

A Survey of Perfluoroalkyl sulfonamides in indoor and outdoor air using passive air samplers

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Introduction

Perfluorooctane sulfonate (PFOS) has recently emerged as a priority environmental pollutant due to its widespread detection in biological samples from remote regions including the Arctic and the Mid-North Pacific Ocean ^{1,2}. Because PFOS is fairly involatile, it is hypothesized that its occurrence in remote regions is the result of atmospheric transport of more volatile precursor compounds such as the perfluoroalkyl sulfonamides (PFASs) ³. PFASs are used in variety of consumer products for water and oil resistance including surface treatments for fabric, upholstery, carpet, paper and leather. In a recent pilot study employing high volume air samples, indoor air concentrations of PFASs were approximately 100 times greater than outdoor levels ⁴. This is of significance because people typically spend about 90% of their time indoors ⁵ and this exposure may serve as an important uptake pathway. Indoor air also serves as a source of PFASs to the outside where PFASs are ultimately transported and distributed throughout the environment. The current study is intended to be a more comprehensive survey of indoor and outdoor air allowing more confident conclusions to be made. Passive air samplers comprised of polyurethane foam (PUF) disks were used. These are quiet, non-intrusive samplers that operate without the aid of a pump or electricity. Air movement delivers chemical to the sampler which has a high retention capacity for persistent organic pollutants (POPs). PUF disks samplers have been previously used successfully to monitor different classes of hydrophobic persistent organic pollutants POPs ⁶⁻⁸.

Material and Methods

Sampling occurred in Ottawa, Canada during the winter of 2002/03. PUF disks passive samplers (14 cm diameter, 1.35 cm thick) were suspended in special chambers (Figure 1) to prevent the deposition of coarse particles and in the case of the outdoor chamber, to eliminate UV sunlight and minimize the effect of wind speed on uptake. Samplers were deployed in 58 homes for approximately 23 days and at seven outdoor locations in the city for approximately 60 days. More details are given elsewhere ⁹. Concurrent passive and low-volume air samples were taken at eight indoor locations (using BGI-400-4 Personal Air Sampling Pump) for the purpose of calibrating the passive samplers. To investigate reproducibility, duplicate PUF disk samplers were deployed at 8 homes and 3 outdoor locations.

PUF disks were Soxhlet extracted for 21 hours in petroleum ether, concentrated to 0.5 ml and transferred to iso-octane by rotary evaporation and nitrogen blow-down. PFASs were analyzed by gas-chromatography electron impact mass spectrometry (GC-EIMS) using a Hewlett-Packard 6890 GC-5973 mass selective detector MSD in selective ion monitoring (SIM) mode. Information on target chemicals is given in Table 1. Confirmation of EtFOSA was performed in negative chemical ionization (NCI) SIM mode, where methane was used as reagent gas with flow of 2.2 mL min^{-1} . 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 , 0.5 min, 3°C min^{-1} to 160°C , then $20^\circ\text{C min}^{-1}$ to 260°C . Splitless injections were $1 \mu\text{L}$ with split opened after 0.5 min, and the injector was at 250°C . The ion source and quadrupole were 230°C and 150°C for EI and 150°C and 106°C , respectively, for NCI analysis.

Table 1. Perfluoroalkylsulfonamides of interest

Compounds	Acronym	Molecular Formula	EI Ions
N methyl perfluorooctane sulfonamidoethanol	MeFOSE	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	526,462
N ethyl perfluorooctane sulfonamidoethanol	EtFOSE	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	540,448
N ethyl perfluorooctane sulphonamide	EtFOSA	$\text{C}_8\text{F}_{17}\text{SO}_2\text{NHCH}_2\text{CH}_3$	512,448
N methyl perfluorooctane sulfonamidethylacrylate	MeFOSEA	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$	526,462

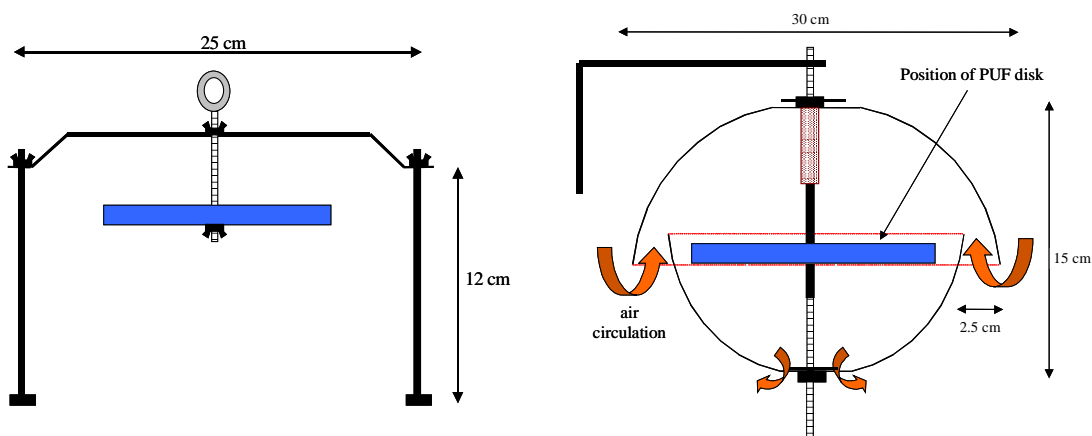


Figure 1. PUF disk passive air samplers used in indoor (left) and outdoor (right) air surveys of perfluorinated compounds.

Results and Discussion

Quality Control/Quality Assurance: Method recoveries for PFASs were determined previously by spiking PUF media just prior to extraction⁴. Total recoveries were $60\% \pm 6\%$ ($n=4$) for MeFOSE, $47\% \pm 7\%$ ($n=4$) for EtFOSE and $47\% \pm 7\%$ for MeFOSEA. Labeled fluorinated sulfonamides were not available at the time of this work. Field blanks (7 indoor and 3 outdoor)

were below the detection limit for EtFOSE, EtFOSA and MeFOSEA. MeFOSE was detected in indoor blanks with a mean value of $209 \pm 50 \text{ pg/m}^3$ and was below detection for outdoor blanks. No blank correction has been applied to the data. Duplicate samplers agreed well with differences ranging from 0.3 to 17%.

Results of the co-located (8 indoor sites) passive and low-vol active samplers indicate that the effective passive air sampling rate was approximately $2.5 \text{ m}^3 \text{ d}^{-1}$ for MeFOSE, EtFOSE and EtFOSEA. This agrees well with sampling rates for polybrominated diphenyl ethers (PBDEs) that were analyzed in the same samples⁹.

Figure 2a shows concentrations of MeFOSE and EtFOSE in indoor and outdoor air. MeFOSE exhibits a log-normal distribution with a geometric mean concentration of 1968 pg m^{-3} . The high level of MeFOSE is probably associated with its use in variety of products for water and oil resistance including surface treatments for fabric, upholstery, carpet and leather. Indoor air concentrations were 25 times higher than outdoors indicating that indoor air is likely to be an important source to the outside. Indoor air concentrations were also high for EtFOSE (geometric mean of 1033 pg m^{-3}) and similarly it was ~13 times greater than outdoor air. EtFOSE is more generally applied to foodwraps although it is also a by-product of other perfluorinated chemicals. No correlation was observed between MeFOSE and EtFOSE concentrations in indoor air. These indoor and outdoor air concentrations are comparable to recently published indoor and outdoor measurements using high volume samplers^{4,10}.

Figure 2b shows results for EtFOSA and MeFOSEA which exhibit concentrations about an order of magnitude lower than MeFOSE and EtFOSE. EtFOSA was detected in more than 90% of the indoor samples analysed with a geometric mean of 54 pg m^{-3} and MeFOSEA was only above the detection limit in 15% of samples with a geometric mean of 38 pg m^{-3} . Again, no correlation was observed between indoor air concentrations of any of the target chemicals.

In conclusion, the results of indoor air from 58 randomly selected residential homes show that some perfluoroalkyl sulfonamides exhibit very high indoor air concentrations. Since people spend majority of their time indoors, the inhalation exposure to these chemicals should be considered in the human exposure assessments. Furthermore, large indoor/outdoor gradients in air concentration exist for MeFOSE and EtFOSE. Therefore indoor air may be a key source of these chemicals to the outdoor-environment. Finally, this study demonstrates the versatility of PUF disks passive samplers for surveying environmental contaminants such as Perfluoroalkylsulfonamides in indoor and outdoor air.

Acknowledgement

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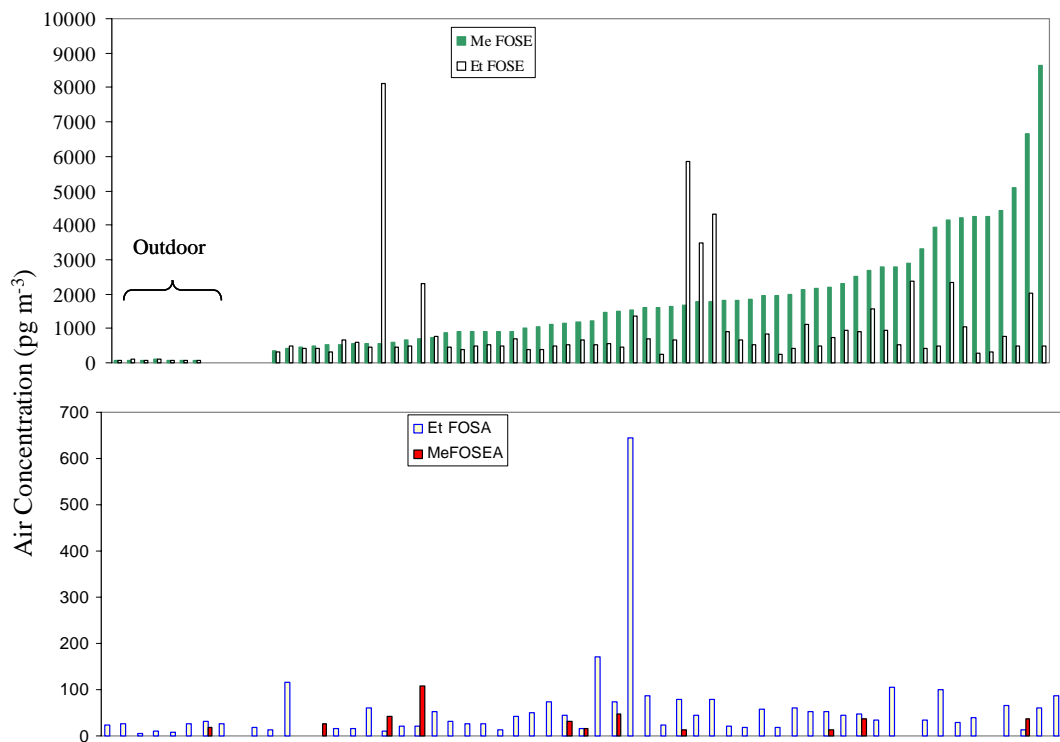


Figure 2. Indoor and outdoor air concentrations of selected perfluoroalkyl sulfonamides (PFASs) in a survey of 58 homes in Ottawa, Canada.