and MeFOSE and EtFOSE that began to plateau after ~ 50 days.

FTOHs Concentrations Ottawa Study Indoor Air Samples

Using the equivalent air volumes for 8:2 FTOH and 10:2 FTOH determined from the calibration study (indicated above), air concentrations were derived from PUF disk samples that were deployed in 52 homes during 2002/03 over 3-week periods. Results are presented in Table 2 and Figure 1. It is important to note that PUF-disks operate as equilibrium samplers for FTOHs. Because they are responsive to changes in air concentrations of FTOHs (due to the low capacity of PUF disks for FTOHs) the results represent the air concentration in the last few hours that the sample was deployed, rather than an average for the entire deployment period, which is the case for passive air samplers that operate in the linear phase.

Geometric mean air concentrations for 8:2 and 10:2 FTOHs were 2065 and $891 \text{ pg}/\text{m}^3$ respectively with a few samples having exceptionally higher concentrations. Average blanks concentrations ($n=7$) were 245 and $44 \text{ pg}/\text{m}^3$ respectively. Air concentrations of 8:2 FTOH and 10:2 FTOH were well correlated ($r^2=0.73$; $p<0.01$), indicating that they likely stem from the same source. Interestingly, the FTOHs (8:2 or 10:2) were not correlated with PFASs (MeFOSE or Et FOSE; $p>0.8$) suggesting that these chemicals stem from different sources.

The geometric mean indoor air concentrations for FTOHs are 20 to 100 times higher than reported for outdoor air (3, 5). This demonstrates the potential role of indoor air as a source to the outside, through ventilation of indoor air. It also demonstrates the potential role indoor air inhalation as an exposure pathway of FTOHs for people.

Air –Dust correlation for FTOHs

FTOHs and PFASs in the dust samples from same homes were reported previously (6) and are shown in Table 2. Figure 2 compares paired dust and air concentrations for the same homes for 8:2 and 10:2 FTOHs. A good agreement with higher dust concentrations correlated to higher indoor air concentrations ($p<0.01$ in both cases) demonstrating that FTOHs in air reflect the levels in dust and likely originate from the same source.

References:

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 Table 1. Summary of low volume air concentrations of target compounds in library air (pg/m³), (n=5).

Compounds	6:2FTOH	8:2FTOH	10:2FTOH	Et FOSA	MeFOSE	EtFOSE
Mean	1680	3350	1700	86	273	188
Min	982	2060	1270	67	161	100
Max	2330	4790	2160	96	395	276

 Table 2 Passive sampler-derived indoor air concentrations (pg/m³) for Ottawa homes.

Compound	8:2FTOH	10:2FTOH	Et FOSA ^a	MeFOSE ^a	EtFOSE ^a
Air Concentrations, Ottawa Homes (n=52), pg/m ³					
Geo mean	2070	891	40	1490	744
Min	261	104	5.9	366	227
Max	28900	9210	646	8190	7740
Dust Concentrations, Ottawa Homes (n=60), ng/g ^b					
Geo mean	55	35	--	113	138
Min	3	2	--	3.3	1.4
Max	16300	8180	--	8860	75400

^aRef 3

^bRef 6

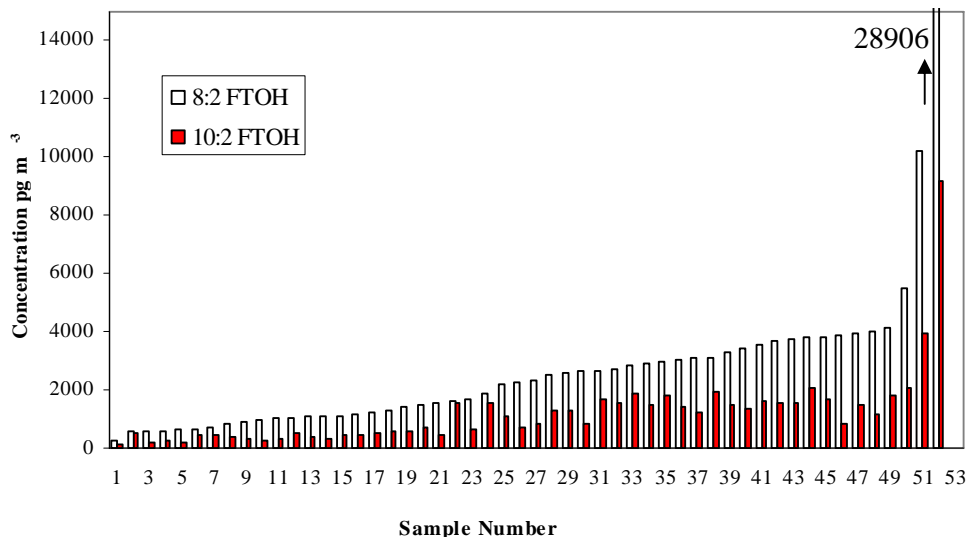


Figure 1. Indoor air concentrations of 8:2 FTOH and 10:2 FTOH from 52 homes in Ottawa, Canada during the winter 2002/2003.

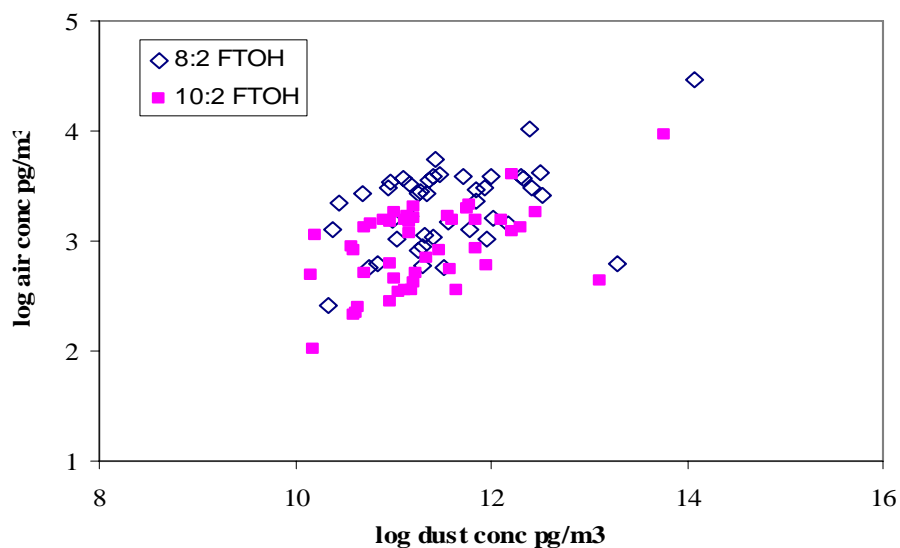


Figure 2. Correlation of air and dust concentrations from the same homes for 8:2 and 10:2 FTOHs. (Note: dust concentrations are expressed as pg/m^3 of dust assuming a dust density of 1g/cm^3 .)