CHARACTERIZATION OF TWO PASSIVE AIR SAMPLERS FOR PER– AND POLYFLUOROALKYL SUBSTANCES

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Introduction

Per- and polyfluoroalkyl substances (PFASs) have received increasing public attention due to their persistence, bioaccumulative potential, and possible adverse effects on human and wildlife. The widespread global distribution of PFASs and their occurrence in biota and humans is believed to arrive through various mechanisms including oceanic transport, air transport and association with aerosols. For measurements in air, passive air samplers (PAS) are ideal due their simplicity and low costs, especially for the purpose of generating spatially resolved data. However, there is some uncertainty regarding the ability of PAS to capture new priority chemical classes in air and how to derive air concentrations. Thus, the aim of this study is to characterize two common PAS for PFASs under filed conditions – the polyurethane foam (PUF) disk and sorbent-impregnated polyurethane foam (SIP) disk. Furthermore, high-volume active air samples (HV-AAS) and low-volume active air samples (LV-AAS) were collected to estimate average ambient air concentrations for PFASs as well as to investigate seasonal trends, in addition to mapping uptake curves of passive samplers with time.

Materials and methods

The target analytes included C_4, C_6, C_8, C_{10} (PFBS, PFHxS, PFOS, PFDS) perfluoroalkane sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$), C_4–C_{12}, C_{14} (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA) perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$), 6:2, 8:2, 10:2 fluorotelomer alcohols (FTOHs, $C_nF_{2n+1}CH_2CH_2OH$), 6:2 fluorotelomermethacrylate (FTMAC) ($C_6F_{13}CH_2CH_2OC(O)C(CH_3)=CH_2$), 8:2, 10:2 fluorotelomer acrylates (FTACs, $C_nF_{2n+1}CH_2CH_2OC(O)CH=CH_2$), perfluorooctane sulfonamide (FOSA, $C_8F_{17}SO_2NH_2$), methyl and ethyl FOSAs ($C_8F_{17}SO_2N(C_nH_{2n+1})H$) and methyl and ethyl perfluorooctane sulfonamidoethanols (FOSEs, $C_8F_{17}SO_2N(C_nH_{2n+1})CH_2CH_2OH$). In addition, 16 mass-labeled internal standards (IS), three injection standards (InjS), and three depuration compounds (i.e., perfluoroheptylethanol (7:2 sFTOH, $C_7F_{15}CH(OH)CH_3$), $^{13}C_8$ PFOS, and $^{13}C_8$ PFOA) were used.

The sampling was conducted over a period of about one year from March 2010 to April 2011 at a semi-urban location in Toronto (Environment Canada field site, 43°46′N, 79°28′W). For passive sampling, SIP-PAS and PUF-PAS were calibrated by deploying them for 7, 21, 28, 42, 56, 84, 112, 140, 168, and 197 days. In addition, SIP-PAS and PUF-PAS were deployed for one month intervals from March 2010 to April 2011 to investigate seasonal trends. Ultimately, four different chamber types were compared for SIP and PUF disks with different gaps between the housings (i.e., original design (used, for example, for the Global Atmospheric Passive Sampling (GAPS) network[3]), top and bottom domes flush, 1 cm gap and 2 cm gap between top and bottom domes). The SIP-PAS and PUF-PAS were spiked with the depuration compounds prior to deployment. In parallel to the PAS, HV-AAS (~330 m^3 over 24 h periods once or twice a week) were collected using glass fiber filters (GFFs) for collecting the particle-phase followed by a PUF/XAD–2 cartridge for trapping the gas-phase compounds. In addition, LV-AAS (~46 m^3 over 14 days) were collected using PUF/XAD–2 cartridge for trapping the gas- and particle-phase compounds. Field blanks and breakthrough tests (for the active samplers, using a second cartridge in series) were also conducted.

The extraction and instrumental analysis based on the methods described elsewhere[1]. Briefly, prior to extraction, the PUF/XAD-2 sandwiches, GFFs, SIPs and PUFs were spiked with an IS mixture containing 16 mass-labelled PFASs. The high volume PUF/XAD-2 sandwiches were Soxhlet extracted using petroleum ether/acetone (85/15, v/v) followed by an extraction with methanol, and the GFFs were extracted by sonication with dichloromethane and then with methanol. The low volume PUF/XAD-2 sandwiches, SIPs and PUFs were extracted by using a pressurized liquid extraction (PLE) system using petroleum ether/acetone (83/17, v/v; 2 cycles) and thereafter with acetonitrile (2 cycles). All extracts were concentrated by rotary evaporation followed by gentle nitrogen blow-down to 0.5–1 mL and then the InjS were added. The separation and detection for the 6:2 FTMAC, FTACs, FTOHs, FOSAs and FOSEs (i.e., petroleum ether/acetone and dichloromethane extracts) was performed using gas chromatography – mass spectrometry (GC/MS) using positive chemical ionization (PCI) and the analysis of PFCAs, PFSAs and PFOSA (i.e., methanol and acetonitrile extracts) were performed by liquid chromatography using a triple quadrupole mass spectrometer interfaced with an electrospray ionization source in negative-ion mode (LC–(–)ESI–MS/MS).

Results and discussion

For quality assurance and quality control, field blanks, limits of detection (LODs), recoveries, duplicate samples and the efficiency of the collection of PFASs were examined. Generally, the field blank concentrations were <10% of the concentrations measured in the samples. The LODs ranged from 0.001–1.33 pg m^{-3} for the HV-AAS (gas- and particle-phase), 0.005–9.69 pg m^{-3} for the LV-AAS, 0.001–3.15 pg m^{-3} for the SIP-PAS and 0.001–9.18 pg m^{-3} for the PUF-PAS. Average recoveries were 78%, 96%, 67%, 81%, and 93% for the LV-AAS, SIP-PAS, PUF-PAS, and gas-phase and particle-phase using HV-AAS, respectively. Duplicate measurements showed excellent agreement and very good reproducibility for all sampling techniques with a mean standard deviation of ~5% for the PFASs. Breakthrough experiments showed breakthrough for the FTOHs, 8:2 FTAC and MeFOSA using HV-AAS (i.e., 6–30% in the back column) and for PFBS and 8:2 FTOH using LV-AAS (i.e., 2–4% in the back column).

The HV-AAS concentrations were used to calculate the uptake profiles for the PAS because the detection frequency of PFASs in the LV-AAS was low due to the lower sample air volume. The equivalent air volume were calculated by dividing the amount of chemical in the passive sampler medium (PSM) (C_{PSM}, pg $sample^{-1}$) by the total concentrations of the target analyte in ambient air using the HV-AAS (C_A, pg m^{-3}). The uptake profiles of PFASs for PUF-PAS and SIP-PAS are shown in Figure 1. For the PUF-PAS, the FOSAs and FOSEs equilibrate after several weeks. The uptake profile of the PFSAs showed a very short linear phase of a few weeks and a long curvilinear phase until the end of the deployment period. The PFCAs, 8:2 and 10:2 FTOH, 6:2 FTMAC, FTACs and FOSA were not detected in the PUF-PAS and therefore no uptake profiles are shown for these chemicals. For the SIP-PAS, the linear uptake profile for the PFSAs was similar compared to the PUF-PAS whereas FOSAs and FOSEs had a longer linear uptake phase in the SIP-PAS (>56 days) compared to the PUF-PAS (<28 days). In general, the linear phase and time to equilibrate for PFASs (except for PFSAs) was much longer using the SIP-PAS which can be seen as great collection improvement in particular for PFCAs and FTOHs in the SIP-PAS.

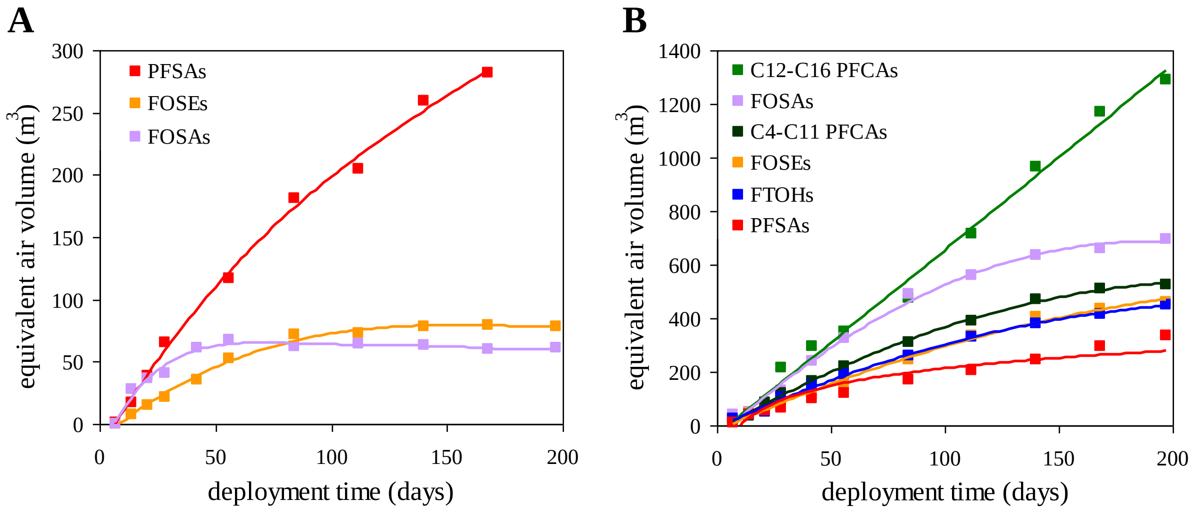

Figure 1. Uptake profiles of PFASs for A) PUF-PAS and B) SIP-PAS.

The sampling rate (m^3 d^{-1}) and passive air sampler partitioning coefficients (K_{PSM-A}) were calculated for individual PFAS using the uptake curve of the chemical in the PAS (further details for calibration of PAS is described elsewhere[2]). The average sampling rate for all PFASs was calculated to be 3.9 m^3 d^{-1}, which is very close to the sampling rate of 4 m^3 d^{-1} reported previously[3]. Thus, a linear sampling rate of 4 m^3 d^{-1} was applied when calculating effective air sample volumes for monthly samples for all PFASs, with the exception of FOSAs and FOSEs in the PUF-PAS, which were shown to equilibrate in less than 1 month (Figure 1). The sample volumes for FOSAs and FOSEs in the PUF-PAS were calculated using the full uptake expression which includes the K_{PSM-A} and characteristics of the PSM (for details see elsewhere[2]) because the uptake curve was already in the curvilinear phase after a few weeks. Overall, the SIP-PAS has the advantage of longer linear uptake periods and a higher capacity for more volatile chemicals in comparison to the PUF-PAS. This is especially important for the PFCAs and FTOHs which were not detectable in the PUF-PAS. However, for chemicals associated with particles the sampling rate may be overestimated because the PAS collect mainly chemicals in the gas-phase and only ~10% of the particle-phase[4].

Depuration compounds are useful for calculating site-specific air sampling rates under different meteorological conditions. For the depuration compounds tested in this study, the $^{13}C_8$ PFOA concentration decreased exponentially for both PAS types during the deployment period with a loss of ~75% after 197 days and ~85% after 168 days for the SIP-PAS and PUF-PAS, respectively. In contrast, the concentration of $^{13}C_8$ PFOS did not change in both PAS types during the whole deployment time of 197 days, whereas 7:2 sFTOH was completely lost after 7 days deployment time. Hence, only $^{13}C_8$ PFOA was suitable for the calculation of the site specific sampling rate. More work is required to identify additional suitable depuration compounds as the depuration compound method for deriving site-specific sampling rates requires confirmation of several ‘suitable’ depuration compounds.

SIP and PUF disks were deployed in different chamber designs to examine the collection efficiency of particles for the PAS. The PFAS concentration did not differ significantly in the four different chamber designs ($p > 0.05$, Student's *t*-test) which indicates that small changes to the chamber designs (e.g., gap between upper and lower domes) has only a small influence on the collection of particles on the PSM. More work is required in this area as the particle-phase sampling efficiency may depend on the type and size distribution of ambient particles.

The air concentration of PFASs measured by the HV-AAS (representing 14-29% of the monthly average) was compared with the air concentration derived by the SIP-PAS and PUF-PAS (representing 100%) using linear regression. Generally, the SIP-PAS showed a good agreement with the air concentration determined by the HV-AAS for all PFAS classes ($R^2 \geq 0.90$). The average difference between the two sampling techniques was less than a factor of two for individual PFASs. Only the concentrations of the PFSAs and PFCAs were slightly lower and higher, respectively, for the SIP-PAS. For the PUF-PAS, the FOSA/FOSE concentrations showed a higher scattering of the data ($R^2 = 0.76$) but the linear regression with the HV-AAS measurements were close to unity. In contrast, the PFSA concentrations showed a good linear regression ($R^2 = 0.90$), but the concentrations were lower compared to the air concentration measured by the HV-AAS which was also observed for the SIP-PAS. Overall, the difference for individual PFASs was within a factor of two using SIP-PAS and PUF-PAS which is considered as a good agreement for comparing PAS derived concentrations with measured air concentration using HV-AAS, especially considering that some variability is due to a different proportion of the air sampled at the site by the two sampling techniques.

Overall, all of the 29 targeted PFASs were detected in air samples. The FTACs, 6:2 FTMAC, FTOHs and shorter chained PFCAs (C_4–C_8) were predominantly present in the gas-phase, whereas the FOSEs, PFSAs and longer chained PFCAs had a high particle-associated fraction. The most abundant PFAS class for the total air concentration (sum of gas- and particle-phase) were the FTOHs representing in average ~80% of the ΣPFASs. The next most abundant compound classes were PFCAs (~7%) and FTACs/FTMACs (~7%). The other PFAS classes represented less than 3% of the ΣPFASs. Total air concentrations for ΣFTOHs ranged from 20–182 pg m^{-3} with 8:2 FTOH as the dominant compound (48% of the ΣFTOHs). The total ΣPFCA concentration ranged from 0.7–20 pg m^{-3} with PFBA as the dominant compound (~54% of the ΣPFCA), and with a tendency of decreasing air concentrations for the longer chain PFCAs. The C_4-based PFASs (e.g., PFBA) are the main replacement compound of the voluntary phase-out C_8-based products (i.e., PFOA and PFOS) which may explain the elevated concentration of PFBA in air at Toronto. Lower total air concentrations were observed for ΣPFSAs (on average 1.0 pg m^{-3}) with PFOS as the predominant compound in this PFAS class (74% of the ΣPFSAs).

The air concentrations of individual PFASs in Toronto were compared using four different sampling approaches over one year (i.e., HV-AAS, SIP-PAS, and PUF-PAS) and six and a half months (i.e., LV-AAS). In general, the results of the LV-AAS and PAS, which allow for a time-integrated sampling over a period of two weeks and one month, respectively, agree well with the HV-AAS concentrations. Interestingly, the majority of PFASs was positively correlated with temperature using HV-AAS ($p < 0.05$, Pearson Correlation). For example, MeFOSE showed highest concentrations in summer (i.e., July and August, monthly average temperature 24–26 °C) with an average of 5.7 pg m^{-3}, whereas about six times lower concentrations were observed in the coldest month in winter (i.e., February, monthly average temperature –5.8 °C) with an average of 0.9 pg m^{-3} (see Figure 2).

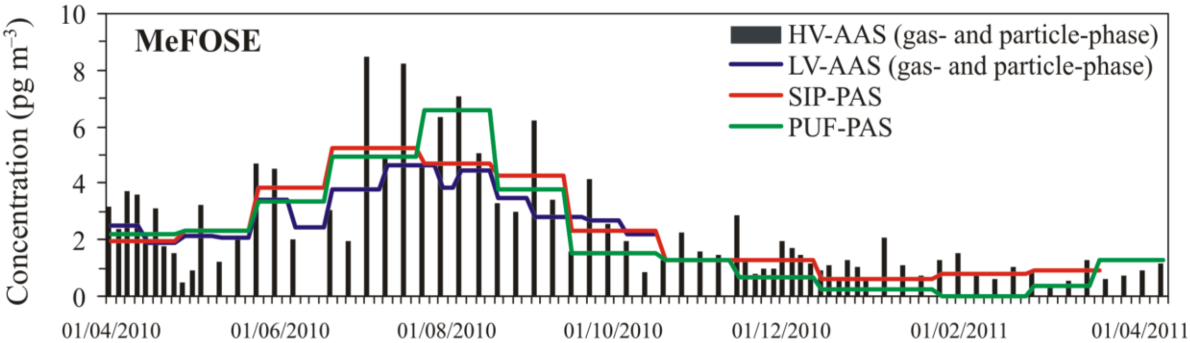

Figure 2. MeFOSE concentrations measured by four different sampling techniques (i.e., HV-AAS and LV-AAS (sum of gas- and particle-phase), and SIP-PAS and PUF-PAS) over one year at Toronto, Canada.

In summary, this study shows for the first time an uptake profile for PFSAs in SIP-PAS and PUF-PAS and for PFCAs in SIP-PAS. The SIP-PAS had the advantage of longer linear uptake periods and a higher capacity for FOSAs, FOSAs, FTOHs and PFCAs in comparison to the PUF-PAS. This is especially important for the PFCAs and FTOHs which are not detectable in the PUF disks due to rapid equilibration. Overall, the results from the PAS were in good agreement with the average air concentrations determined by the HV-AAS and LV-AAS. Seasonal trends were found for the majority of PFASs which showed highest concentrations in summer and lowest concentrations during the winter. Temperature was a key factor governing air concentrations for these PFASs during the year. Ultimately, all sampling approaches investigated were suitable to monitor PFASs in ambient air and to capture seasonal trends.

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References

1. Ahrens, L, Shoeib, M, Harner, T, Lane, D A, Guo, R, Reiner, E J. (2011) *Anal. Chem.* 83(24): 9622–9628
2. Shoeib, M, Harner, T. (2002) *Environ. Sci. Technol.* 36(19): 4142–4151
3. Pozo, K, Harner, T, Lee, S C, Wania, F, Muir, D G, Jones, K C. (2009) *Environ. Sci. Technol.* 43(3): 796–803
4. Klánová, J, Èupr, P, Kohoutek, J, Harner, T. (2008) *Environ. Sci. Technol.* 42(2): 550–555