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Perfluorinated Sulfonamides in Indoor and Outdoor Air and Indoor Dust: Occurrence, Partitioning, and Human Exposure

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Perfluorinated alkyl sulfonamides (PFASs) which are used in a variety of consumer products for surface protection were investigated through a comprehensive survey of indoor air, house dust, and outdoor air in the city of Ottawa, Canada. This study revealed new information regarding the occurrence and indoor air source strength of several PFASs including *N*-methylperfluorooctane sulfonamidoethanol (MeFOSE), *N*-ethylperfluorooctane sulfonamidoethanol (EtFOSE), *N*-ethylperfluorooctane sulfonamide (EtFOSA), and *N*-methylperfluorooctane sulfonamidethylacrylate (MeFOSEA). Passive air samplers consisting of polyurethane foam disks were calibrated and used to conduct the indoor and outdoor survey. Indoor air concentrations for MeFOSE and EtFOSE (1490 and 740 pg m^{-3}, respectively) were about 10−20 times greater than outdoor concentrations, establishing indoor air as an important source to the outside environment. EtFOSA and MeFOSEA concentrations were lower in indoor air (40 and 29 pg m^{-3} respectively) and below detection in outdoor air samples. For indoor dust, highest concentrations were recorded for MeFOSE and EtFOSE with geometric mean concentrations of 110 and 120 ng g^{-1}, while concentrations for EtFOSA and MeFOSEA were below detection and 7.9 ng g^{-1} respectively. MeFOSE and EtFOSE concentrations in house dust followed levels in indoor air. However, resolution of the coupled air and dust data (for the same homes) was not successful using existing K_{OA}-based models for surface-air exchange. The partitioning to house dust was greatly underpredicted. The difficulties with existing models may be due to the high activity coefficient of PFASs in octanol and/or a situation where the dust is greatly oversaturated with respect to the air due to components of the dust being contaminated with PFASs. A human exposure assessment based on median air and dust concentrations revealed that human exposure through inhalation (100% absorption assumed) and dust ingestion were ∼40 and ∼20 ng d^{-1}, respectively. However, for children the dust ingestion pathway was dominant and accounted for ∼44 ng d^{-1}.

Introduction

Perfluorooctane sulfonate (PFOS) has 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 and its persistent and bioaccumulative nature (*1*−*3*). PFOS and other perfluoroalkyl compounds have also been detected in human blood from several areas around the world (*4*−*7*). The mechanism by which PFOS appears in biological samples in remote regions is not understood. Because it has a low volatility and high water solubility, PFOS itself is unlikely to undergo long-range atmospheric transport. It is hypothesized that its occurrence in remote regions is the result of atmospheric transport of more volatile and neutral airborne contaminant precursors such as the perfluoroalkyl sulfonamides (PFASs) (*8*, *9*). PFOS-related chemicals such as PFASs are used in a variety of consumer products for water and oil resistance including surface treatments for fabric, upholstery, carpet, paper, and leather, in fire-fighting foams, and as insecticides (*10*). Research on perfluorinated chemicals has increased dramatically in the past three years in an effort to understand the environmental fate, concentrations, and toxicity of these chemicals (*11*).

PFASs were first detected in air at urban and rural sites in Canada with concentrations ranging from 13 to 393 pg m^{-3} (*8*). They have also been measured in air in North America with highest concentrations observed near a carpet manufacturing facility in Griffin, Georgia (60−1500 pg m^{-3}) (*12*). Indoor air was shown to be a source of PFASs to the outside (*13*). Indoor air concentrations were about 2 orders of magnitude higher than outdoor levels. Furthermore, PFASs in indoor air were associated with the particle phase (∼60%), whereas predictions from models based on K_{OA} (octanol−air partition coefficient) and supercooled liquid vapor pressure (p_L^0) indicated that they should be entirely in the gas phase.

To better assess the long-range transport and fate pathways of PFASs, more information is needed regarding their physical chemical properties and partitioning to relevant media, e.g., soil, vegetation, aerosols. Partitioning to dust particles is particularly important for evaluating exposure and intake of PFASs in indoor environments. People spend, on average, more than 90% of their time indoors and this exposure may serve as an important uptake pathway (*14*). For children, exposure to contaminated house dust may represent a particular concern since children spend a lot of time on floors and carpets where dust accumulates; they frequently put their hands and other objects in their mouths, increasing their ingestion uptake. Overall, infants and toddlers ingest about twice as much dust as adults (*15*). Although, the effect of PFOS and other fluorinated compounds is not fully understood and still investigated, some research points to the role of PFOS as an inhibitor of gap-junction intercellular communication (*16*) and as a tumor promoter (*17*).

In this study polyurethane foam (PUF) disk passive air samplers were used to conduct a survey of PFASs in indoor and outdoor air. The use of PUF disk samplers for measuring air concentrations of persistent organic pollutants (POPs) has already been demonstrated (*18*−*20*). The samples collected in this study were previously analyzed to yield indoor air concentrations of brominated flame retardants (*21*). In addition to air samples, house dusts from the

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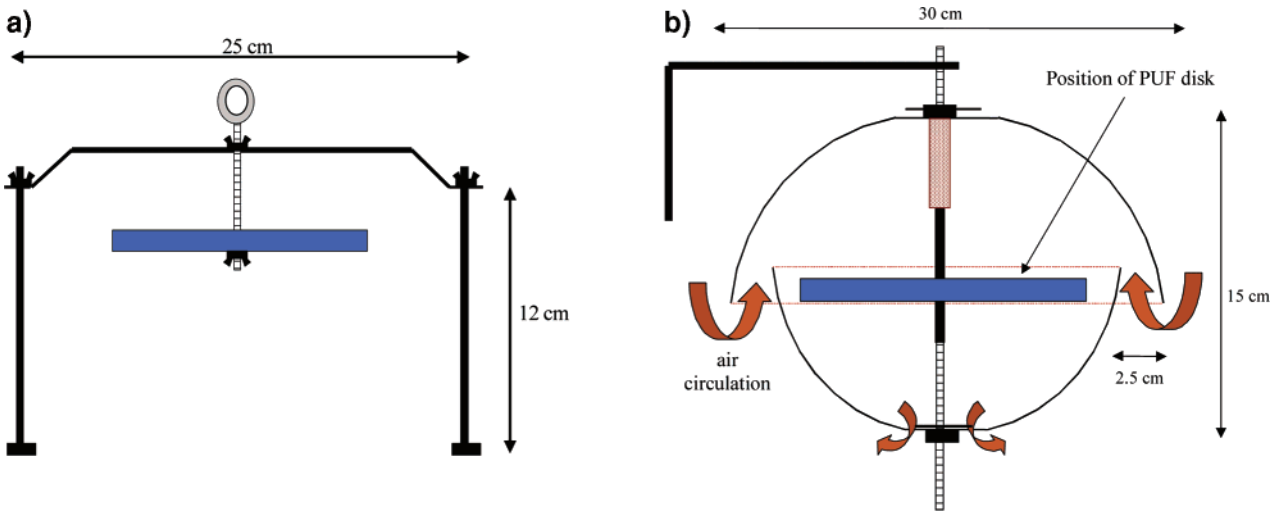

FIGURE 1. Schematic diagram of indoor (a) and outdoor (b) passive air samplers.

occupants' vacuum bags or central vacuum containers were also analyzed. These combined results for PFAS concentrations in air and dust are used to evaluate (i) the role of indoor environments as sources of PFASs to the outside, (ii) partitioning of PFAS between air and dust, and (iii) human exposure to PFASs through inhalation and ingestion of dust.

Methods

Sample Collection. Indoor air and dust were collected from 59 of 66 randomly selected homes in the city of Ottawa, Canada, during the winter of 2002/03. Outdoor samples were collected at seven sites across the city (*21*). Passive samplers consisted of PUF disks (14 cm diameter, 1.35 cm thick, surface area 365 cm^2, mass 4.40 g, volume 207 cm^3, PacWill Environmental, Stoney Creek, ON) that were individually suspended in special chambers to prevent the deposition of coarse particles in indoor homes (Figure 1a) and to eliminate UV sunlight and minimize the effect of wind speed on uptake in the outdoor chambers (Figure 1b). Samplers were deployed for approximately 21 days indoors and for approximately 70 days at 7 outdoor locations. Other sampling details are given elsewhere (*21*). Throughout the sampling period, clean PUF disk travel blanks ($n = 7$) were transported and stored with real samples and then treated as samples during analysis. Method detection limit (MDL) values for analytes were calculated as the mean of the travel blank levels + 3 standard deviations. Reproducibility of PUF disks samplers was tested by deploying duplicate samplers at seven homes and three outdoor locations.

Passive samplers were calibrated against low-volume air samples at eight indoor locations. Low-volume samples were collected at a rate of approximately 2 L min^{-1} using a BGI-400-4 personal air sampling pump (BGI Incorporated, Whatham, MA). Breakthrough was evaluated by fitting two PUF plugs (22 mm outer diameter; 76 mm length for the front PUF and 38 mm length for the second) into the sampler head (ORBO-1000, inside diamater (i.d.) 22 mm, from Supelco, USA). The sampler inlet was oriented horizontally, and no glass fiber filter was used in order to mimic the passive samplers. Both active and passive samplers were deployed simultaneously for 17−20 days in indoor locations, mainly offices and laboratories.

Dust was collected from 66 homes as follows: For homes that used floor model vacuum cleaners, the bags were detached from the cleaner and placed in a sealed polyethylene sample bag (Fisher Scientific Ltd., Nepean, Ontario). For central vacuum cleaners, dust stored in the reservoir container was transferred directly into the sealed bags using a glove-covered hand. Upon arrival in the laboratory (few hours later), the bag was then cut open with clean scissors and the content of the bag was transferred to a vibratory siever (AS200 digit Analytical Sieve Shaker, Retsch GmbH&Co.KG, 42781 Haan, Rheinische Str.36, Germany). This consisted of a No. 16 sieve (U.S.A. Standard Testing Sieve, A.S.T.M.E-11 Specification, opening 1.18 mm) above a No. 100 sieve (U.S.A. Standard Testing Sieve, A.S.T.M.E-11 Specification, opening 150 μm) followed by a collection pan. After sealing the top, the vibratory siever was run for 10 min at an amplitude of 80. The dust was allowed to settle for 15 s, and the collection pan was removed and replaced with a new one. The siever was run for an additional 5 min. Any visible hairs were removed from the first collection pan using tweezers and/or a brush. Dust from the collection pans was transferred to a 190 mm i.d. × 100 mm tall crystallizing dish. When the entire sample was sieved, the dust from the crystallizing dish was sieved one more time for 3 min. Three grams of the resulting fine dust (<150 μm) was then transferred to a 20-mL clear wide-mouth bottle with an aluminum liner screw cap. The remainder was stored in 125-mL preweighed jars (VWR International Ltd, Montreal, Quebec), using a stainless steel spatula. The dust samples were stored at −20 °C until analysis. Sodium sulfate was placed in the same types of bottles and stored together with processed dust samples to serve as a combined storage and analytical method blank.

Extractions. PUF samples were Soxhlet extracted for 21 h in petroleum ether, concentrated to 0.5 mL, and transferred to isooctane by rotary evaporation and nitrogen blow down. Samples containing visible particles were filtered through a glass pipette packed with glass wool using petroleum ether eluate. Recoveries of *N*-methylperfluorooctane sulfonamidoethanol (MeFOSE), *N*-ethylperfluorooctane sulfonamidoethanol (EtFOSE), *N*-ethylperfluorooctane sulfonamide (EtFOSA), and *N*-methylperfluorooctane sulfonamidethylacrylate (MeFOSEA) (~120 ng), were determined by spiking PUF disks just prior to extraction. Extractions were performed in two stages, first using petroleum ether for 21 h, followed by acetone for 21 h. Dust extractions were performed by weighing approximately 0.25 g of dust and Soxhlet extracting with dichloromethane (DCM) for 24 h. To test recoveries, approximately 10 dust samples were extracted two times (24 h each) using DCM. Mirex (0.1 ng) was added as an internal standard before analysis to correct for volume and instrument response. No cleanup of extracts was performed for PUF or dust samples.

TABLE 1. Structural and Analytical Information for the PFASs Investigated in This Study

compounds	acronym	molecular formula	EI ions	NCI ions
N-methyl perfluorooctane sulfonamidoethanol	MeFOSE	$C_8F_{17}SO_2N(CH_3)\ CH_2CH_2OH$	526, 462	483, 400
N-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	$C_8F_{17}SO_2N(CH_2\ CH_3)CH_2CH_2OH$	540, 448	483, 400
N-ethyl perfluorooctane sulfonamide	EtFOSA	$C_8F_{17}SO_2NHCH_2\ CH_3$	512, 448	483, 400
N-methyl perfluorooctane sulfonamidethylacrylate	MeFOSEA	$C_8F_{17}SO_2N(CH_3)\ CH_2CH_2OCOCH{=}CH_2$	526, 462	483, 400

TABLE 2. Analytical Details for PFASs by EI-MS Analysis: IDLs, MDLs, and Method Recoveries

compounds	IDL (pg)	MDL[a] (pg m^{-3})	% recovery (SD) PUF ($n = 4$)
MeFOSE	6.1	7.1	87 (5)
EtFOSE	4.5	5.4	89 (6)
EtFOSA	1.2	0.01[b]	87 (5)
MeFOSEA	5.1	0.05[b]	64 (5)

[a] MDL calculated as average blank ($n = 7$) +3 standard deviations assuming a sample air volume of 70 m^3. [b] Calculated as $^2/_3$ IDL assuming air volume of 70 m^3.

Chemicals. The target compounds and their molecular formulas are given in Table 1. All PFASs were obtained from the 3M Company, with purities >90%.

Analysis. 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. Confirmation was performed on selected samples using negative chemical ionization (NCI) in 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 with helium as the carrier gas. The GC oven temperature was 60 °C, 0.5 min, 3 °C min^{-1} to 160 °C, then 20 °C min^{-1} to 260 °C. Splitless injections were 1 μL with split opened after 0.5 min and the injector at 250 °C. The ion source and quadrupole were kept at 230 and 150 °C for EI and 150 and 106 °C, respectively, for NCI analysis. Analysis details are given in Table 1. Standards were included every 12 samples to monitor changes in instrument sensitivity. Subsets of all dust samples were sent for total organic and inorganic carbon analysis (Laboratory Services, University of Guelph, ON).

Results and Discussion

Quality Control Quality Assurance. Samples qualified if the target/qualifier ion ratios (Table 1) were within 20% of the values in the standards. The MDL equivalent air concentrations (mean of the travel blank levels + 3 standard deviations) were 7 and 5 pg m^{-3} for MeFOSE and EtFOSE, respectively, assuming an air volume of 70 m^3 (Table 2). EtFOSA and MeFOSEA were not detected in the travel blanks. In these cases the MDL value was considered to be equal to two-thirds of the instrument detection limit (IDL). The IDL was calculated from the lowest concentration analytical standard that could be integrated and corresponds to a chromatographic peak with a signal/noise ratio of 3/1. Results are given in Table 2. Targets were not detected in sodium sulfate blank extracts ($n = 3$). Since all blank samples were below detection, MDLs of the targets in dust were assigned based on IDL as discussed above. No blank correction was applied to reported air and dust concentrations.

PUF recoveries showed that more than 98% of target compounds were extracted by the first petroleum ether extract with only trace amounts in the second acetone extract. This was consistent with previous work (*13*). Overall, recoveries were greater than 87% with the exception of MeFOSEA for which recoveries were lower at 64% (Table 2). For dust samples, all target analytes were contained entirely in the first extract, indicating that a single 24-h extract with DCM was sufficient. Results for samples were not recovery corrected. It should be noted that, at the time of the study, isotopically labeled neutral perfluorinated compounds were not available for performing surrogate recoveries.

Good agreement was obtained for all 10 sets of duplicate samplers with percentage differences not exceeding 10% with the exception of one set (17% for MeFOSE) (Table 3). For sites where duplicate samplers were deployed, the average of the two values is reported.

Results of the breakthrough tests for the low-volume sampler showed that although some breakthrough of target analytes to the second PUF did occur it was less than 25%. Therefore, the sum of the front and back PUFs was used to evaluate the PUF disk sampling rate.

Calibration Study: Passive Sampler Uptake Rate. The PUF disk air sampling rate was determined by calibrating them against low-volume air samplers. Side-by-side sampling was conducted at eight indoor locations and is described in detail by Wilford et al. (*21*). The resulting sampling rate for the PFASs was approximately 2.5 $m^3\ d^{-1}$, in good agreement with the sampling rate previously determined for polybrominated diphenyl ethers (*21*). On the basis of this rate, an air volume of approximately 52.5 m^3 was sampled for the 21-day indoor deployment and approximately 175 m^3 for the 70-day outdoor period.

A sampling issue exists with the calibration method which is due to the PUF disk samplers collecting mainly gas-phase chemicals (*21*), whereas the low-volume samplers represent both gas- and particle-phase contributions. This results in an underestimate for the passive air sampling rate of 2.5 $m^3\ d^{-1}$ and explains why this value is lower than the usual value of 3.5−4 $m^3\ d^{-1}$ derived in other studies using the same PUF disks (*18*−*20*). Consequently, passive sampler-derived gas-phase concentrations could be biased high up to ∼40% as results of lower sampling rate indicated above (note: since concentrations are calculated as (amount of analyte on PUF disk/(sampling rate × number of days the PUF disk was exposed)). However, the extent of the bias will depend on the suspended dust concentrations in each home which vary and which were not part of the sampling strategy for this study.

Indoor and Outdoor Air Concentrations of PFAS. Passive sampler-derived air concentrations for the target compounds in indoor and outdoor air are presented in Figure 2 and Table 4.

MeFOSE. Highest air concentrations were observed for MeFOSE which was log normally distributed in indoor air with a geometric mean value of 1490 pg m^{-3} (Figure 2a), compared to the arithmetic mean value of 1970 pg m^{-3}; this was approximately 18 times greater than the outdoor value of 82 pg m^{-3}. The only other indoor air concentrations for MeFOSE were reported by Shoeib et al. (*13*) for a survey of homes and laboratories. In that study MeFOSE also dominated and ranged from 11 to 8000 pg m^{-3}. Outdoor air concentrations of MeFOSE have been reported recently. First, in Toronto (urban) and Long Point (a rural location on the north shore of Lake Erie) concentrations ranged from 86 to 123 and 34 to 36 pg m^{-3}, respectively (*8*). Outdoor air concentrations for residential areas in Toronto were also

TABLE 3. Comparison of PFASs Air Concentrations at Sites Where Duplicate PUF Disk Samplers Were Deployed

	Me FOSE			Et FOSE			Et FOSA		
sample	sample A	sample B		sample A	sample B		sample A	sample B	
time (days)	concn (pg m^{-3})	concn (pg m^{-3})	% difference	concn (pg m^{-3})	concn (pg m^{-3})	% difference	concn (pg m^{-3})	concn (pg m^{-3})	% difference
22	597	610	2.2	629	649	3.4	BDL[b]	BDL	
21	462	431	6.7	6760	6140	9.2	BDL	BDL	
23	1670	1380	17	359	346	3.8	15	14	8.2
27	2410	2550	5.5	1960	1980	0.7	87	91	4.1
28	3530	3870	9.5	246	243	1.0	32	33	0.9
21	7210	6440	10	404	401	0.8	72	67	7.2
22	1520	1580	4.4	557	572	2.8	BDL	BDL	
69[a]	83	83	0.0	87	87	0.3	BDL	BDL	
76[a]	77	75	2.3	80	79	1.4	BDL	BDL	
74[a]	77	75	2.7	83	88	6.9	BDL	BDL	

[a] Outdoor PUF disk samples. [b] BDL = below method detection limit (MDL, see Table 2).

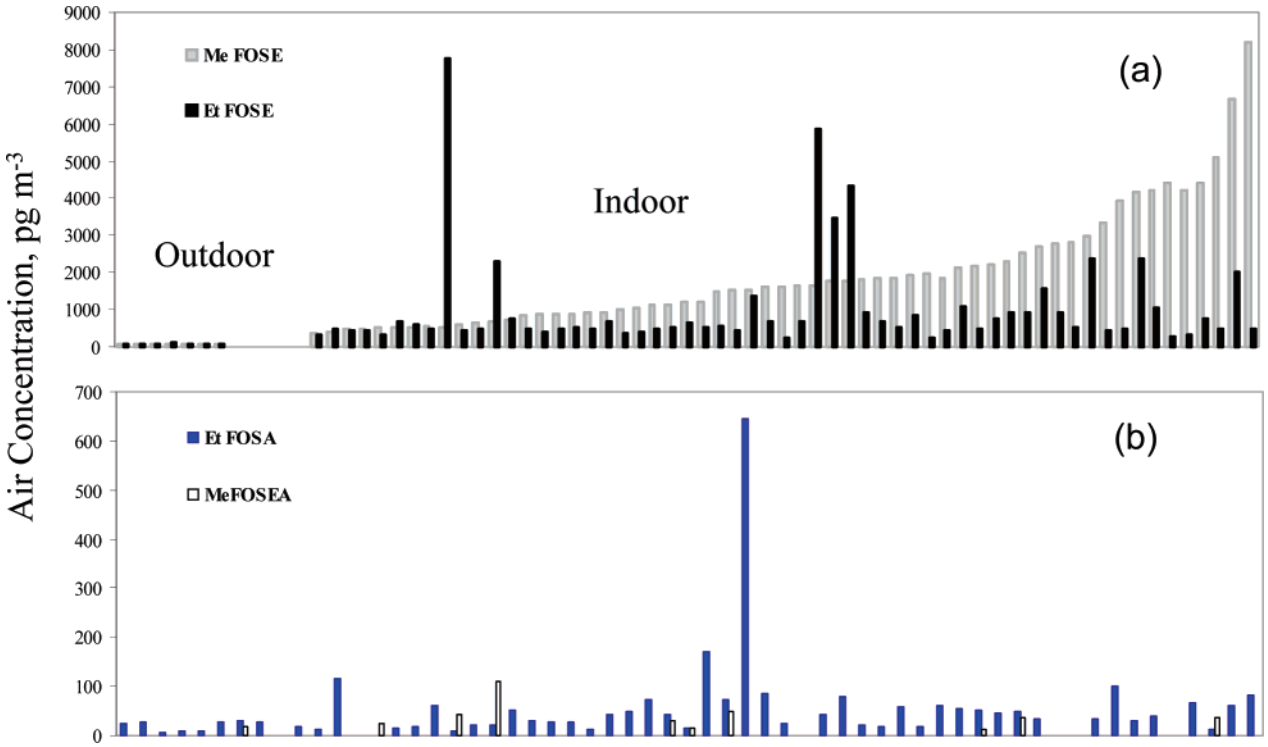

FIGURE 2. Passive sampler-derived air concentrations (pg m^{-3}) in outdoor and indoor air for (a) MeFOSE and EtFOSE and (b) EtFOSA and MeFOSEA. Sample order is the same in a and b and follows increasing concentrations of MeFOSE.

reported with values ranging from 16 to 32 pg m^{-3} (*13*). MeFOSE concentrations reported in several locations in North America ranged from 20 pg m^{-3} to almost 400 pg m^{-3} in Griffin, Georgia; this elevated value was attributed to a high density of potential point sources (carpet treatment facilities) in the region (*12*).

EtFOSE. Results for EtFOSE are shown in Figure 2a arranged according to the same sample order used to demonstrate the log normality for MeFOSE. Although EtFOSE concentrations are also log normally distributed, they are only weakly correlated to MeFOSE ($p = 0.15$), indicating that they may arise from different sources. The geometric mean indoor air concentrations for EtFOSE was 744 pg m^{-3}, about 8.5 times greater than the outdoor value of 87 pg m^{-3}.

Such high indoor air concentrations of EtFOSE were not expected. To our knowledge, EtFOSE is mainly used for treating food wrapping. It is possible however, that EtFOSE may also occur as a byproduct in the manufacture of other fluorochemical compounds for carpet and fabric treatments or that other important uses exist which have not yet been considered. Outdoor air concentrations ranged from 51 to 393 pg m^{-3} in Toronto to 68 to 85 pg m^{-3} at Long Point (*8*). Results for Toronto reported by Shoeib et al. (*13*) were 5−1900 pg m^{-3} in indoor air and 8−10 pg m^{-3} in outdoor air. EtFOSE air concentrations in a survey across North America ranged from below detection to a high of ~200 pg m^{-3} in Reno, Nevada (*12*).

EtFOSA and MeFOSEA. Indoor air concentrations for EtFOSA and MeFOSEA (Figure 2b) were about an order of magnitude lower than for MeFOSE and EtFOSE (Figure 2a). Results in Figure 2b are arranged according to the same sample sequence used in Figure 2a. EtFOSA was detected in more than 90% of the indoor samples and had a geometric mean value of 40 pg m^{-3}. Outdoor samples were below detection. Outdoor air concentrations for EtFOSA ranged from below detection to ~60 pg m^{-3} in Reno Nevada (*12*), while 14 pg m^{-3} was reported in Toronto (*8*).

In this study, MeFOSEA was above the detection limit in only 15% of samples with a geometric mean of 29 pg m^{-3}. MeFOSEA was not detected in outdoor samples. The only

TABLE 4. Concentrations of PFAS in Indoor and Outdoor Air Samples and Indoor Dust[a]

	MeFOSE	EtFOSE	EtFOSA	MeFOSEA
Outdoor Air, pg m^{-3}				
minimum	76	80	BDL[b]	BDL
maximum	99	106	BDL	BDL
arithmetic mean (SD)	83 (7.8)	88 (8.3)	BDL	BDL
geometric mean	82	88	BDL	BDL
no. detections	7	7	0	0
Indoor Air, pg m^{-3}				
minimum	366	227	5.94	12.0
maximum	8190	7740	646	109
arithmetic mean (SD)	1970 (1610)	1100 (1420)	59 (91)	35 (27)
geometric mean	1490	744	40	29
no. detections	59	59	52	10
Indoor Dust, ng g^{-1}				
minimum	3.3	1.4	BDL	0.7
maximum	8860	75440	BDL	44
arithmetic mean (SD)	412 (1180)	2200 (9750)	BDL	14 (15)
geometric mean	113	138	BDL	7.9
no. detections	66	66	0	16

[a] Note: average organic carbon content of dust samples was 23.9% ± 6.0. [b] BDL = below method detection limit.

previous measurement of MeFOSEA in air was in the study by Shoeib et al. (*13*) where levels in indoor air ranged from below detection to ~5 pg m^{-3}, with one house exhibiting a high value of 283 pg m^{-3}.

PFAS Concentrations in Indoor Dust. Results for dust samples are shown in Figure 3 and Table 4. To our knowledge these are the first measurements of these compounds in indoor dust although PFOS and perfluorooctanoic acid (PFOA) were detected in house dust in Japan with concentrations ranging from 11 to 2500 and 69 to 3700 ng g^{-1}, respectively (*22*).

Consistent with the indoor air measurements, highest concentrations in dust were observed for MeFOSE (geometric mean of 113 ng g^{-1}) and EtFOSE (138 ng g^{-1}). Results for dust were also log normally distributed as shown for MeFOSE in Figure 3 where results are again arranged according to samples with increasing dust concentrations of MeFOSE. No correlation exists between MeFOSE and EtFOSE dust concentrations ($p > 0.5$). EtFOSA was not detected in indoor dust. MeFOSEA was detected in ~30% of dust samples with a geometric mean value of ~ 8 ng g^{-1}.

Dust-Air Partitioning of PFASs. It is useful to evaluate the dust-air partitioning of PFASs in order to address concerns regarding the environmental fate of these compounds and to evaluate the potential for human expsosure via dust ingestion and inhalation. One might speculate that, if these chemicals (specifically MeFOSE and EtFOSE) arise from a range of indoor sources, indoor environments may effectively act as equilibration chambers. In this scenario, chemicals strive to distribute themselves equally (in fugacity terms) between media in an approach to equilibrium. It is likely that home ventilation (i.e., replacement of indoor air with outdoor air) plays a key role in preventing indoor air concentrations from becoming excessively high. Home ventilation is also a pathway for delivery of contaminated indoor air to the outside environment.

As this study was conducted during the winter period when outdoor air temperatures were typically below freezing in Ottawa, we can assume that windows and doors were closed and that ventilation rates in these homes were relatively low and controlled mainly by the furnace systems and human traffic. These were ideal conditions for the dust-air equilibration scenario. Figure 4 compares paired dust and air concentrations for the same homes for MeFOSE and EtFOSE. Although there is considerable scatter in the data, there is generally a good agreement with higher dust concentrations correlated to higher indoor air concentrations ($p < 0.001$). Dust concentrations in Figure 4 were converted to a mass/volume basis (pg contaminant in cubic meter of dust) using a value of 1 kg L^{-1} for the density of dust. This was based on several preliminary tests that involved adding dust to water, shaking, and observing that the bulk of the dust remained suspended in water.

Previous work has shown that the K_{OA}-based model of particle−gas partitioning greatly underpredicts particulate fractions for MeFOSE and EtFOSE in suspended indoor dust (*13*). In that approach, the K_{OA}-based model results were compared to the particle/gas partition coefficient K_P (m^3 μg^{-1}) calculated from measured data as $K_P = C_P/C_A$ where C_P is the concentration of chemical on particles (ng μg^{-1} particles) and C_A is the concentration in air (gas phase) (ng m^{-3}).

In this study, an analoguos model, the Karickhoff model, is used to predict concentrations on dust from air concentrations of PFASs. If air−dust equilibrium is assumed, the concentration on dust can be predicted from air concentration C_{AIR} using

$$K_{DA} = 0.411\rho_D f_{OC} K_{OA} = C_{DUST}/C_{AIR} \quad (1)$$

where K_{DA} is the dust air partition coefficient, ρ_D the density of dust, and f_{OC} is the organic carbon content of dust. Supplement 1 provides a more detailed explanation of the model and background. Log K_{OA} values for MeFOSE and EtFOSE were 7.70 and 7.78, respectively (*13*). Values of f_{OC} were determined for each dust sample and on average were 0.23 ± 0.06, and dust density was 1 kg L^{-1} as discussed previously.

The concentration on dust that is predicted using eq 1 is compared to the measured dust concentrations in Figure 5. The results indicate that the Karickhoff model greatly underpredicts (by about 1 order of magnitude) the extent to which MeFOSE and EtFOSE are associated with particles. This is consistent with the earlier finding by Shoeib et al. (*13*) where an analogous K_{OA} model (see Supplement 1) was used to compare particle-phase and gas-phase components of PFASs from high volume indoor air samples. These findings suggest that either the K_{OA}-based model needs to be recalibrated for PFASs or that K_{OA} is not a suitable correlation parameter for dust/particle to air partitioning of PFASs. To properly test the usefulness of K_{OA} in this regard would require partitioning data for several PFASs that span a range of K_{OA} values—essentially plotting the observed partition coefficients against K_{OA} on a log−log basis and observing a slope close to unity.

The failure of the existing K_{OA}-based partitioning models is likely due to large interaction effects of the surfactants in octanol. For instance, an underlying assumption in K_{OA} model is that the chemical's activity coefficient in octanol is similar to its activity coefficient in the absorbing medium (i.e., dust). The activity coefficient in octanol estimated from the values of p_L^0 and K_{OA} reported by Shoeib et al. (*13*) result in a value of approximately 150 for MeFOSE and 30 for EtFOSE. This is about 1 order of magnitude higher than the average value for more than 200 organic chemicals (*23*) and may explain the uncharacteristic partitioning behavior (in terms of K_{OA}) of the PFASs.

Another possibility for the failure of the K_{OA}-based model is that the dust and air are in disequilibrium; the dust may contain components that are highly contaminated with PFASs. The PFASs may be either too tightly bound to these materials or have insufficient time to reach equilibrium with indoor air.

Statistical Analysis. An attempt was made to relate air and dust concentrations to house characteristics obtained through the questionnaire. Because air and dust were already

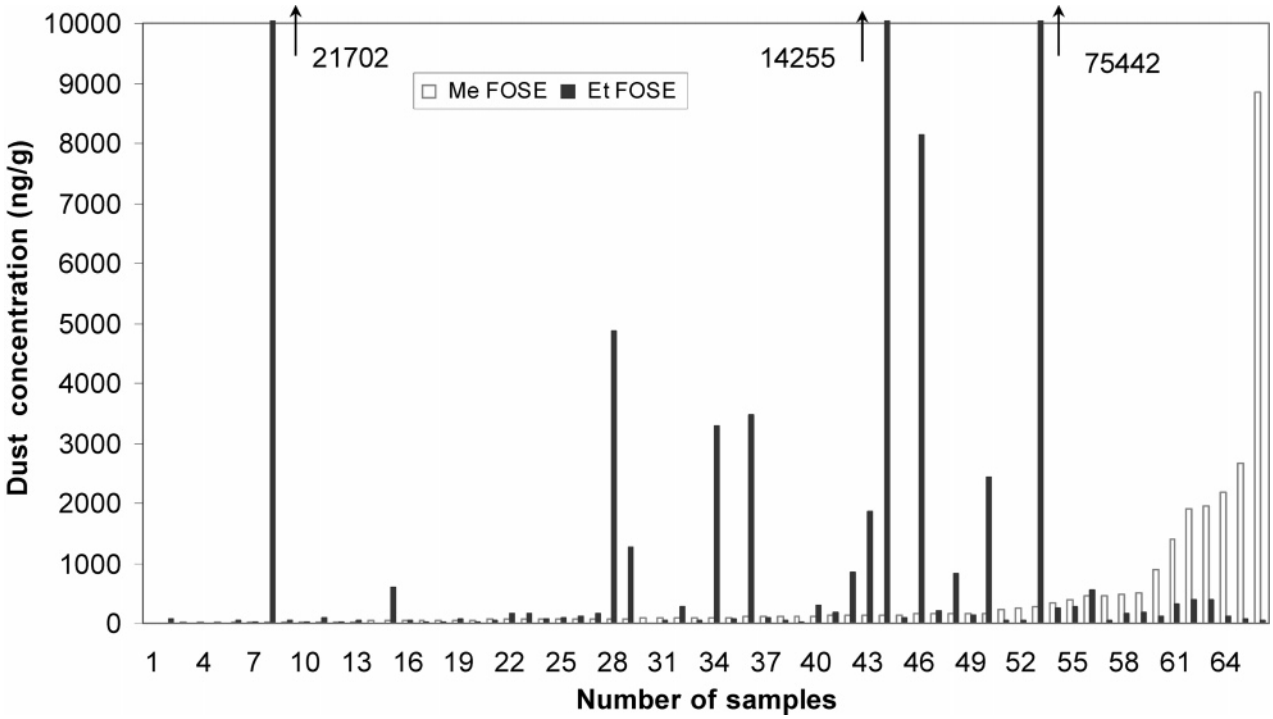

FIGURE 3. Concentration of MeFOSE and EtFOSE in house dust collected from 66 homes. Sample order follows increasing concentrations of MeFOSE.

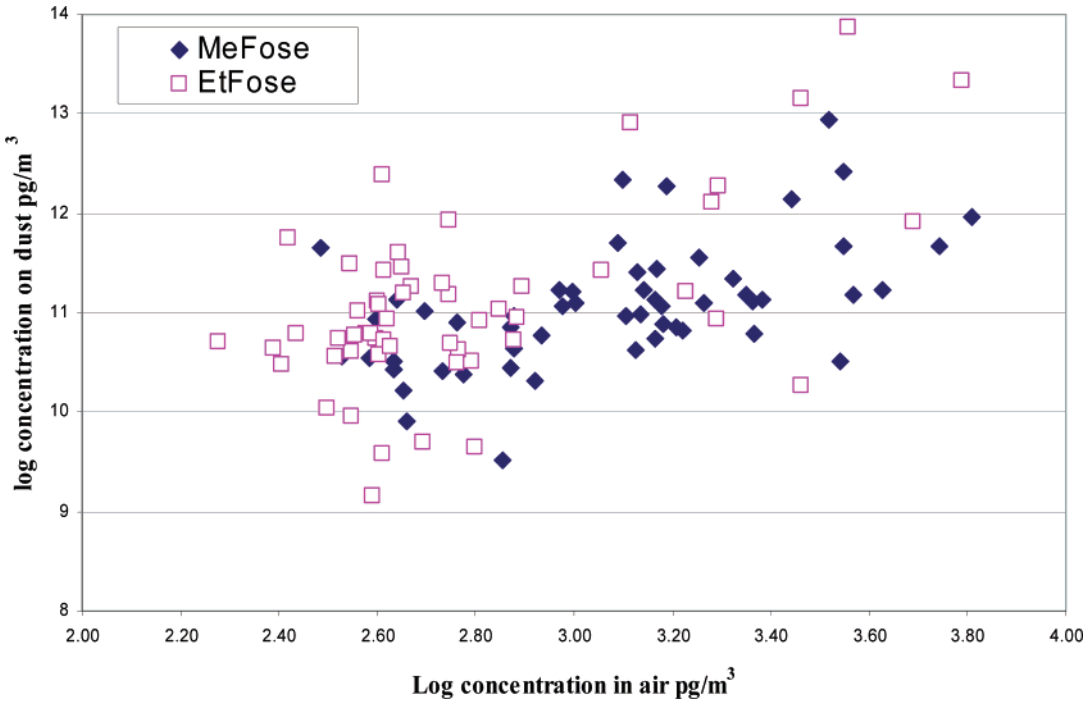

FIGURE 4. Correlation of air and dust concentrations from the same homes for MeFOSE and EtFOSE. Note that dust concentrations are expressed as pg m^{-3} of dust assuming a dust density of 1 kg L^{-1}.

correlated (Figure 4), it was sufficient to carry out the evaluation on just the air data. The results of the statistical analysis showed some marginally significant trends; for instance, there were higher levels of MeFOSE ($p = 0.035$) and total MeFOSE + EtFOSE ($p = 0.037$) in the seven homes where new fabric (probably treated) was applied to furniture during the previous 6-month period. Also a marginally significantly lower level of MeFOSE ($p = 0.024$) and significantly lower levels of MeFOSE + EtFOSE ($p = 0.0084$) were observed in multihomes (i.e., homes in apartment buildings) compared to single-house homes. No correlations were observed between levels of PFASs and house age and/or extent of carpeting. Unfortunately, questions dealing with home ventilation rates were not adequately captured in the questionnaire, and hence this factor was not further evaluated.

Human Exposure. PFOS has been detected in human sera from around the world (*6*, *7*, *24*). It is not known whether this uptake occurs directly (i.e., as PFOS) as it was detected in house dust (*22*) and/or by biotransformation of some precursor to PFOS, such as the PFASs (*9*). It has also been suggested that PFASs may be degraded to PFOS directly in

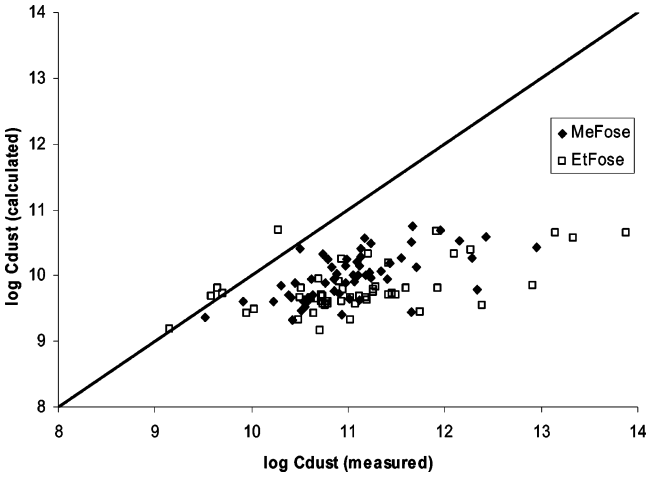

FIGURE 5. Measured and predicted dust concentrations for MeFOSE and EtFOSE using air data and eq 1.

TABLE 5. Estimated Human Exposure to PFASs via Inhalation and Ingestion of Dust

	10th percentile	median	90th percentile
inhalation (male), ng d^{-1}	17	41	127
inhalation (female), ng d^{-1}	16	39	119
inhalation (child), ng d^{-1}	12	27	82
dust ingestion (adult), ng d^{-1}	5	20	412
dust ingestion (child), ng d^{-1}	10	44	825

the atmosphere (*8*). The high level of PFAS in indoor air and dust where people spend most of their time urges the need to estimate human exposure via inhalation and dust ingestion pathways. Exposure to contaminated dust is particularly of concern for children; not only do children spend a lot of time on floors and carpets where dust accumulates but they frequently put their hands and other objects into their mouths, increasing their ingestion of dust. Overall, infants and toddlers ingest about twice as much dust as adults per day. (*15*)

On the basis of measured PFAS concentrations in air and dust, a simple estimation for human exposure was performed. In the absence of inhalation absorption efficiency information for PFASs, 100% absorption (worst case scenario) was assumed. Light activity inhalation rates of 20, 19, and 13 L min^{-1} for male (m), female (f), and children up to 10 years old, respectively, were used in these calculations (*25*). Children's inhalation rates were not found to be significantly different across gender. It was assumed that 16 h per day were spent on light activity. The remaining time of the day was spent resting or outdoors. Exposure while at rest or outdoors was deemed to be not important to the calculation (and not included) due to low inhalation rates during rest and low outdoor air concentrations. The US Environemntal Protection Agency (EPA) (*15*) estimates that children (1−6 years of age) ingest ∼200 mg dust day^{-1}, while the figure for adults is 100 mg day^{-1}.

Table 5 summarizes the calculations for the three exposure scenarios: (1) using the lowest 10th percentile air and dust concentrations of MeFOSE and EtFOSE, (2) using median levels, and (3) using 90th percentile levels. In most cases the dominant pathway for adult exposure is via inhalation. For instance, under scenario 2 (median air and dust concentrations), inhalation and dust ingestion result in 60 ng day^{-1} taken up; almost two-thirds of this is due to inhalation. However, for children, dust ingestion is dominant and in the range 44 ng day^{-1} compared to 27 ng day^{-1} via inhalation. For people living in the 10% of homes with highest air and dust levels (90th percentile), ingestion is the dominant pathway, accounting for 412 ng day^{-1} compared to ∼130 ng day^{-1} by inhalation. For children in this same situation, dust uptake is estimated to be ∼825 ng day^{-1}—an order of magnitude greater than the inhalation value of 82 ng day^{-1}.

It should be emphasized that results in Table 5 represent the worse case scenario (i.e., 100% absorption assumed and indoor air concentrations taken in winter time when ventilation is low). Levels of PFAS in indoor air are expected to vary seasonally and decrease during the milder periods (e.g., summer) when windows are open and indoor air is diluted by relatively cleaner outdoor air.

The main implications of this work are: (i) Indoor air and dust are an important human exposure route for PFASs, especially MeFOSE and EtFOSE. It will be interesting to make comparisons with dietary exposure as these data become available. (ii) Indoor air is an important source of PFASs to the outside environment, again, especially for MeFOSE and EtFOSE. If indoor air is in fact the dominant source, it should be possible to make fairly good estimates of environmental emission rates based on the data presented here and information on home ventilation. It is also necessary to investigate if there are other point sources of PFASs (aside from indoor air, e.g., industrial, manufacturing) that may be important. (iii.) Last, this study confirms findings from previous work (*13*) and suggests that K_{OA}-based partitioning models underpredict particulate (or dust) fractions of PFASs. This is an area for further study and has implications for our understanding of the transport and fate pathways for PFASs.

Supporting Information Available

Detailed explanation of the K_{DA} model and background. This material is available free of charge via the Internet at http://pubs.acs.org.

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