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Development of an air sampling method for quantifying 12 legacy and emerging PFAS with the OSHA Versatile Sampler (OVS) tube and analysis by HPLC-MS/MS

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ABSTRACT

This study evaluates an air sampling method for quantifying twelve legacy and emerging per- and polyfluoroalkyl substances (PFAS) with the OSHA Versatile Sampler (OVS) tube. We expanded the application of the OVS tube beyond perfluorooctanoic acid (PFOA) by adding multiple acidic PFAS classes including perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), undecafluoro-2-methyl-3-oxahexanoic acid (HFPO-DA, commercially known as GenX), and the sodium salt of 4,8-dioxa-3H-perfluorononanoic acid (DONA-Na). A two-step spiking approach was employed to introduce PFAS to the OVS tube. Non-volatile PFSAs and DONA-Na were statically spiked onto glass fiber filters and XAD-2 media, and then semi-volatile PFCAs and HFPO-DA were introduced via vapor generation with active airflow from spikes applied to the polytetrafluoroethylene (PTFE) retaining ring within the OVS tube. PFAS were quantified by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) with calibration ranges of 0.5–200.0 ng/mL (1.0–200.0 ng/mL for HFPO-DA) and analytical limits of detection (LODs) of 0.1–1.5 ng/mL (equivalent to air sampling LODs of 0.4–6 ng/m^3). Extraction of OVS media with methanol yielded mean recoveries of 97.1–100.1 %. Spiked PFAS compounds at air concentrations of 0.1–20 μg/m^3 (0.1–5 μg/m^3 for DONA-Na) were retained on the OVS tube over a 28-day storage period at 23 °C (mean recoveries: 91–103 %) with breakthrough <5 % for all analytes. These findings establish the OVS tube as a reliable sampling device for monitoring occupational air exposures to a broader range of PFAS compounds, providing critical support for health risk assessment and exposure mitigation in workplace environments.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are integral to various industrial processes, consumer products, and aqueous film-forming firefighting foams due to the strength of the fluorine-carbon bonds providing high chemical and heat resistance [1,2]. Several PFAS have been linked to adverse health outcomes such as developmental effects, immune system suppression, and hormone disruption [3–6]. Recently, the International Agency for Research on Cancer (IARC) classified perfluorooctanoic acid (PFOA) as carcinogenic (Group 1) to humans due to evidence of tumor development in animal studies, and perfluorooctane sulfonate (PFOS) was classified as possibly carcinogenic (Group 2B) to humans [7].

While concerns regarding PFAS exposures are typically associated

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with environmental sources such as drinking water [8], indoor and outdoor air [9–13], and soil [14], their prevalence in occupational settings such as in manufacturing and construction processes (0.33 million tons produced yearly from 2010 to 2019) [15] underscores a critical yet often overlooked route of exposure [16,17]. PFAS compounds vary widely in their chemical and physical properties. Volatile species such as fluorotelomer alcohols (FTOHs) predominantly exist in vapor or aerosol phases [9,18,19], whereas semi-volatile or non-volatile species like perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs)] tend to adsorb to dust or solid surfaces [11,20–25]. Given these variations, workers may be exposed to PFAS through inhalation, dermal contact, or ingestion, depending on the materials used, their applications, and environmental factors [26–29].

Previous studies have measured PFAS levels in air and dust in various work environments, including firefighting stations, ski-waxing rooms, textile manufacturing, e-waste recycling, and floor stripping/waxing [19,30–37]. Despite the potential health risks associated with PFAS exposures, there is a significant gap in standardized methodology for monitoring airborne PFAS [13], especially for air monitoring in workplace atmospheres. Unlike water quality monitoring, where guidelines and regulations for PFAS levels have been more rigorously defined [38–40], the lack of standardized methods for workplace monitoring pose a challenge in understanding and mitigating risks. The German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) was the first governmental organization to establish 8-h occupational exposure limits (OELs) for PFOA and PFOS at 5 and 10 μg/m^3, respectively [41]. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommend 8-h threshold limit values (TLVs) for perfluoroisobutylene (PFIB), perfluorobutyl ethylene (PFBE), and ammonium perfluorooctanoate (APFO) that have been adopted by multiple governmental agencies, but there are currently no established airborne exposure limits for PFAS in the United States [42–44].

The Occupational Safety and Health Administration (OSHA) Versatile Sampler (OVS) was designed to capture airborne chemicals in both vapor and particulate states [45,46]. Kaiser et al. (2005) introduced an analytical air sampling method for collecting PFOA utilizing the OVS tube sampler and analysis by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) [47]. The OVS sampler used was a glass tube sampler containing a 0.3-μm nominal porosity glass fiber filter (GFF) and two beds of hydrophobic polymer (XAD-2) sorbent separated by polyurethane foam (PUF) plug. The method involved spiking PFOA standards (loadings corresponding to a concentration range of 0.47–47.4 μg/m^3 for a 480 L air sample) directly onto the OVS tube, followed by solvent evaporation and active air sampling at flow rates of 1–15 L/min for 8–24 h sampling periods. Recovery of PFOA from the OVS media exceeded 90 % across all loadings with storage stability under ambient and refrigerated conditions for up to 60 days. These observations suggest the OVS tube is a suitable air sampler for monitoring PFOA in workplace environments.

We adapted the method described by Kaiser et al. (2005) to encompass additional PFAS encountered in occupational environments [16,23]. We also investigated an air generation technique tailored to circumvent direct PFAS application to the sampler media—enhancing the fidelity of simulating environmental capture conditions via OVS tubes. Given the absence of established OELs for the majority of PFAS, this study utilized the MAK Commission PFOA OEL of 5.0 μg/m^3 as a provisional OEL for measuring potentially harmful levels of airborne PFAS [41]. This work details the evaluation of the OVS tube for sampling twelve legacy and emerging PFAS at airborne concentrations equivalent to 0.01–2.0 times the reference PFOA OEL.

2. Materials and methods

2.1. PFAS analytical method

2.1.1. Chemicals and standards

Methanol (MeOH; HPLC grade; 99.9 %), acetonitrile (Optima LC/MS grade; 99.9 %), de-ionized water (H_2O; Type II), ammonium acetate (NH_4OAc; crystalline/HPLC; 97 %) were all purchased from Fisher Scientific (Waltham, MA, USA). Perfluorobutanoic acid (PFBA; 99.5 %), perfluoropentanoic acid (PFPeA; 99.7 %), perfluorohexanoic acid (PFHxA; 99.7 %), perfluoroheptanoic acid (PFHpA; 99.4 %), and perfluorooctanoic acid (PFOA; 96.1 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Perfluorobutanesulfonic acid (PFBS; 99 %), perfluoropentanesulfonic acid (PFPeS; 100 %), perfluorohexanesulfonic acid (PFHxS; 95 %), perfluoroheptanesulfonic acid (PFHpS; 100 %), perfluorooctanesulfonic acid (PFOS; 100 %), and undecafluoro-2-methyl-3-oxahexanoic acid (HFPO-DA; 100 %) were purchased from SynQuest (Alachua, FL, USA). Certified reference material (CRM) solutions of the sodium salt of 4,8-dioxa-3H-perfluorononanoic acid (DONA-Na; 50 μg/mL solution in methanol), sodium perfluoro-1-[1,2,3–13C3] hexanesulfonate (13C3-PFHxS; 50 μg/mL solution in methanol), sodium perfluoro-1-[1,2,3,4–13C4]octanesulfonate (13C4-PFOS; 50 μg/mL solution in methanol), perfluoro-*n*-[2,3,4–13C3]butanoic acid (13C3-PFBA; 50 μg/mL solution in methanol), perfluoro-*n*-[1,2–13C2]hexanoic acid (13C2-PFHxA; 50 μg/mL solution in methanol), and 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-13C3-propanoic acid (13C3–HFPO-DA; 50 μg/mL solution in methanol) were purchased from Wellington Laboratories (Guelph, ON, Canada). Additionally, perfluoro-*n*-(1,2–13C2)octanoic acid (13C2-PFOA; 1284.78 μg/mL solution in methanol) was obtained from DuPont (Wilmington, DE, USA).

2.1.2. Preparation of PFAS stock solutions

Individual PFAS stock solutions (excluding DONA-Na) were prepared at 1000 μg/mL by dissolving the corresponding neat solid or liquid compounds in a 1:1 (v/v) mixture of MeOH:H_2O to a 10 mL final volume. Solvents were added using verified solvent dispensers. DONA was only available as a sodium salt (DONA-Na) dissolved in MeOH at 50.0 μg/mL. A mixed PFAS stock solution (10 μg/mL) in 1:1 MeOH:H_2O was prepared by combining appropriate volumes of individual PFAS stock solutions (1000 μg/mL each) and DONA-Na (50.0 μg/mL) and diluting to a 10 mL final volume. Similarly, a mixed internal standard (IS) solution was prepared at approximately 1.0 μg/mL by combining appropriate volumes of individual stock IS in 1:1 MeOH:H_2O to a 5 mL final volume. PFAS stock solutions were also corrected for material purity and salt complex (DONA-Na).

2.1.3. Instrumental conditions

HPLC-MS/MS analysis with negative electrospray ionization was performed by Bureau Veritas North America (Novi, MI, USA) using a Waters 2795 Alliance HPLC system coupled to a Waters Micromass Quattro MS/MS (Waters Corp., Milford, MA, USA). The chromatographic conditions and optimized MS/MS parameters for the PFAS mass transitions are shown in the **Supporting Information (SI)** Tables S1 and S2, respectively. Six ^{13}C-labelled IS compounds were included in the mass spectrometric method for quantitation.

2.1.4. Preparation of PFAS calibration standards

Calibration stock standard solutions (N = 8; range: 0.5–200.0 ng/mL) were prepared in MeOH via serial dilutions of the 10 μg/mL mixed PFAS stock solution and 50 μg/mL DONA-Na stock solution to 10 mL final volumes. Analytical standards for HPLC-MS/MS analysis were prepared by mixing 200 μL of each calibration stock solution with 10 μL of the IS solution (1.0 μg/mL) in a 300 μL conical polypropylene autosampler vial. Analysis was performed using a single injection of each calibration standard to the HPLC-MS/MS method described in Section 2.1.3. Calibration curves for individual PFAS adjusted with their

respective IS were created using a second-order polynomial fit algorithm with a weighted (x^{-1}) regression.

2.1.5. Limits of detection and quantitation for the analytical method

The analytical limits of detection (LOD) and quantitation (LOQ) were determined using the standard error of regression of a low-level calibration curve consisting of four levels per analyte injected in duplicate, and a methanol reagent blank. Calibration standard levels used for the LOD/LOQ determination ranged from 0 to 5.0 ng/mL dependent upon the analyte because instrument responses varied.

The calculations for the analytical LOD/LOQ followed the guidelines outlined in the NIOSH Manual of Analytical Methods (NMAM) 5th edition [48]. A non-weighted linear regression curve was generated from the peak area responses of the 0–5.0 ng/mL calibration standards. The predicted responses ($\hat{Y}_i$) were determined for each corresponding X value, and the standard error of the regression, S_y is calculated via Eq (1):

$$S_y = \left[\sum (\hat{Y}_i - Y_i)^2 \Big/ (N-2)\right]^{1/2} \quad (1)$$

where, Y_i and N are the observed mean response and number of data points, respectively. The calculated LOD and LOQ are then estimated from Eqs (2) and (3) respectively:

$$LOD = 3 \times S_y / m \quad (2)$$

$$LOQ = 3.33 \times LOD \quad (3)$$

in cases where the mean blank response value "B" significantly differs from the intercept "b" of the regression or if the intercept is negative, the formula in Eq (4) was utilized:

$$LOD = (3S_y + B - b) / m \quad (4)$$

2.1.6. OVS media extraction and sample preparation for HPLC-MS/MS analysis

A custom OVS tube (SKC, cat# 226-30-16-BV; 11 mm inner diameter; 13 mm outer diameter × 60 mm length) was used in this study (Fig. S1). The OVS tube contained a 12-mm GFF retained by a polytetrafluoroethylene (PTFE) ring followed by two sections of XAD-2 sorbent (front section, 270 mg; back section, 140 mg) separated by a PUF plug. The back section of the XAD-2 sorbent is retained by a second PUF plug. PTFE rings were soaked in methanol for 2 h and then analyzed by HPLC-MS/MS to test for potential leaching of targeted PFAS. Extractions of OVS tube media sections were performed by placing them individually (or combined as specified) into separate glass test tubes, followed by addition of 2 mL of MeOH and shaking for 60 min (2 cycles/sec). The extracts were then filtered through an Acrodisc syringe filter (0.45 μm) into 4 mL amber glass vials. For HPLC-MS/MS analysis, 200 μL of the extracts were spiked with 10 μL of mixed IS solution (1.0 μg/mL) in a polypropylene autosampler vial. Appropriate dilutions of the extracts were performed using MeOH to ensure PFAS concentrations fell within the calibration range.

2.2. Method evaluation criteria

2.2.1. Preparation of PFAS spiking solutions

Four PFAS mixed spiking solutions were prepared in 1:1 MeOH:H_2O by combining calculated volumes of individual PFAS standards to a final volume of 10 mL (see Table S3). Two high-concentration mixed spiking solutions (H-Mix) were prepared at 150 μg/mL: H-Mix #1 containing the five PFCAs and HFPO-DA, and H-Mix #2 containing the five PFSAs only. These H-Mix solutions, along with the DONA-Na standard (50 μg/mL in MeOH), were used to achieve the top three mass loading at 0.1 ×, 0.5 ×, and 2.0 × OEL (see Section 2.2.2). Two low-concentration mixed spiking solutions (L-Mix) were prepared at 3 μg/mL: L-Mix #1 containing the five PFCAs and HFPO-DA, and L-Mix #2 containing the five PFSAs and DONA-Na to achieve the low-level mass loading at 0.01 × OEL.

For solvent testing in the preliminary PFAS vapor generation evaluation (see Section 2.2.3), two more mixed spiking solutions at 150 μg/mL were prepared in 10 mL of acetonitrile. H-Mix #3 contained five PFCAs and HFPO-DA, while H-Mix #4 contained only five PFSAs.

2.2.2. Extraction efficiency of OVS media

The extraction efficiency from OVS media was tested at 24, 240, 1200, and 4800 ng per media section, equivalent to 0.05, 0.5, 2.5, and 10.0 μg/m^3 in 480 L of air volume (Table S4). These levels correspond to 0.01 ×, 0.1 ×, 0.5 × and 2.0 × the provisional OEL (5.0 μg/m^3) set by the German MAK Commission for PFOA [41]. Notably, since both media sections within the same OVS tube were spiked at the same levels, the total concentrations for the entire OVS tube were doubled, corresponding to 0.1, 1, 5, and 20 μg/m^3 in 480 L air volume. Six replicates of each mass loading level were prepared on both the GFF and front XAD-2 sorbent (XAD_f) sections in the OVS tube, along with 6 blank tubes to evaluate extraction efficiency. Extraction efficiency (%) is defined as the percentage of a target analyte that is successfully retrieved from the media, calculated using Eq (5).

$$\text{Extraction Efficiency (\%)} = \left(\frac{\textit{Amount of analyte extracted}}{\textit{Amount of analyte introduced}}\right) \times 100 \quad (5)$$

A total of eighty-four GFF and XAD_f media sections were transferred into separate disposable glass test tubes for media spiking. Additionally, six GFF and XAD_f media sections were also placed into separate disposable glass test tubes to serve as media blanks. These media sections were then directly spiked with appropriate volumes from H-Mix #1, H-Mix #2, and DONA-Na standard to achieve the target mass loading of 240, 1200, and 4800 ng/media-section. To achieve the 24 ng/media-section mass loading, an L-Mix combining all 12 PFAS (3 μg/mL in 1:1 MeOH:H_2O) was used.

The spiked media were air-dried at room temperature for 90 min, followed by extraction and analysis (see Section 2.1.6). The extracts from both GFF and XAD-2 media at 0.5 × and 2.0 × OEL levels were diluted 20-fold with MeOH prior to analysis to fall within the calibration range.

2.2.3. Limits of detection and quantitation for the air sampling method

The air sampling LODs and LOQs were determined using the NIOSH evaluation criteria [48]. The OVS media (GFF and XAD_f analyzed separately) were spiked in duplicate at seven levels ranging from 0.2 to 20.0 ng (equivalent to 0.4–41.7 ng/m^3 with 480 L air sampled). The media sections were transferred to disposable glass test tubes for spiking, and two additional GFF and XAD_f media sections were allocated for media blanks. The spiked media were allowed to air-dry for 90 min at room temperature. Although spiking was performed exclusively on the GFF and XAD_f media, the PTFE ring was combined with the GFF, and the middle PUF was combined with the XAD_f in separate disposable glass tubes. These combined components were extracted together to replicate the field sample preparation process. The extracted samples were then prepared for HPLC-MS/MS analysis following the method described in Section 2.1.6. Non-weighted linear regression curves to determine the sampling LODs/LOQs were generated as described in Section 2.1.5, and the standard error of regression was used to determine the LOD/LOQ. It should be noted that not all seven levels were used for calculating the LOD/LOQ for each analyte. The four levels appropriate for each analyte response that ranged from below the expected LOD to no more than 10 × the expected LOD were used. These ranges were 0.2–2.0 ng for PFBS and DONA-Na, 2.0–20.0 ng for HFPO-DA, and 0.5–5.0 ng for all other analytes.

2.3. Air sampling with the OVS tube

2.3.1. Preliminary evaluation of PFAS volatilization and collection behavior

A pilot vapor generation technique was initially evaluated to understand the volatilization and collection behavior of PFAS on sampler media. This evaluation was essential for establishing the methodology by which various PFAS were introduced onto OVS tube media for further testing, ensuring accurate representation of their behavior in air sampling applications. The volatility and collection behavior of 11 PFAS were evaluated only at 0.5 × OEL in spiking solvents 1:1 MeOH:H_2O and acetonitrile. DONA-Na was excluded from the vapor generation test because its salt form is non-volatile. Air sampling was performed over a 480-min period at ambient temperature (23 °C) and relative humidity (RH; 62 %), with a nominal flow rate of 1 L/min. The setup and protocol for the vapor generation along with the results are fully described in **Text S1 and** Table S5. Preliminary testing demonstrated successful vapor generation of PFCAs and HFPO-DA, with 87.4–108.0 % recoveries mainly on the GFF. Volatilization was more efficient with 1:1 MeOH:H_2O, whereas acetonitrile resulted in higher residues on the initial spiking site (PTFE ring). In contrast, PFSAs did not volatilize, with 100 % of residues recovered from the PTFE ring, reflecting their inherent low volatility and strong surface affinity. Accordingly, a two-step spiking approach tailored to PFAS volatility and optimized for real-world environmental capture conditions was proposed for their introduction to the OVS tube, enabling comprehensive PFAS air sampling evaluation following NIOSH NMAM guidance [48].

2.3.2. PFAS introduction to the OVS tube

The introduction of 12 PFAS into the OVS tube utilized the two-step spiking approach. In the first step, non-volatile PFSAs and DONA-Na were applied to the OVS tube media (GFF and XAD_f) using a static liquid spike. The GFF media was first removed from the OVS tube to avoid direct contact with XAD_f and was subsequently placed on crimp caps for further spiking. The solvent was allowed to evaporate at room temperature for 60 min. Following evaporation, the GFF media sections were reassembled into the OVS tubes, which were then capped and stored overnight in preparation for the next air sampling steps. The second step involved vapor generation to introduce volatile PFCAs and HFPO-DA. These compounds were spiked onto the PTFE ring positioned and suspended above the PFSAs and DONA-Na-spiked media within the same OVS tube (Fig. S2). Air sampling was performed over a 480-min period at a nominal flow rate of 1 L/min. Vapor generation spiking occurred at the start of the air sampling, with the solvent observed to evaporate within the initial minutes of the sampling process as air passed through the OVS tube.

Following the NIOSH NMAM guidance [48], PFAS were introduced to the OVS tube at four mass loadings according to Table S6. Using the static liquid spike method, PFSAs and DONA-Na were spiked on both GFF and XAD_f media sections at concentrations corresponding to 0.01 × , 0.1 × , 0.5 × OEL (5.0 μg/m^3), with PFSAs additionally spiked at 2.0 × OEL and DONA-Na at 1.0 × OEL per media section, based on a total sampled air volume of 480 L. PFCAs and HFPO-DA were then introduced onto the PTFE ring within the same tube at concentrations corresponding to 0.01 × , 0.1 × , 0.5 × , and 2.0 × OEL.

To achieve these mass loadings, PFAS stock solutions prepared in 1:1 MeOH:H_2O, H-Mix and L-Mix, as well as DONA-Na (50 μg/mL), were used (see Section 2.2.1). Static liquid spikes from PFSAs and DONA-Na spiking solutions were then applied to both the GFF and XAD_f sections to achieve the required mass loadings (Table S6). The spiked media at the three lower concentration levels were allowed to dry for 60 min, while the highest concentration level dried for 90 min. At the start of active air sampling, the PTFE ring was spiked with PFCAs/HFPO-DA solutions at the target mass loadings using the vapor generation liquid spike method.

2.3.3. Active air sampling following sample introduction

Active air sampling was performed to assess the collection efficiency, retention efficiency, and breakthrough of the OVS media. The spiked OVS tubes were assembled on a lab-constructed 42-port air sampling manifold connected to a vacuum pump (Fig. S3). Air sampling was performed over a 480-min period at 23 °C (20 % or 80 % RH), with a nominal flow rate of 1 L/min. A Miller-Nelson test atmosphere generator (Assay Technology, Livermore, CA, USA) was used to generate air at the specified temperature and RH. Flow rate for each OVS tube was measured at the beginning and end of air sampling using a DryCal DC-Lite flow meter (*data not shown*). Temperature and RH were measured over the course of the sampling event using a traceable hygrometer/thermometer. After sampling for 8 h, OVS tubes were removed from the sampling manifold, capped, and stored overnight in ambient laboratory conditions. Extractions were performed the following day to determine the collection and retention of PFAS within the four distinct OVS tube components [PTFE ring, GFF, XAD_f and middle PUF, back XAD-2 sorbent (XAD_b)]. One replicate for PFPeA and HFPO-DA at the 0.5 × OEL spike level were both eliminated from the collection efficiency, retention efficiency, and breakthrough calculations because their total recoveries fell below the >75 % NIOSH NMAM acceptance criteria [48] and they were determined to be statistical outliers by the Grubbs' test at 95 % confidence level based on all recovery data from the active air sampling procedure ($n = 24$) [49].

2.3.4. Storage stability

The stability of PFAS in OVS tubes was evaluated over a 28-day period for mass loadings equivalent to 0.01 × and 2.0 × OEL (0.5 × OEL for DONA-Na). These loadings correspond to the amounts expected from sampling 480 L of air. Utilizing the liquid static spike method, the GFF and XAD_f sections of the OVS tube were individually spiked; the GFF was spiked on the crimp cap as described previously. This method resulted in each OVS tube receiving twice the concentration (see Table S7). After spiking, the solvent was allowed to evaporate, and the media was reassembled within the tubes. OVS tubes were stored in light-shielded bags at room temperature until extraction and analysis on the designated storage day. Each section of the OVS tube—GFF + PTFE ring, XAD_f + middle PUF, and XAD_b—was extracted separately as described in Section 2.1.6. Six replicates were spiked per concentration level at each storage interval (days 0, 7, 14, 21, and 28), yielding a total of thirty replicates per level. Additionally, ten blank OVS tubes were analyzed for quality control purposes.

3. Results and discussion

3.1. Analytical performance

3.1.1. Calibration curve and analytical limits of detection and quantitation

The calibration performance of the HPLC-MS/MS method for the 12 PFAS was sensitive and demonstrated acceptable regression fit correlation ($R^2 > 0.9996$) within the concentration range of 0.5–200.0 ng/mL (Table 1). HFPO-DA displayed the least favorable negative electrospray ionization response of the PFAS [50,51], requiring a higher minimum calibration standard of 1.0 ng/mL. PFBA exhibited previously reported chromatographic anomalies, including peak splitting and broadening due to early retention behavior and solvent strength (Fig. 1) [52]. However, this peak splitting did not affect the integration of PFBA's chromatographic peak or the accuracy of its calibration curve, which maintained a high correlation ($R^2 = 0.9999$) across the studied calibration range. Chromatographic peaks corresponding to both branched and linear isomers of PFHxS and PFOS were observed and integrated together to determine their concentration. The back-calculated concentrations from the calibration curves were within ±10 % absolute error of the expected concentrations for each standard level and for each analyte. The quadratic regression fit for each analyte, chromatograms of a 10.0 ng/mL standard, and the linear regression plot used to determine

Table 1
Calibration results and analytical limits of detection and quantitation.

PFAS	Calibration			LOD/LOQ	
	Calibration range (ng/mL)	R^2	Concentration (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)
PFBA	0.5–200.0	0.9999	0.5–5.0	0.5	1.7
PFPeA		0.9998	0.1–1.0	0.1	0.50
PFHxA		0.9999	0.1–1.0	0.1	0.34
PFHpA		0.9997	0.25–2.0	0.3	0.83
PFOA		0.9997	0.1–1.0	0.1	0.45
PFBS		0.9999	0.1–1.0	0.1	0.42
PFPeS		0.9999	0.25–2.0	0.3	0.84
PFHxS		0.9998	0.1–1.0	0.2	0.72
PFHpS		0.9999	0.25–2.0	0.3	0.83
PFOS		0.9999	0.25–2.0	0.3	0.83
DONA-Na		0.9998	0.1–1.0	0.1	0.50
HFPO-DA	1.0–200.0	0.9999	0.5–5.0	0.8	2.6

R^2 = coefficient of determination; LOD = limit of detection; LOQ = limit of quantification.

the analytical LODs/LOQs for individual PFAS can be seen in the **SI** (Fig. S4).

The analytical LOD and LOQ values of all analytes ranged from 0.1 to 0.8 ng/mL and 0.3–2.6 ng/mL, respectively, as shown in Table 1. PFPeA, PFHxA, PFOA, PFBS, and DONA-Na demonstrated the lowest LOD at 0.1 ng/mL, with corresponding LOQs ranging from 0.34 to 0.50 ng/mL. HFPO-DA had the highest LOD and LOQ values, at 0.8 ng/mL and 2.6 ng/mL, respectively. PFHpA, PFPeS, PFHpS, and PFOS showed similar LODs of 0.3 ng/mL and LOQs of approximately 0.83 ng/mL.

3.1.2. *Air sampling limits of detection and quantitation*

Analysis of GFF and XAD-2 media blanks revealed that all measured PFAS were either not detected or present at concentrations below the lowest calibration standard. Minor peaks for PFBA, PFPeA, and PFHxA were observed below the lowest standard (<0.5 ng/mL) on both GFF and XAD-2 media. All other compounds were not detected (ND). These results imply minimal to no PFAS contamination in the media blanks.

The sampling LOD values ranged from 0.2 to 3 ng (equivalent to 0.4 to 6 ng/m^3), with most compounds showing an LOD of 0.2 ng for both GFF and XAD$_f$, except HFPO-DA, which had an LOD of 3 ng for both media. The LOQ values for all analytes and media types ranged from 0.67 to 2.0 ng, except for HFPO-DA, which had LOQs of 9.1 ng for GFF and 8.6 ng for XAD$_f$. PFBA and PFPeS showed LOQ values of 2.0 ng and 1.0 ng, respectively, for both media types, while PFOS had LOQs of 0.67 and 0.69 ng for both GFF and XAD$_f$, respectively. Overall, HFPO-DA exhibited the highest quantitation limits, indicating that the method is less sensitive for this analyte compared to other PFAS [50,51]. The results for LOD and LOQ values for both media types are summarized in Table 2.

3.2. *Extraction efficiency*

Extraction efficiencies for individual PFAS in GFF and XAD-2 spiked media are shown in Fig. 2 (see Table S8 for more information). Acceptable extraction efficiencies within the range of 75 %–125 % of the theoretical values [48] were achieved for all 12 PFAS across the two media types. Extraction efficiencies for PFCAs across all spike levels (24–4800 ng) on GFF ranged from 91.8 % to 106 %, with a mean efficiency of 100 % ± 4.4 % (N = 120). On XAD-2, extraction efficiencies ranged from 92.6 % to 113 %, with a mean efficiency of 104 % ± 4.9 %. For PFSAs, extraction efficiencies on GFF were observed between 89.3 % and 104 %, with an average of 97.1 % ± 4.2 %, whereas on XAD-2, efficiencies spanned from 96.8 % to 110 %, with a mean of 105 % ± 3.9 %.

For HFPO-DA, extraction efficiencies on GFF ranged from 94.2 % to

Table 2
Results of the air sampling LODs/LOQs calculated for GFF and XAD-2 media spiked with 0.2–2.0 ng of the PFAS standard mixture (with blank subtraction).

PFAS	Mass Collected on OVS Tube				Air Sampling Concentration[a]			
	LOD (ng)		LOQ (ng)		LOD (ng/m^3)		LOQ (ng/m^3)	
	GFF	XAD$_f$	GFF	XAD$_f$	GFF	XAD$_f$	GFF	XAD$_f$
PFBA	0.2	0.2	2.0	2.0	0.4	0.4	4.2	4.2
PFPeA	0.3	0.2	1.0	0.67	0.6	0.4	2.1	1.4
PFHxA	0.5	0.6	1.6	1.9	1	1	3.3	4.0
PFHpA	0.2	0.3	0.79	1.0	0.4	0.6	1.7	2.1
PFOA	0.2	0.2	0.67	0.67	0.4	0.4	1.4	1.4
PFBS	0.2	0.2	0.66	0.66	0.4	0.4	1.4	1.4
PFPeS	0.2	0.2	1.0	1.0	0.4	0.4	2.1	2.1
PFHxS	0.2	0.3	0.67	1.1	0.4	0.6	1.4	2.3
PFHpS	0.2	0.2	0.67	0.67	0.4	0.4	1.4	1.4
PFOS	0.2	0.2	0.67	0.69	0.4	0.4	1.4	1.4
HFPO-DA[b]	3	3	9.1	8.6	6	6	19	18
DONA-Na	0.2	0.2	0.67	0.67	0.4	0.4	1.4	1.4

LOD = limit of detection; LOQ = limit of quantification; GFF = glass fiber filter; XAD$_f$ = front XAD-2 sorbent.
[a] The calculated LOD and LOQ for each analyte collected on OVS tube media was converted to air concentration (ng/m^3) by dividing the mass per sample (ng) by the total air sampled (0.48 m^3) over an 8-h period with a flow rate of 1 L/min.
[b] Spike range for HFPO-DA was 2.0–20.0 ng.

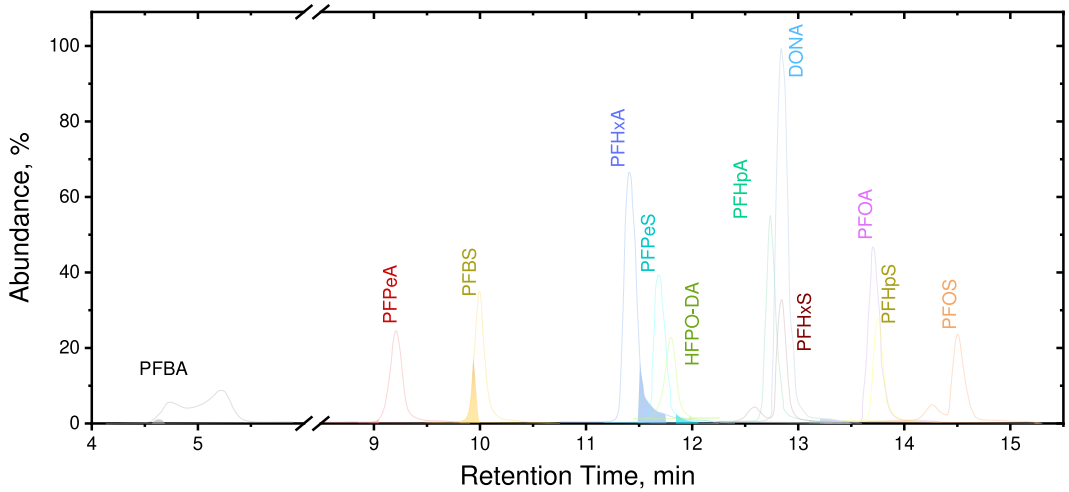

Fig. 1. HPLC-MS/MS chromatogram for a 5 ng/mL mixture of 12 PFAS using a Waters 2795 Alliance HPLC coupled to a Waters Micromass Quattro MS/MS system.

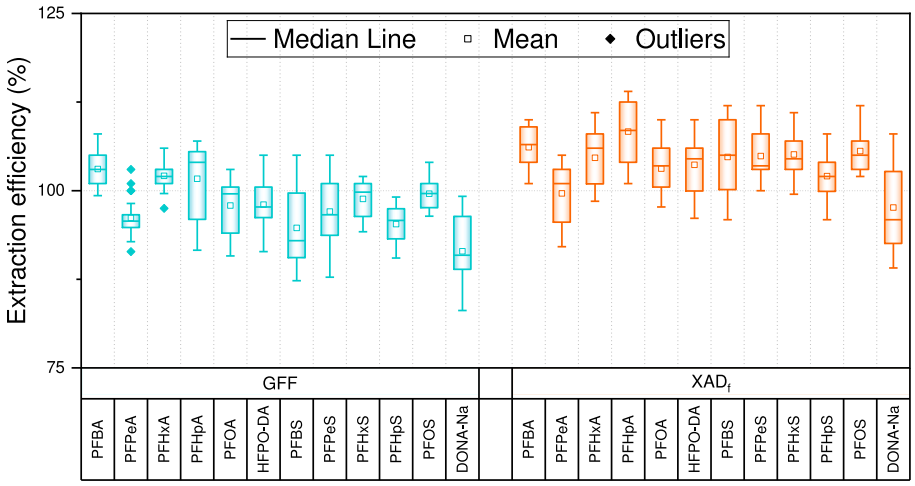

Fig. 2. Box-and-whisker plots displaying the mean extraction efficiencies of individual PFAS spiked onto GFF and XAD$_f$ media at 0.01–2.0 × OEL per media section.

101 %, with an average of 98.0 % ± 3.3 % (N = 24). On XAD-2, efficiencies ranged from 98.3 % to 107 %, with an average of 104 % ± 4.3 %. For DONA-Na, efficiencies on GFF ranged from 85.1 % to 97.6 %, with an average of 91.4 % ± 4.7 % (N = 24), while on XAD-2, efficiencies ranged from 91.7 % to 107 %, with an average of 97.6 % ± 6.3 %. These results indicate that XAD-2 generally exhibited higher extraction efficiencies, with a broader range and slightly higher mean values compared to GFF across most compounds and spike levels, reflecting its suitability for capturing the target list of PFAS in this study.

3.3. Air sampling of PFAS

3.3.1. Media blanks

Table S9 provides the results for six media blanks sampled alongside spiked media, analyzed at 20 % and 80 % RH, with three blanks per RH level. Results are expressed in ng per section. If analyte peaks were absent or below the lowest calibration standard, they were recorded as ND. Of all the PFAS tested, only PFHxA was detected at 80 % RH in the range of 1.8–3.1 ng/section, while at 20 % RH, levels were generally not detected with minimal concentrations between 0.7 and 0.8 ng per section. The presence of PFHxA in media blanks indicates background contamination likely from the sampling equipment, laboratory environment, or analytical reagents, a common occurrence observed in the literature [53–55]. Moreover, the detected PFHxA levels at 80 % RH suggest that higher humidity enhances PFHxA adsorption or transfer onto sampling media. Therefore, for PFHxA, air sampling results were corrected only for 0.01 × OEL level at both RH levels, across all media types. No further adjustments were necessary for levels above this, as the 20-fold dilution significantly reduced any matrix effects from the media. To manage variability in PFHxA background levels associated with reagents, labware, and instrumentation, it is recommended to implement blank corrections for OVS tubes on both a per-preparation and per-analysis batch basis.

3.3.2. PFCAs and HFPO-DA

The OVS tube demonstrated high efficiency in collecting and retaining analytes, with average total OVS recovery ranging from 91.4 % to 98.9 % across all spiked concentrations and RH levels (Fig. 3). However, the vaporization, collection, and retention dynamics of the compounds showed clear dependencies on both their spiked concentration and the RH levels (Fig. 4a). The results of collection and retention of PFCAs and HFPO-DA across the different OVS tube sections for the four tested sampling levels at 20 % and 80 % RH are presented in Table S10 and S11.

The vapor generation of PFCAs and HFPO-DA showed concentration dependence, increasing at concentrations above 0.01 × OEL. At the 0.01 × OEL spike level (24 ng), the analytes exhibited minimal vapor generation with the majority remaining as residues on the PTFE ring and less than 10 % being collected on the GFF or XAD$_f$ sections under both RH levels studied. The unexpected concentration-dependent behavior in vapor generation suggested that lower concentrations might not effectively volatilize from the PTFE ring surface. Despite some variability,

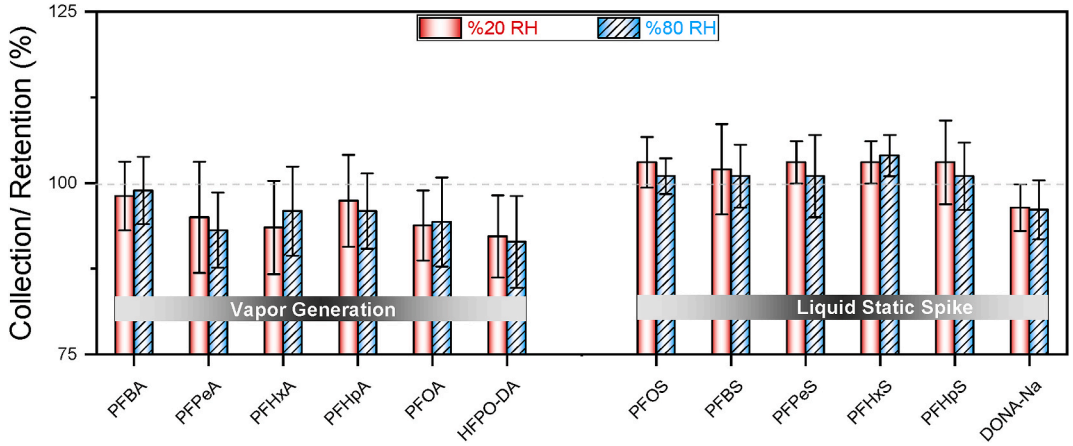

Fig. 3. Mean OVS collection and retention efficiencies for individual PFAS during 8-h air sampling at a nominal flow rate of 1 L/min, utilizing both vapor generation (PFCAs/HFPO-DA) and liquid static spiking (PFSAs/DONA-Na) methods. Data are presented across four spike levels (Table S6) and two RH levels (80 % and 20 %).

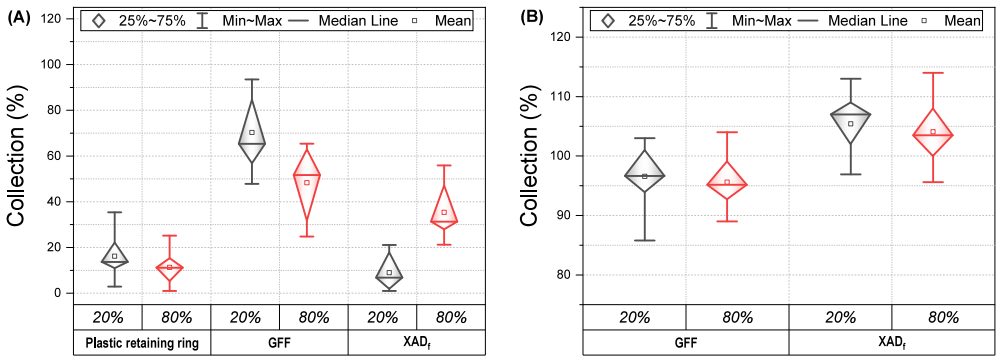

Fig. 4. Mean collection efficiency of individual OVS sections during 8-h air sampling at a nominal flow rate of 1 L/min, using vapor generation and liquid static spiking methods. Data for each section are averaged at 20 % and 80 % RH, across: A) 0.1–2.0 × OEL per media section for PFCAs and HFPO-DA, and B) 0.01–0.5 × OEL per media section for PFSAs and DONA-Na. Results for 0.01 × OEL for PFCAs and HFPO-DA, as well as 2.0 × OEL PFSA (1.0 × OEL DONA-Na), exhibited distinct behavior and are therefore addressed in the text.

higher spike levels (0.1–2.0 × OEL) demonstrated consistent vapor generation with approximately >80 % of the initially spiked concentration being collected on the GFF and XAD$_f$ sections. Additionally, a trend of decreasing residue on the PTFE ring with increasing concentration was observed. This behavior can be explained by the spiking procedure, in which small droplets of PFAS solution were added to the limited surface area of the PTFE ring. At lower PFAS spike levels, the small volume quickly saturates and adsorbs to the PTFE surface resulting in minimal migration [56]. At higher PFAS spike levels, multi-layer adsorption can develop with the first molecular layer adhering to the PTFE surface and additional layers are weakly bound and prone to migration within the OVS tube [57].

RH levels significantly influenced vapor generation and analyte distribution among the OVS tube sections, with the extent of the effect varying based on the analyte spike level. At the lowest spike level (0.01 × OEL), RH exhibited minimal impact on analyte vaporization and distribution across the GFF and XAD$_f$ sections. Approximately 92 % and 90 % of analyte residues remained on the PTFE ring at 20 % and 80 % RH, respectively. However, at higher spike levels (≥0.1 × OEL), increased mean recovery ranges were observed on the PTFE ring at 20 % RH (3–35 %) compared to 80 % RH (1–25 %), suggesting that high RH may promote analyte vaporization from the PTFE ring. Additionally, high RH levels facilitated analyte migration from GFF to XAD$_f$ at 0.1–2.0 × OEL levels. At 20 % RH, the GFF section retained 48–94 % of the spiked sample, while 1–21 % migrated to the XAD$_f$ section. In contrast, at 80 % RH, the GFF collected a reduced proportion (25–65 %) of the sample, with greater migration to the XAD$_f$ (21–56 %). Analytes in the XAD$_b$ section were predominantly not detected or detected at concentrations below the acceptable breakthrough threshold (<5 %) [48].

3.3.3. PFSAs and DONA-Na

The retention efficiencies of statically spiked PFSAs (0.01–2.0 × OEL) and DONA-Na (0.01–1.0 × OEL) on the GFF and XAD$_f$ sections of the OVS tube are summarized in Table S12 (20 % RH) and Table S13 (80 % RH). Retention efficiency (%) is defined as the percentage of a specific analyte that is retained by the media in relation to the amount of analyte that was initially introduced into the OVS tube, calculated using Eq (6).

The OVS tube demonstrated consistent total retention efficiencies across all spiked concentrations and RH levels, with mean retention efficiencies between 96.1 % and 103 % (Fig. 3). Unlike the PFCAs, the retention dynamics of PFSAs and DONA-Na were not influenced by RH or spike levels within the range of 0.01–0.5 × OEL per media section (Fig. 4b).

Retention patterns on individual GFF and XAD$_f$ sections remained relatively constant across RH levels. Moreover, analyte concentration did impact retention on GFF sections. Near-complete recovery (96.0–105 %) was achieved for GFF and XAD$_f$ sections at spike levels of 0.01 × , 0.1 × , and 0.5 × OEL per media section. At the 2.0 × OEL spike level (1.0 × OEL for DONA-Na), significant portions (28.0–71.4 %) of the statically spiked analytes on GFFs migrated to XAD$_f$ sections. This migration was influenced by the analyte chain length, with shorter-chain PFSAs showing more pronounced migration to XAD$_f$ sections, and this has been observed previously with high-volume air sampling of gaseous PFOA [58]. The migration of DONA-Na (58.1–65.3 %) paralleled that of PFPeS (64.8–69.3 %) and PFHxS (53.8–58.8 %). Notably, RH did not appear to affect the migration behavior. Due to analyte migration from GFF to XAD$_f$, XAD$_f$ sections exhibited high PFAS recoveries from 139.2 to 190.3 %. All XAD$_b$ sections (*data not shown*) displayed either "ND" levels or less than 0.1 % of the amount found on the XAD$_f$ section. This performance underscores the effectiveness of the XAD-2 sorbent in retaining PFSAs and DONA-Na, maintaining its efficiency at the highest spike level with a total PFAS mass loading of 81.6 μg on the OVS tube.

The observed migration of PFSAs and DONA-Na from the GFF to the XAD$_f$ section at the highest spike level may be attributed to the uneven distribution of the spiked samples on the GFF. Despite employing a systematic approach to introduce the spikes—applying small droplets of the stock solution evenly over the GFF surface—this method may have resulted in non-uniform deposition leading to insufficient interaction between the analytes and the GFF matrix. Weak interactions likely facilitated the migration of loosely bound analytes following the expected volatility trend of the compounds (C4 > C5 > C6 > C7 > C8). Moreover, the additional collection of PFCAs and HFPO-DA vapor on the GFF might have further saturated the GFF surface, exacerbating the migration of loosely bound analytes to the XAD$_f$.

$$\text{Retention Efficiency (\%)} = \left(\frac{\textit{Amount of analyte retained by media}}{\textit{Amount of analyte introduced to the OVS tube}}\right) \times 100 \quad (6)$$

3.4. Storage stability

The results demonstrate the target PFAS were stable on OVS tubes over a 28-day period at room temperature. The OVS tubes exhibited mean recoveries of 95.2 %–107 % for all 12 PFAS over a 28-day period, with relative standard deviations (RSDs) below 9 % across all combined concentration levels. Analysis of media blanks ($N = 10$) revealed no detectable analyte peaks, except for PFBA and PFOS which consistently displayed minor peaks corresponding to concentrations well below their lowest calibration points. Table S14 summarizes the OVS tube storage stability for all PFAS, presenting the mean recoveries of spiked media sections at 0.01 × and 2.0 × OEL levels (0.5 × OEL for DONA-Na) combined.

The analytes were stable on both GFF and XAD_f media at the lowest concentration level (0.01 × OEL per media section), with mean recoveries ranging from 93.1 % to 97.5 % for GFF and 103 % to 105 % for XAD_f over all storage periods (Table 3). A substantial migration of all analytes from GFF to XAD_f was observed at the 2.0 × OEL (and 0.5 × OEL for DONA-Na) during the first week of storage, with no further migration at subsequent time points. The average migration of total GFF-spiked mass ranged from 76.1 % to 80.3 % with the most volatile compound (PFBA) showed an average migration of 89.1 %. Across all storage periods and concentration levels, PFAS were either not detected or concentrations were less than 0.2 % of the amount spiked onto the XAD_f section, indicating storage-related migration in the OVS tube is not a concern with minimal breakthrough from the GFF and XAD_f sections.

4. Conclusions

This study evaluated air sampling of PFAS using OVS tubes with GFF and XAD-2 media, offering a reliable method for assessing airborne exposures. The developed HPLC-MS/MS method demonstrated acceptable sensitivity, precision, and quadratic fit ($R^2 > 0.9996$) over a broad calibration range. The sampling method LODs (0.2–0.6 ng/media section) and LOQs (0.66–2.0 ng/media section) were suitable for trace-level analysis, with HFPO-DA exhibiting higher LOD (3 ng/media section) and LOQ (8.6–9.1 ng/media section) thresholds due to its lesser negative electrospray ionization efficiency [50,51]. The OVS tube displayed average collection and retention efficiencies of 91.4–104 % across the target PFAS classes at both 20 % and 80 % RH. While 80 % RH promoted analyte migration from GFF to XAD-2 at higher spike levels, analyte breakthrough in the OVS tube remained negligible. Extraction efficiencies for all PFAS were 85.1–113 % with XAD-2 outperforming GFF in precision and range. Storage stability tests highlighted acceptable analyte recoveries (90.8–114 %) over 28 days at room temperature, with minimal variability across storage periods and concentration levels (RSDs <5.8 %). While short-term redistribution of analytes among the OVS tube media was observed, no further redistribution occurred after the first week and no breakthrough was observed. This research establishes a framework for PFAS air sampling and analysis with the OVS tube and would be appropriate for future monitoring efforts in varied environmental and occupational conditions. Future work comparing the air sampling efficiency of the OVS tube to cost-effective filter cassettes and investigating the collection of emerging non-volatile and semi-volatile PFAS of concern [9,12,13] with OVS tubes and filter cassettes is recommended.

Table 3
Average PFAS recoveries from individual GFF and XAD-2 media spiked at two concentration levels and stored for up to 28 days at room temperature.

	Recovery of PFCAs and HFPO-DA (% ± SD)				Recovery of PFSAs and DONA-Na (% ± SD)			
	0.01 × OEL/ section		2.0 × OEL/ section		0.01 × OEL/ section		2.0 × OEL/ section[a]	
Day	GFF	XAD_f	GFF	XAD_f	GFF	XAD_f	GFF	XAD_f
0	97.5 ± 4.8	102 ± 2.7	104 ± 4.3	104 ± 5.3	95.2 ± 4.5	103 ± 3.7	102 ± 5.5	106 ± 5.4
7	96.8 ± 4.3	104 ± 3.4	21.0 ± 6.1	187 ± 4.8	96.2 ± 4.1	105 ± 4.1	20.9 ± 3.0	191 ± 8.7
14	95.9 ± 3.6	104 ± 3.4	20.5 ± 6.1	181 ± 9.4	95.1 ± 3.3	104 ± 3.0	20.7 ± 3.5	188 ± 7.7
21	96.8 ± 2.5	105 ± 2.3	21.3 ± 4.7	184 ± 5.1	93.1 ± 2.6	104 ± 2.0	19.7 ± 3.1	188 ± 7.9
28	96.3 ± 3.9	102 ± 3.6	23.9 ± 6.3	186 ± 5.0	94.2 ± 2.4	104 ± 3.5	23.4 ± 4.3	187 ± 3.2

OEL = occupational exposure limit; GFF = glass fiber filter; XAD_f = front XAD-2 sorbent.
[a] 0.5 × OEL for DONA-Na.

CRediT authorship contribution statement

Wael H. Abdelraheem: Writing – original draft, Visualization, Project administration, Methodology, Formal analysis, Conceptualization. **Jennifer L. Roberts:** Writing – review & editing, Resources, Project administration, Methodology, Conceptualization. **Kristine S. Kurtz:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Investigation, Formal analysis. **Robert P. Streicher:** Writing – review & editing, Methodology, Conceptualization. **Zachary G. Robbins:** Writing – review & editing, Visualization, Validation.

Notes

The authors declare no competing financial interest.

Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention (CDC). Mention of any company or product does not constitute endorsement by NIOSH/CDC.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2025.129205.

Data availability

Datasets are available online at the CDC data repository at https://data.cdc.gov/.

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