



Characterization of per- and polyfluoroalkyl substances on fire suppression system piping and optimization of removal methods

Johnsie R. Lang^{a,*}, Jeffery McDonough^b, T.C. Guillette^a, Peter Storch^c, John Anderson^d, David Liles^e, Robert Prigge^e, Jonathan A.L. Miles^f, Craig Divine^g

^a Arcadis G&M of North Carolina, Inc., 5420 Wade Park Boulevard, Suite 350, Raleigh, NC, 27607, USA

^b Arcadis, 630 Plaza Drive Suite 200 Highlands Ranch CO 80129, USA

^c Arcadis, 120 Edward Street, Brisbane Queensland 4000, Australia

^d Arcadis, 482 Congress Street, Suite 501, Portland, ME 04101, USA

^e Arcadis G&M of North Carolina, Inc., 4915 Prospectus Drive Unit G, Durham, NC, 27713, USA

^f Arcadis 1 Whitehall Riverside, Leeds, LS1 4BN, UK

^g Arcadis, Irvine, CA, USA

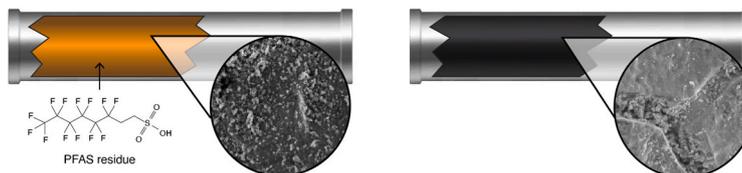
HIGHLIGHTS

- Fluorine free foam transition without proper cleaning can result in PFASs rebound.
- AFFF piping accumulated approximately 10 $\mu\text{g}/\text{cm}^2$ PFAS following decades of exposure.
- XPS revealed decreases in fluorine on the surface of AFFF piping after extraction.
- AFFF concentrate pipe segments were imaged with SEM.

GRAPHICAL ABSTRACT

Current problem: PFAS rebounds in fluorine-free foam when added to pipes with PFAS residue.

Solution: Cleaning pipes with Fluoro Fighter removes PFAS residue significantly better than MeOH or water, eliminating PFAS rebound.



ARTICLE INFO

Handling Editor: Myrto Petreas

Keywords:

PFAS
AFFF
Fire suppression
Foam transition
SEM
XPS

ABSTRACT

Fire suppression systems are known to be impacted with residual, entrained per- and polyfluoroalkyl substances (PFASs) because of historical use of aqueous film forming foam (AFFF) and fluoroprotein foam. Amphiphilic PFASs aggregate at liquid:solid interfaces creating a hydrophobic layer which reduces the effectiveness of water to remove PFAS from layered surfaces. When fire suppression systems are transitioned to fluorine free foam (F3) without appropriate cleaning, residual PFASs associated with the surfaces of the fire suppression system can contaminate the replacement F3. Release of residual PFASs from fire suppression systems into F3 has been documented; however, little is known about the residual PFASs associated with the surfaces of the fire suppression systems. More information is needed to develop methods to appropriately remove PFASs from fire suppression systems to prevent costly and inefficient foam transitioning and preserve the PFAS-free benefit of F3. The objective of this work was to evaluate the distribution and composition of PFASs on hangar piping exposed to PFAS-containing firefighting foam for a prolonged period. Two assessment methods were used: 1) extractions with methanol, water, and a proprietary aqueous organic solvent (Fluoro Fighter™); and 2) direct imaging

* Corresponding author.

E-mail addresses: Johnsie.lang@arcadis.com (J.R. Lang), mcdonough.jeff@gmail.com (J. McDonough), theresa.guillette@arcadis.com (T.C. Guillette), Peter.Storch@arcadis.com (P. Storch), john.anderson@arcadis.com (J. Anderson), David.Liles@arcadis.com (D. Liles), Robert.Prigge@arcadis.com (R. Prigge), craig.divine@arcadis.com (C. Divine).

<https://doi.org/10.1016/j.chemosphere.2022.136254>

Received 16 May 2022; Received in revised form 25 August 2022; Accepted 26 August 2022

Available online 12 September 2022

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methods of the surface. Extractions were analyzed with mass spectrometry and combustion ion chromatography. Results indicate pipe in contact with PFAS-containing firefighting foam can amass approximately $10 \mu\text{g}/\text{cm}^2$ of surface-associated PFAS residual following decades of exposure. Fluoro Fighter demonstrated higher PFAS removal per surface area of pipe than methanol ($p = 0.007$) or water extraction ($p < 0.0001$). Scanning electron microscope (SEM) images of the hangar piping reveal deposits suspected to be self-assembled PFAS layers, as evidenced by examination of pipe surfaces using X-ray photoelectron spectroscopy (XPS), which revealed atomic fluorine on the surface of the pipe.

1. Introduction

Aqueous film forming foam (AFFF) and fluoroprotein foam which contain per- and polyfluoroalkyl substance (PFASs) have been historically used and stored in fire suppression systems, like those used for aircraft hangars and aviation rescue and firefighting (ARFF) vehicles (ITRC, 2017). PFAS-containing firefighting foam formulations can include a range of hydrocarbon-based surfactants (H-surfactants) and fluorocarbon-based surfactants (F-surfactants) engineered to yield comparatively superior fire extinguishment capabilities (Back, 2020). Until 2001, the 3 M Company manufactured widely used formulations of AFFF containing perfluorooctane sulfonic acid (PFOS – C8) and its precursors (Place and Field, 2012; Houtz et al., 2013). Concurrently, several smaller manufacturers sold AFFF containing compounds (e.g. 8:2 and 6:2 fluorotelomers) which could form perfluoroalkyl carboxylates of equal or shorter chain length (D'Agostino and Mabury, 2014; Harding-Marjanovic et al., 2015). After 3 M ceased sales of PFOS containing AFFF in 2001, the fluorotelomer formulations dominated the AFFF market, and they primarily contained 6:2 fluorotelomer (C6) (Place and Field, 2012; Backe et al., 2013; Houtz et al., 2013).

Regulations restricting the use and release of PFASs are being proposed and promulgated throughout the world, with several enacted regulations addressing the use of PFAS-containing firefighting foam (Queensland, 2016; Congress, 2019; Legislature, 2019; Senate, 2020; Congress, 2021a; Espinosa et al., 2021; Legislature, 2021a, b). In addition to regulated usage, firefighting foam users are transitioning to fluorine free foam (F3) to reduce environmental liability in the event of a release, to reduce the cost of expensive containment systems and management of generated waste streams, and to avoid reputational damage. In 2016, Queensland, Australia was one of the first governments to ban PFAS use in firefighting foam (Queensland, 2016). The US 2020 National Defense Authorization Act (NDAA) specifies immediate prohibition of controlled release of PFAS containing AFFF and contains a requirement for the Secretary of the Navy to publish a specification for F3 use and ensure it is available for use by the Department of Defense (DoD) on October 1, 2023 (Congress, 2021b).

Internal surfaces of fire suppression systems are impacted by residual PFASs due to prolonged exposure to fluorosurfactants (Ross and Storch, 2020). When firefighting foam systems are transitioned to F3, residual PFASs on the wetted surface can leach into F3 potentially jeopardizing compliance with applicable regulations and prevention of environmental liability. Ross and Storch (2020) report total measured PFAS concentrations in F3 following exposure to existing AFFF infrastructure of more than 1 g/L (sum of 28 PFAS by TOP assay). Methods for removing residual PFASs from existing fire suppression systems are urgently needed as an alternative to costly replacement of equipment and infrastructure. Fire suppression system cleaning methods relying on serial water flushes generate large volumes of liquid waste for disposal (Institute, 2020). Due to uncertainties about current practices for disposal of PFAS containing liquids, it is important to minimize the creation of liquid waste streams (USEPA, 2020).

PFAS are typically amphiphilic surfactants due to the molecular structure of a hydrophilic functional group combined with a hydrophobic perfluoroalkyl chain. Longer perfluoroalkyl chains results in more pronounced surfactant properties (Krafft and Riess, 2015). Given the amphiphilic nature of long chain PFASs, when they encounter

surfaces, they will arrange themselves to maximize electrostatic interactions and minimize hydrophobic interactions (Rojas, 2002). The large surface area of perfluoroalkyl chains coupled with the low polarizability of the fluorine atoms results in enhanced hydrophobicity and low van der Waals interactions. These characteristics encourage a rigid molecular structure facilitating self-assembly of F-surfactants, previously observed as micelles and/or spherical vesicles in liquids and lamellar phases and bilayer aggregates at phase interfaces (Krafft et al., 1993; Gladysz, 2004). Zhang et al. (2016) previously used scanning electron microscopy (SEM) to show novel fluorosurfactants self-assemble into spherical, bilayer vesicles in acetonitrile/water mixed solvents (Zhang et al., 2016). These properties result in surface-associated PFASs within fire suppression systems requiring special consideration and innovative cleaning methods.

A literature search has identified no previous publications documenting the composition of PFASs associated with internal surfaces of fire suppression systems. To transition from PFAS-containing firefighting foam to F3 more effectively, knowledge about surface-associated PFASs within these systems is needed. The objective of this research is to 1) evaluate the distribution and composition of PFASs on actual fire suppression system piping exposed to PFAS-containing firefighting foam for prolonged periods and 2) to optimize the efficacy of cleaning methods. This is a case study of one foam concentrate pipe sample representing a potentially small number or a single type of AFFF.

2. Materials and methods

2.1. Fire suppression system pipe sample collection, processing, and extractions

Fire suppression system pipe (6.99 cm [cm] interior diameter, 7.62 cm outer diameter) was obtained from a commercial airport hangar in Sydney, Australia. Prior to removal from the hangar, the 304 stainless-steel pipes held PFAS-containing firefighting foam for more than three decades (variable formulations of both long and short chain PFASs). The pipe removed was identified as 304 stainless-steel on the as-built drawings for the building. Although the formulation of PFAS-containing firefighting foam varied historically, a sample of the PFAS-containing firefighting foam residual encountered while collecting the pipe sample was collected and analyzed for PFAS with and without total oxidizable precursor (TOP) assay by ALS Environment Australia (ALS).

Approximately 20 m of 304 stainless-steel foam concentrate pipe was removed and cut into 1-m lengths from the straight run sections of the system between flanges. The 1-m sections were individually placed into labelled high-density polyethylene (HDPE) bags and secured with a cable tie. The pipe sections were crated and shipped by air to the Arcadis Treatability Laboratory (ATL) in Durham, North Carolina (NC) and arrived within two weeks of the shipment date.

Pipe cutting, preparation, and extraction was completed at the ATL. Prior to pipe cutting and preparation, pipe was stored at room temperature. After extraction, pipe was stored at 4 °C before shipment to analytical laboratories for PFAS analysis. A Wen Model 3970 band saw was utilized to cut the pipe into individual pipe sample coupons. Individual pipe sample coupons were randomly cut from sections throughout the bulk pipe sample to a length of approximately 10.16 cm, weighed, and then sub-divided into sections to allow for submergence in

the extraction media (Table S1 and Fig. 1).

Fresh pipe is defined as pipe as removed from the field (i.e. non-extracted pipe). Individual pipe sample coupons were extracted in 200–300 mL (mL) of methanol (MeOH - Fisher Scientific high pressure liquid chromatograph [HPLC] grade), tap water (City of Durham, NC public water supply), or a proprietary aqueous organic solvent produced by the author's company (Fluoro Fighter™ - Safety Data Sheet [SDS] provided in the supplemental information [SI]) within reaction vessels (Table S1). MeOH extraction is commonly used for extraction of PFASs from solids, but there are significant health and safety hazards introduced by handling MeOH at a field site. (NIOSH) Fluoro Fighter has been previously used to remove PFAS from fire suppression piping, with no major health and safety issues (Ross and Storch, 2020). Fluoro Fighter was developed for optimized PFAS removal based on Hansen Solubility Parameters (Hansen, 2007). Some current cleaning procedures rely on water flushing only during the transition from PFAS-containing foam to F3 (Group, 2020; Institute, 2020).

The liquid level in each extraction vessel was sufficient to completely cover the individual pipe sample coupons. MeOH extractions were sonicated for 15 min at the beginning and end of the soaking period using a Fisher Scientific FS30 Ultrasonic Bath at 40 kHz (kHz), while the Fluoro Fighter extractions were not sonicated. Water extractions were performed in treatments with and without sonication (Table S1). The MeOH extractions were sonication to mimic soil extraction procedures (Strynar et al., 2012). The Fluoro Fighter extractions were performed without sonication because this technique is not typically implemented during field work. MeOH extractions were completed at room temperature only, while the Fluoro Fighter extraction was performed at room temperature, 40 °C and 80 °C and the water extraction was performed at room temperature and 40 °C. For MeOH and water extractions, the extraction time was 24 h. For the Fluoro Fighter extractions, the majority of extractions were completed using a 24-h extraction time, but five samples were extracted at 2 h, five samples at 12 h, and five samples at 48 h to assess variable extraction times. To assess residuals following single extractions, four of the MeOH extracted pipes were reextracted using the same 24-h soaking and sonication procedure. Using the same procedure, a single replicate was re-extracted a third time in MeOH to assess PFAS residual following two previous extractions. Fluoro Fighter and water extracted pipes were not re-extracted.

After extraction, the various media was decanted from the reaction vessel and stored at 4 °C; aliquots (15 mL for MeOH and 125 mL for water/Fluoro Fighter) of extraction media were decanted into pre-cleaned glass containers and shipped overnight to McGill University (McGill; Montreal, Quebec, Canada), Clarkson University (Clarkson; Potsdam New York, USA), Eurofins Test America (TA; Sacramento, CA), and Pace Analytical (Baton Rouge, LA) on ice. Additionally, extracted pipe was shipped to Surface Science Western, (SSW; London, Ontario,

Canada).

2.2. Pipe sample coupon extraction analysis

PFAS analysis was performed by ALS, McGill, TA, or Pace using liquid chromatography with tandem mass spectroscopy (LC-MS/MS). ALS, Pace, and TA are all Environmental Laboratory Accreditation Program (ELAP) certified for PFAS analysis and samples were analyzed in compliance with the Quality Systems Manual (QSM) for Environmental Laboratories Version 5.3 Table B-15 (Dod/DoE, 2021). The presence of Fluoro Fighter in samples creates significant matrix interference in obtaining complete oxidation of the sample during TOP assay. In order to reduce matrix effects, Fluoro Fighter extraction samples were diluted 1:10,000X with deionized (DI) water samples prior to TOP assay. Water samples were not diluted prior to analysis. For pre-TOP assay analysis of MeOH extractions, samples were diluted 1:10X with DI water and directly injected into the LC-MS/MS. For TOP assay analysis of MeOH extractions, 120 µL of sample was initially brought to dryness to remove effects of MeOH on the oxidation process.

For all samples analyzed by TOP assay, the initial solution was centrifuged (21000 g for 5 min), then an aliquot of supernatant was taken out and diluted with internal standard solution for final instrumental analysis. As shown in Table S2, with the exception of McGill, all TOP analysis performed by commercial laboratories followed the TOP procedure detailed in Houtz et al., (2012). McGill laboratory utilized 200 µL of sample, instead of 250 µL (Table S2). Specifically, sample was diluted with water was added into the TOP tube, sonicated for 20 min, then 656 µL of potassium persulfate at 175 mM in HPLC-water was added (final concentration of 60 mM), followed by the addition of 57.4 µL of 5 M NaOH (a final concentration of 150 mM). After inverting for mixing, the TOP tubes with the aqueous solution were put into the heated water bath (85 °C) for 6 h. After the reaction time, these tubes were removed from the water bath and waited until cooling down. Subsequently, 10 µL of HCl 6 M and 100 µL of methanol were sequentially added, with the tubes inverted for mixing. After that, 70 µL of TOP sample, 140 µL of internal standard solution at 6.25 ppb (in MeOH), and 140 µL of methanol were added into a separate vial (2 mL). After vortexing, an aliquot of 180 µL of the supernatant was transferred to an injection vial for instrument analysis by LC-MS/MS.

MeOH and elevated temperature Fluoro Fighter extractions were also analyzed prior to TOP assay. A list of PFAS included for analysis is summarized in Table S3. For pipe extraction concentrations, measured values (micrograms/liter; µg/L) were converted to micrograms (µg) of total detected PFAS (post TOP assay) per centimeters squared of interior pipe surface area (µg/cm²) using the extraction volumes (in liters; L) and the interior pipe surface area (cm²) for each pipe sample coupon (µg/L * L/cm² = µg/cm²).

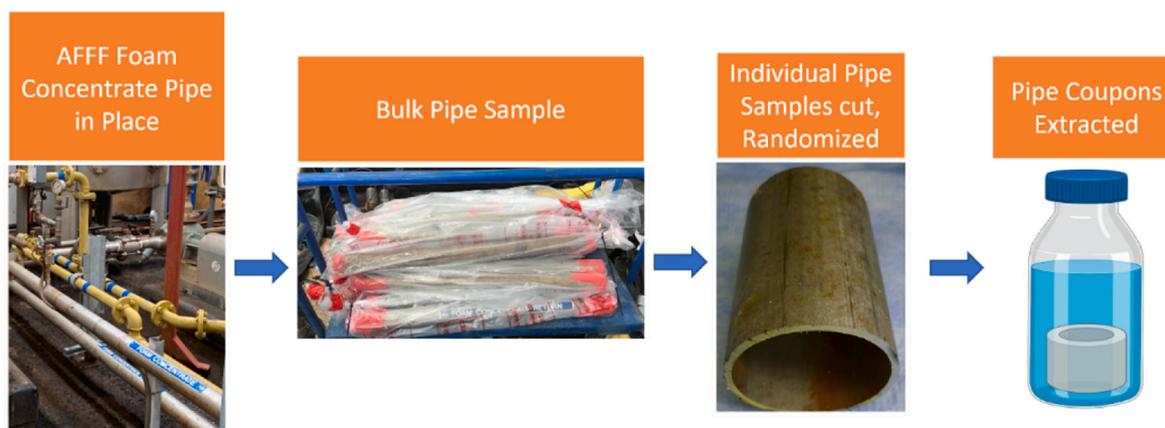


Fig. 1. Pipe sample coupon extraction workflow. All images shown are actual pipe used for experiments.

The total organic fluorine (TOF) and total fluorine (TF) in the MeOH extractions and a subset of the water and Fluoro Fighter extractions was measured using combustion ion chromatography (CIC) and ion chromatography (IC) (Schultes et al., 2018). Inorganic fluoride concentrations were measured using IC and subtracted from the total fluoride concentration measured with CIC to obtain TOF concentrations in the samples. The TOF was converted to μg of TOF per cm^2 of interior pipe surface area ($\mu\text{g}/\text{cm}^2$) as indicated for PFASs. For comparison purposes, organofluoride associated with PFASs (post TOP assay) was determined based on stoichiometry per PFAS analyte and compared to TOF as TOP-OF.

2.3. Imaging of the pipe surface

Samples of the pipe were shipped to SSW for analysis with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM imaging was performed using a Hitachi SU8230 Regulus ultra-high resolution field emission scanning electron microscope. Profiles of the surface were collected with a scan length of 4.8 mm, a scan speed of 200 $\mu\text{m}/\text{s}$ and a sampling rate of 100 Hz. The image was filtered using a Gaussian filter with a cut-off wavelength of 0.8 mm. XPS was performed using a Kratos AXIS Supra X-ray photoelectron spectrometer. XPS can detect all elemental deposits, except hydrogen and helium, probes the surface of the sample to a depth of 7–10 nm (nm), and has detection limits ranging from 0.1 to 0.5 atomic percent (%) depending on the element (Shard, 2014). The survey scan analyses were carried out with an analysis area of 300 $\mu\text{m} \times 700 \mu\text{m}$ and a pass energy of 160 eV.

One replicate from each treatment was randomly selected to be imaged. Fresh pipe and pipe sample coupons following MeOH, water, or Fluoro Fighter extraction were cut into a single 2.54 cm \times 2.54 cm section at the ATL prior to shipment. Surface imaging was performed directly on the pipe surface as received without further processing. In addition to the interior surface of each pipe, the exterior surface of the fresh pipe sample was also imaged to provide a non-exposed surface image. In order to assess the variability of the XPS fluorine measurement, the 80 °C Fluoro Fighter extracted pipe sample was analyzed in five distinct pipe surface locations.

To understand the profile roughness of the various pipe surfaces, an industrialized standard (ISO 4287) with a cut off wavelength of 0.8 mm was used to estimate both the average roughness (Ra) and the root mean square roughness (Rq). To calculate roughness, the profile was filtered using a Gaussian filter, removing waviness and form error (e.g., the tilt) from the profile. The first and the last 0.4 mm portions of the profile were excluded for roughness estimation. The remaining 4.0 mm portion of the profile was divided to five 0.8 mm sampling segments, each of which was used to calculate roughness. The roughness estimation was done using Apex 3D Advanced software. Pipe average roughness (Ra) and root mean square roughness (Rq) were calculated using the average height and the root mean square height of all the data points against the mean plane. Areal roughness is estimated from an area, while traditional profile roughness is only estimated from a single scan.

2.4. Statistical evaluation

Comparison of the different extractions based on measured concentrations of PFASs (means with standard deviation) were analyzed statistically by a non-parametric, Kruskal–Wallis one-way analysis of variance (ANOVA) test. Data were checked for normal distribution with a Shapiro–Wilk test and residual plot. Significance was set to a probability value of $p \leq 0.05$. A Dunn's post-hoc test was used as a follow up to compare the mean of each measured PFASs concentration for the different extractions. Comparison of the difference in heat extractions (22 °C vs 40 °C) were analyzed by Kruskal–Wallis ANOVA test, with significance set to a probability value of $p \leq 0.05$ and Dunn's post-hoc test to compare individual groups. Data were analyzed in the R statistical programming environment (Version 4.1.2) and visualized with

Graphpad Prism (Version 9, La Jolla, CA, USA).

3. Results

3.1. PFAS-containing firefighting foam

Analytical results for the PFAS-containing firefighting foam drained from the pipe in the hangar suggest the presence of a considerable quantity of unknown perfluoroalkyl acid (PFAA) precursors as evidenced by a comparison of pre- and post-TOP assay results (Table S4 and Table S5). Total average measured concentration post-TOP assay (2.4 g/L) was in the lower range of the previously reported concentrations for AFFF concentrates (Houtz et al., 2013). 6:2-fluorotelomer sulfonic acid (6:2-FtS) is observed to represent 98.6% of the pre-TOP assay average \sum PFASs. Despite some residual precursors detected in the post-TOP assay results (e.g., 6:2-FtS and 8:2-FtS), there is a definitive and expected shift in the post-TOP assay results to perfluorocarboxylic acids (PFCAs). Approximately 98.1% of the post-TOP assay average \sum PFASs are represented by PFBA, PFPeA, and PFHxA at concentrations exceeding the stoichiometric conversion of the 6:2-FtS dominant pre-TOP assay results. This suggests PFAA precursors within the pre-TOP assay results were undetectable with the available list of PFAS analytes.

3.2. Pipe extraction TOP assay results by varying media

PFAS concentrations in the pipe extractions indicate the total measured PFASs post-TOP assay removed from the pipe interior surface area was variable based on extraction media (Kruskal–Wallis test $H(3) = 22.93$, $p < 0.0001$ - Fig. 2a and Table S5). A Dunn's post hoc test determined Fluoro Fighter removed statistically significant higher amounts of PFASs from the pipe surface compared to MeOH ($p = 0.007$) and water ($p < 0.0001$). The differences between the average extraction concentrations demonstrated Fluoro Fighter removed approximately 2.5X more PFASs than MeOH and 2.9X more than water. As some current guidance documents recommend water flushing to clean fire suppression systems (Group, 2020; Institute, 2020), the apparent connection between PFAS concentrations and the extraction media demonstrate the risk of using water as a cleaning agent which is shown to leave considerable PFASs in place post cleaning. These results indicate Fluoro Fighter was more effective at extracting PFASs from the pipe interior surface compared to MeOH, which is used by laboratories for PFAS extraction of non-biological solids (Strynar et al., 2012). A comparison of water extractions with and without sonication revealed sonication did not significantly increase the level of PFAS extracted.

The distribution of PFAS in the post-TOP assay MeOH and water extraction samples was similar with PFPeA making up ~60% of the total (Table S5). Low level detections of PFAA precursors (6:2-FtS and 8:2-FtS) in the MeOH extraction samples suggest the oxidative digest associated with the TOP assay was partially incomplete. Representative PFAAs in water and MeOH extractions were similar in distribution but demonstrated a difference in the magnitude of the concentration may be indicative of the comparatively limited capability of water to remove surface associated PFASs from fire suppression systems. The MeOH extraction results demonstrated multiple long chain PFCAs not detected in the water or Fluoro Fighter extraction results. Since the lower limit of quantitation were much higher for the Fluoro Fighter extraction analysis compared to water or MeOH extractions, identification of low-level long chain PFCAs in the Fluoro Fighter extractions could not be determined.

3.3. MeOH Re-extraction pipe extraction TOP assay results

Results indicate the majority of PFAS was removed in the first methanol extraction with the re-extractions showing strong agreement and demonstrating a mean which was 6% ($\pm 2\%$) of the single MeOH extraction mean (Fig. 2b). All of the measured PFASs post-TOP assay for

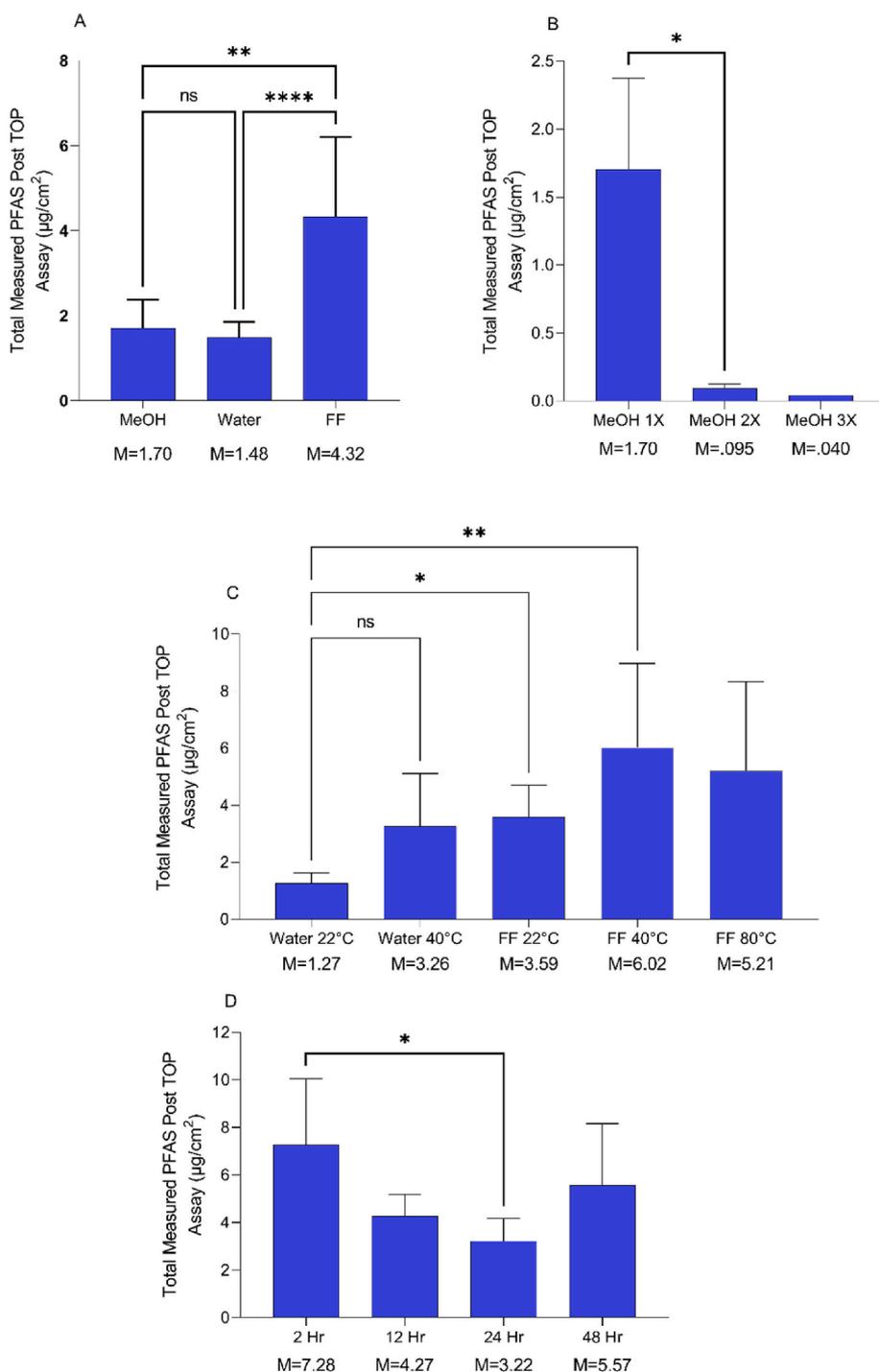


Fig. 2. (A) Average total measured PFASs extracted from pipe sample coupons using various extraction media (error bars represent one standard deviation from the mean) for MeOH (n = 5), tap water (n = 10), and Fluoro Fighter (n = 18); **p = 0.007, ****p < 0.0001, Kruskal Wallis test between MeOH, Tap Water, and Fluoro Fighter, Dunn's post-hoc. NS = not significant. (B) Average total measured PFASs extracted from pipe sample coupons with methanol once (MeOH 1x, n = 5), twice (MeOH 2X, n = 4) and three times (MeOH 3X, n = 1); *p = 0.02, Mann-Whitney U test between MeOH 1X and MeOH 2X (C) Average total measured PFASs extracted from pipe sample coupons with Tap Water (22 °C, n = 5; 40 °C, n = 5) and Fluoro Fighter (FF) at room temperature (22 °C, n = 5), 40 °C (n = 5), and 80 °C (n = 3), *p = 0.05, **p = 0.002, Kruskal Wallis test between Tap Water 22 °C, Tap water 40 °C and Fluoro Fighter 40 °C, Dunn's post-hoc. Not tested, 80 °C due to sample size (n = 3). NS = not significant. (D) Average total measured PFASs extracted from pipe sample coupons with Fluoro Fighter (FF) at 2 h (2 Hr, n = 5), 12 h (12 Hr, n = 5), 24 h (24 Hr, n = 5), 48 h (48 Hr, n = 5), *p = 0.01, Kruskal Wallis, Dunn's post-hoc. M = mean amount of PFAS (µg/cm²) extracted from pipe per replicates. Analysis of extraction media performed using modified USEPA Method 537.1 with TOP assay.

the MeOH 2X extraction were PFCAs, characterized by PFBA (27.1%), PFPeA (55.8%), PFHxA (14.8%), and PFHpA (2.6%) (Table S5). The measured total PFAS concentration observed from the 3X MeOH extraction was 53 µg/L. Two compounds represented the total PFAS concentration in the 3X MeOH extraction, PFBA (37.6%) and PFPeA (62.9%).

3.4. Pipe extraction TOP assay results by varying temperature

Fluoro Fighter solution at increased temperature (40 °C) demonstrated approximately 1.87X PFAS removal as compared to Fluoro Fighter solution at room temperature (Fig. 2c). Fluoro Fighter

extractions at 22 °C were significantly different compared to the room temperature (22 °C) water extractions results based on results of Kruskal Wallis test, with Dunn's post-hoc comparison (p = 0.05). Increased temperatures of Fluoro Fighter at 40 °C were significantly different compared to the room temperature (22 °C) water extractions results based on results of Kruskal Wallis test, with Dunn's post-hoc comparison (p = 0.002). Though the 80 °C Fluoro Fighter extraction results did show a higher amount of total PFASs concentration compared to 22 °C Fluoro Fighter extraction, it was not included in the statistical analysis due to the reduced samples (n = 3). Commonly, heated solvents can increase the dissolution of mass of compound they solvate. Both elevated temperatures had higher variation in the total PFAS extracted with Fluoro

Fighter than the 22 °C, and this may be due to heterogeneity of the PFAS on the surface of the pipes.

Water at increased temperature (40 °C) also demonstrated enhanced removal compared to water at room temperature (Fig. 2c); however this was not significant according to a Kruskal Wallis test ($p = 0.21$). When water extractions at increased temperature (40 °C) were compared to Fluoro Fighter at room temperature, the results were not significantly different ($p = 0.86$), indicating Fluoro Fighter at ambient temperature removes similar levels of PFAS compared to heated water. Similar removal for heated water compared to Fluoro Fighter at room temperature has implications for situations where elevated temperatures cannot be maintained during the cleaning process.

There were three PFCAs and one PFSA detected in the increased temperature treatments not detected in the room temperature Fluoro Fighter treatment: PFHpA, PFOA, PFNA, and PFOS (Table S5). The detections of additional compounds could be due to historical AFFF use containing longer chain PFAS which could be contained in the deeper the surface assembled PFAS bilayers. There were no detections of precursors suggesting the TOP assay likely completely converted any applicable precursors into PFCAs.

3.5. Pipe extraction TOP assay results by varying extraction times

Fluoro Fighter extractions completed with shorter extraction periods demonstrated higher PFAS concentrations compared to the 24-h Fluoro Fighter extractions (Fig. 2d). The 2-h extraction time was significantly different from the 24-h extractions ($p = 0.01$, Kruskal Wallis, Dunn's post-hoc). Higher concentrations for shorter extractions times were surprising as the dissolution of PFAS from the surface was not expected to occur quickly. It is unclear if dissolution and resolidification on the surface is occurring in the longer time period or if these differences could be due to variability in PFAS concentrations on the pipe surface. Longer chain PFCAs were present in some of the 48-h extractions indicating the longer time periods are helpful with longer chain dissolution, even though concentrations were not large enough to affect total PFAS removal (Table S5).

3.6. Pipe extraction Pre-TOP assay results

The subset of extraction samples analyzed with pre-TOP assay provides insight into the PFAS composition on the pipe (Table S4). For the pre-TOP assay data, extractions using Fluoro Fighter with elevated temperatures did not demonstrate significantly higher total measured PFAS concentrations compared to water, but did show elevated PFAS concentrations compared to methanol. These conclusions differ from the post-TOP assay data conclusions and highlight the need for TOP assay to assess total PFAS loads in fire suppression systems. 6:2 FTS comprised the majority of PFAS in the pre-TOP assay, which indicates use of a PFAS-containing foam synthesized via fluorotelomerization in the pipe system. For the MeOH extractions, the total measured pre-TOP assay concentrations were approximately 7% of the post-TOP assay concentrations, which was similar to the AFFF concentrate foam removed from the system (Tables S4 and S5). For the MeOH re-extractions, two samples of 2X and 3X had higher pre-TOP assay concentrations than post-TOP assay concentrations. This could be attributed to analytical variability at the lower end of concentrations, and/or the potential of intermediate compound formation not fully captured by the post-TOP assay PFAS targeted list. It is possible the presence of MeOH leads to the formation of PFCAs methyl esters which are not captured analytically (Hanari et al., 2014). Given that pre-TOP assay result concentrations were much lower for 2X and 3X MeOH extractions, it is also probable that analytical variance attributed to this.

3.7. Pipe Extraction TOF Results

A summary of the TOF results for the various extraction media is

presented in Table S6. For extraction media where inorganic fluorine (F^-) was detected, it was subtracted from the TF to obtain the measured TOF concentration. For purposes of comparison with pipe sample coupon extraction using TOP assay, the concentrations of individual PFAAs (and residual precursors) were stoichiometrically converted to the equivalent fluorine concentration. For clarity, this form of organofluorine will be referred to as TOP-OF.

In comparison to the TOP-OF results, the TOF suggest more organofluorine was extracted and more comparable organofluorine extraction occurred among the various extraction media. A ratio comparison of the TOP-OF and TOF for all extraction media was performed to evaluate the potential for analytical or extraction biases in the data (Table S6). Differences in TOP-OF and TOF are likely due to potential limitations associated with the TOP assay that have been discussed in the literature, such as incomplete oxidation of unknown precursors due to matrix interference, precursor transformation into ultra-short chain PFASs (<C4) cannot be measured by modified Method 537.1, and there may be losses of PFAAs during in the analytical procedure (Houtz and Sedlak, 2012; Boiteux et al., 2016; Munoz et al., 2016; Robel et al., 2017). It is anticipated these identified limitations associated with the TOP assay would bias the TOP-OF low in comparison to the TOF measurements.

For the MeOH extractions, the average TOP-OF:TOF ratio is 27.6% ($\pm 2.8\%$) and serves as a comparative benchmark for water and Fluoro Fighter extraction media because the TF was below quantitation limits. The average TOP-OF:TOF for the water extraction medium is 16.1% ($\pm 4.2\%$) and for the Fluoro Fighter extraction medium is 47.2% ($\pm 13.6\%$). Both the water and Fluoro Fighter extraction media used tap water from the City of Durham, and the background inorganic fluoride (F^-) was expected to be < 0.1 ppm based on the city water quality reports. The level of F^- measured in the Fluoro Fighter was consistent and in the range of expected concentrations. The water results were surprising as they demonstrated variable levels of F^- and two of the three samples measured showed concentrations below the expected City of Durham levels. The application of CIC to provide a secondary quantification of organofluorine to substantiate the TOP assay PFAS concentrations for these types of extraction media is not typical. Therefore, further development of the TOF method may be required for accurate analysis for this application. For example, samples were directly injected into the CIC instrument, without sample preparation. A preparatory extraction with modified Extractable Organic Fluorine (EOF) may mitigate these apparent interferences and yield more consistent results in future studies.

3.8. SEM imaging of pipe sample coupons

SEM imaging of piping surfaces was used to visualize the residuals containing PFASs on the interior surface of the pipe. Images are presented in Fig. S1 for fresh pipe, pipe extracted with various extractions of MeOH, pipe extracted with water, and pipe extracted with Fluoro Fighter. At low magnification (accelerating voltage of 5.00 kV, distance 11.5 mm, 5.0 K magnification) on the surface of the fresh pipe, an apparent layer of deposited material is observed, obscuring the pipe surface. For the pipe surfaces extracted with various media, varying amounts of deposits appear to partially cover the smooth pipe surface, suggesting some removal of the observed deposits and some residuals left behind (Fig. S1). Because the pipe used for this project was only ever exposed to PFAS-containing firefighting foam, this deposit is suspected to be attributable to the PFAS-containing firefighting foam. Note, rust of the stainless-steel pipe wetted surface could also play a role in the surface deposit residual chemistry. Both the exterior and the interior surfaces of the fresh pipe (i.e. unextracted) were imaged with SEM. The exterior of the fresh pipe was imaged to provide a visual comparison of a representative pipe sample without prolonged exposure to PFAS-containing firefighting foam; however, it cannot be ruled out that the exterior surface may have contacted PFAS-containing firefighting foam.

3.9. XPS imaging of pipe sample coupons

Elemental fluorine composition data produced by XPS is demonstrated in Fig. 3A for fresh pipe and pipe following extraction with water, MeOH, and Fluoro Fighter. The XPS results seem to confirm the observed deposits on the pipe surfaces in the SEM images contained fluorine, which is assumed to be associated with PFASs with respect to the corresponding PFAS concentrations measured in the extraction media (Fig. 1). XPS suggests residual fluorine deposits remained on the wetted surface after extractions for all media evaluated. The highest residual fluorine measurements were associated with fresh pipe and the lowest residual fluorine measurements were associated with elevated temperature Fluoro Fighter extractions (Fig. 3A). In agreement with the analytical data from the extractions, the water extraction does show some fluorine removal, though comparatively less than MeOH and Fluoro Fighter extraction media. Since XPS is a novel method for determining fluorine residuals on AFFF concentrate pipe surfaces, future work is needed to further validate this procedure on additional pipe types.

Except for the water extraction, the sulfur response appears to closely follow the fluorine response (Fig. 3B and Fig. S2). Given the elevated concentrations of 6:2-FtS (Table S4) and the potential for unknown/unquantified precursors to contain some form of sulfur, this may be related to the observed decreases in fluorine and indicate removal of surface-associated PFASs. Iron, silica, and phosphorus are observed to increase in comparison to the fresh pipe for pipe extracted with Fluoro Fighter (Table S7). As XPS is a surface technique, the XPS may have become more sensitive to the elemental composition of the 304 stainless steel pipe as the deposits were cleaned off by the various extractions. Silicon and copper are well known to be associated with various stainless steels, either as trace components or to impart specific functionality like corrosion resistance. Nickel was not detected on the pipe surface by XPS even though it was expected as it is a common constituent of 304 stainless steel pipe. The lack of nickel detection could be due to the overlapping of the nickel and iron peaks on the XPS results or could be caused by the low probing depth on the surface of the pipe for this type of analysis.

3.10. Pipe surface roughness

The fresh pipe sample demonstrated the highest values for Sa, Sq, Ra,

and Rq, indicating all extraction methods provided some level of surface roughness reduction (Table S8). Increasing extraction temperatures demonstrated a decrease in Ra and Rq values compared to room temperature Fluoro Fighter, indicating a smoother surface. There was no apparent pattern for both Ra and Rq between the other extractions (MeOH or Tap Water). Since this is a novel use of pipe surface roughness measurements in correlation with PFAS and total fluorine surface residuals, further validation of the methods should be completed in a future study.

4. Conclusions

Industry data confirm PFAS rebound into replacement F3 from improperly or incompletely cleaned fire suppression systems where PFAS-containing firefighting foams were used historically (Ross and Storch, 2020). The results of this research can be used to improve industrial cleaning of fire suppression systems transitioning away from PFAS-containing firefighting foam in favor of F3. This manuscript contains the first known published SEM imaging of residual deposits on the interior surface area of AFFF concentrate piping following decades of exposure. For all extraction media evaluated in this project, XPS suggests residual fluorine deposits remained after extractions. This may demonstrate the appreciable PFAS residuals anticipated to be stored within fire suppression systems. This brings great importance to using the appropriate cleaning agent when cleaning fire suppression systems so as not to jeopardize replacement F3 with residual PFASs. It also likely suggests a combination of multiple cleaning techniques (e.g., soaking or temperature manipulation) will be necessary to efficiently remove the greatest percentage of residual PFASs, while generating the least amount of concentrated liquid waste. Note, there are no additional disposal constraints for the Fluoro Fighter beyond traditional PFAS contaminated aqueous phase disposal criteria.

The results of this project suggest variable effectiveness of extraction media to remove surface associated PFASs from pipe surfaces. TOP assay results for the extraction media demonstrated Fluoro Fighter removed more surface-associated PFASs in comparison to equivalent extractions using MeOH or water. Based on these results, it appears the use of heated Fluoro Fighter provides the largest PFAS residual removal from the pipe surfaces. Qualitative comparison of apparent deposits on the pipe sample coupon surfaces via SEM imaging suggest a single Fluoro Fighter extraction may have removed more of these deposits than a single water

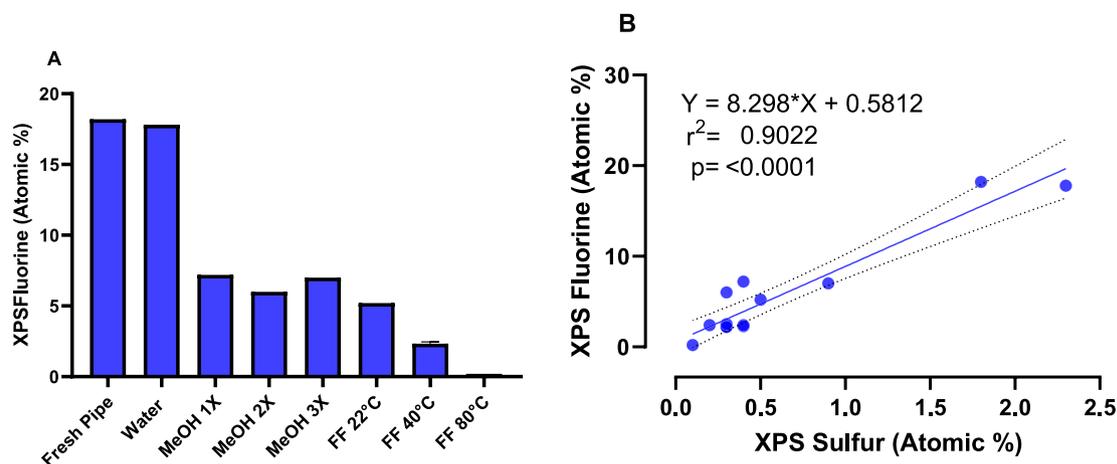


Fig. 3. (A) X-ray photoelectron spectroscopy (XPS) analysis of elemental area count on the surfaces of fresh pipe, pipe extracted with a single water extraction, pipe extracted with single, double, and triple MeOH (1X, 2X, 3X) extractions, pipe extracted with a single Fluoro Fighter extraction, pipe extracted with Fluoro Fighter at 40 °C, and pipe extracted with Fluoro Fighter at 80 °C. (B) XPS Fluorine and Sulfur atomic % linear regression ($r^2 = 0.9022$, $p < 0.0001$) for all pipes extracted.

extraction and two serial MeOH extractions. As XPS results confirm the elemental composition of those deposits contained fluorine, these deposits are likely to be (at least in part) surface associated PFASs. Analysis of the various extraction media was also performed with CIC for TOF measurements, but the atypical application of this method may have confounded the results as evidenced by large sample variance and conflicting results with the other lines of evidence (e.g., PFAS analysis, SEM, and XPS).

Data presented herein should be interpreted carefully as PFAS-containing firefighting foams can vary drastically in their synthesis and composition, which would be expected to result in unique PFAS residuals within fire suppression systems. Note, the sample consisted of straight pipe sections only and it is unknown if PFAS residue might accumulate more or less in piping bends and valves under turbulent flow conditions. While the TOP assay was used to purposefully transform unquantifiable precursors compounds into PFAAs that can be analyzed via available methods, it is possible some PFASs remained unaccounted for due to limitations associated with the TOP assay.

Author contributions

Johnsie R. Lang: Conceptualization, Methodology, Data Curation, Resources, Writing - Original Draft, Supervision, Writing - Review & Editing, Funding acquisition; **Jeffery McDonough:** Conceptualization, Data Curation, Writing - Original Draft; **T.C. Guillette:** Investigation, Data Curation, Writing - Original Draft, Visualization; **Peter Storch:** Conceptualization, Methodology, Writing - Review & Editing; **John Anderson:** Data Curation, Writing - Review & Editing; **David Liles:** Investigation, Resources, Methodology; **Robert Prigge:** Investigation, Resources; **Jonathan A. L. Miles:** Conceptualization, Resources, Writing - Original Draft; **Craig Divine:** Conceptualization, Methodology, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgements

The authors would like to acknowledge Qantas Airways Limited for supplying the PFAS-containing firefighting foam pipe from their Australian hangar. The research was funded by the Environmental Security Technology Certification Program (ESTCP; grant ER20-5364) through the United States Department of Defense.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.136254>.

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