

NIST Technical Note NIST TN 2313

Per- and Polyfluoroalkyl Substances in Textiles Present in Firefighter Gloves, Hoods, and Wildland Gear

Andre L. Thompson Andrew C. Maizel Meghanne Tighe Samuel Escobar-Veras Alix E. Rodowa Bruce Benner Audrey F. Tombaugh Jessica Reiner Michelle Donnelly Ryan Falkenstein-Smith John Kucklick Catherine Rimmer Rick D. Davis

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Abstract

Firefighter turnout gear has been found to contain per- and polyfluoroalkyl substances (PFAS) and is a potential source of PFAS exposure to firefighters. However, previous evaluations of firefighter exposure to PFAS through personal protective gear has exclusively examined jackets and pants. In contrast, turnout gear contains other protective articles that contact firefighter skin, including hoods and gloves. Additionally, wildland firefighters typically wear gear that includes a shirt and pants, each made of a single layer, to allow easier movement relative to the heavy jacket and pants worn by structural firefighters. To determine the identity, concentration, and prevalence of PFAS potentially present in unused textiles present in firefighting hoods, gloves, and wildland gear, fifty-five nonvolatile, semivolatile, and volatile PFAS were quantified in thirtytwo textiles taken from gloves and hoods used by structural firefighters as well as wildland firefighter shirts and pants. Between zero and nine individual PFAS were observed above their respective reporting limits in each textile, with the highest numbers of detections and highest concentrations of PFAS present in wildland gear textiles, compared to glove textiles, which had the second highest, and hood textiles which had the lowest. 6:2 fluorotelomer methacrylate (6:2 FTMAC) and 6:2 fluorotelomer alcohol (6:2 FTOH) are both fluorotelomerization-derived PFAS with six perfluorinated carbons, which were quantified at the highest concentrations of any PFAS reported here, up to 2980 μ g/kg \pm 820 μ g/kg (mean \pm standard deviation of triplicate measurements of single textile) and 1250 μg/kg ± 330 μg/kg, respectively. These two PFAS, however, were only detected in wildland firefighting gear textiles. Also observed in the wildland gear textiles were perfluorocarboxylic acids (PFCAs) with seven or fewer perfluorinated carbons at individual concentrations below 20 μg/kg. Four PFAS were observed in most of the glove layers: perfluorobutanoic acid, perfluorobutane sulfonic acid, perfluorobutane sulfonamide, and *N*-methyl perfluorobutane sulfonamide, with *N*-methyl perfluorobutane sulfonamide observed at the highest concentration, up to 117.2 μg/kg ± 7.0 μg/kg. Five different PFAS were observed across all the hoods, but concentrations were less than 1 μg/kg. PFAS concentrations varied widely among each textile type, suggesting that the amount of PFAS present in unused firefighter gear may depend on the textiles used in gear manufacturing.

Keywords

Gloves; hoods; moisture barrier; outer shell; per- and polyfluoroalkyl substances; PFAS; thermal liner; turnout gear; wildland gear textiles; Firefighter.

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Preface

This National Institute of Standards and Technology Technical Note (NIST TN 2313) is the third publication provided in response to Section 338 of the William M. (Mac) Thornberry National Defense Authorization Act for Fiscal Year 2021, titled the "Guaranteeing Equipment Safety for Firefighters Act of 2020." This act directed NIST to: "complete a study of the contents and composition of unused personal protective equipment worn by firefighters." The first two reports, NIST TN 2248 "Per- and Polyfluoroalkyl Substances in New Firefighter Turnout Gear Textiles" and NIST TN 2260 "Per- and Polyfluoroalkyl Substances in Firefighter Turnout Gear Textiles exposed to Abrasion, Elevated Temperature, Laundering, or Weathering", described the type, amount, and prevalence of PFAS measured from as-received and laboratory stressed structural firefighter jacket and pants fabrics.

This publication is the first report of measured PFAS concentrations in unused structural firefighter glove layers, unused structural firefighter hoods, and unused wildland firefighting gear. Similar to the first two reports, the current report is a targeted analysis of 55 nonvolatile, semivolatile, and volatile PFAS analytes detected using liquid chromatography/tandem mass spectrometry and gas chromatography/mass spectrometry. An upcoming report examines PFAS in these same firefighter components after laboratory stressing.

This NIST TN was produced through the combined efforts of researchers in the Fire Research Division of the NIST Engineering Laboratory and the Chemical Sciences Division of the NIST Material Measurement Laboratory.

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Author Contributions

Bruce Benner: Methodology; Investigation; **Rick Davis:** Conceptualization, Funding acquisition; Project administration; Resources; Supervision; **Michelle Donnelly:** Resources; **Samuel Escobar Veras:** Investigation; **Ryan Falkenstein-Smith:** Methodology, Investigation; **John Kucklick:** Validation; **Andrew Maizel:** Conceptualization, Formal Analysis, Investigation, Methodology, Supervision, Validation, Writing; **Jessica Reiner:** Methodology, Validation, Writing – review & editing; **Catherine Rimmer:** Resources; **Alix Rodowa:** Methodology, Investigation, Validation, Writing – review & editing; **Andre Thompson:** Conceptualization, Investigation, Methodology, Resources, Supervision, Writing; **Meghanne Tighe:** Investigation, Supervision; **Audrey Tombaugh:** Investigation.

Executive Summary

This National Institute of Standards and Technology Technical Note (NIST TN 2313) characterizes the per- and polyfluoroalkyl substances (PFAS) present in unused structural firefighter gloves and hoods and unused wildland firefighter shirts and pants. Fifty-five individual PFAS, solvent-extracted from 15 layers in four unused firefighter gloves, eight textiles from unused firefighter hoods, and nine unused wildland firefighting gear textiles, were analyzed using gas or liquid chromatography-mass spectrometry analysis. The gear type is the only difference between this report and our two prior reports (NIST TN 2248 and TN 2260).

Across all unused structural firefighter glove layers, structural firefighter hood textiles, and wildland firefighter textiles, 19 PFAS were quantified above the reporting limits, with two PFAS (i.e., 6:2 fluorotelomer methacrylate; 6:2 FTMAC, and 6:2 fluorotelomer alcohol; 6:2 FTOH) present above 200 µg/kg in at least one textile. Among the textiles examined here, summed PFAS concentrations were highest in unused firefighter wildland gear textiles and lowest in unused structural hood textiles. Summed PFAS concentrations in an unused wildland textile totaled as high as 4240 µg/kg ± 890 µg/kg. Among unused firefighter glove layers, moisture barrier layers had the highest summed PFAS concentrations, totaling 118.9 μ g/kg ± 7.1 μ g/kg. The highest summed PFAS in an individual unused firefighter hood textile was 0.6 μ g/kg \pm 0.1 µg/kg.

This is the first publication to report PFAS in unused structural firefighter glove layers, structural firefighter hood textiles, and wildland firefighter textiles. Unused firefighter wildland gear textiles contain similar PFAS concentrations to structural firefighter turnout gear. Additional research examining PFAS after stressing firefighter hoods, glove layers, and wildland gear textiles, after long-term stressing of structural and firefighter gear, and after exposure to fire scenes are still needed for a fuller understanding of firefighter's risk of PFAS exposure.

1. **Introduction**

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic compounds commonly used in a wide variety of commercial products [\[1\],](#page-68-1) including as durable water repellent (DWR) treatments that impart chemical and water resistance to textiles used in firefighter turnout gear [\[2\].](#page-68-2) There is growing concern about PFAS negatively affecting human health and the environment [\[3\].](#page-68-3) There have also been studies of health effects found in animals following oral exposure to PFAS, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) [\[4\].](#page-68-4) Oral exposure of 2150 mg/kg ammonium perfluorooctanoate (i.e., the ammonium salt of PFOA) in male and female albino rats resulted in the deaths of all rats in one day [\[4\],](#page-68-4) while treatment of Rhesus monkeys with 30 mg/kg/day ammonium perfluorooctanoate resulted in the death of one male and two females between seven and 12 weeks (group size 10/sex) [\[4\].](#page-68-4) The United States Environmental Protection Agency recently released a draft on the toxicity assessment and maximum contaminant level goals for PFOA and PFOS as likely human carcinogens [\[5\].](#page-68-5)

Firefighters have been found to have higher serum PFAS concentrations than the general public [\[6\]-](#page-68-6)[\[14\].](#page-69-0) Firefighters may be occupationally exposed to PFAS during their work activities, including the use of aqueous film-forming foams (AFFF) [\[6\]](#page-68-6)[,\[11\],](#page-69-1)[\[15\]](#page-69-2)[-\[17\]](#page-69-3) firefighter gear that has been treated with fluorinated polymers [\[2\],](#page-68-2)[\[18\]](#page-69-4)[-\[19\]](#page-69-5) or the accumulation of PFAS during firefighting activities or dust from firefighter stations [\[20\].](#page-69-6) While a link between the use of firefighter gear and elevated serum PFAS concentrations has not been established, many of the PFAS identified in firefighter gear textiles, such as 6:2 fluorotelomer alcohol (6:2 FTOH), 6:2 fluorotelomer methacrylate (6:2 FTMAC), and *N*-methyl perfluorobutanesulfonamido ethanol (MeFBSE) [\[18\]-](#page-69-4)[\[19\],](#page-69-5)[\[21\]](#page-69-7)[-\[22\],](#page-69-8) have not been quantified in firefighter serum.

To protect against exposure to heat and to prevent from becoming water-soaked, structural firefighters typically wear "turnout gear," which includes a coat and pants and also equipment that protects extremities, including a hood, helmet, and gloves [\[23\],](#page-70-0) which must meet the National Fire Protection Association (NFPA) 1971 standard: Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting [\[24\].](#page-70-1) Like turnout gear pants and jackets, gloves are also composed of an outer shell, thermal layer, and moisture barrier, though some gloves also contain an inner liner. Multiple reports have identified PFAS in other articles of firefighter gear [\[15\],](#page-69-2)[\[18\]](#page-69-4)[,\[21\]](#page-69-7)[-\[22\]](#page-69-8) and gloves and hoods may come into direct contact with the sensitive skin of firefighters' hands and face. Additionally, while previous studies have examined PFAS in turnout gear worn by structural firefighters, wildland firefighters typically wear different gear, including a shirt and pair of pants, each made of a single layer.

This publication describes research performed in response to the Fiscal Year 2021 National Defense Authorization Act (H.R. 6395) [\[25\],](#page-70-2) which directed the National Institute of Standards and Technology (NIST) to examine the identity, prevalence, and concentration of PFAS in the personal protective equipment worn by firefighters. NIST has already published reports

examining PFAS in new firefighter turnout gear textiles [\[21\]](#page-69-7) and firefighter turnout gear textiles exposed to abrasion, elevated temperature, laundering, and weathering [\[22\].](#page-69-8) This report will provide additional insight into the type and prevalence of PFAS that firefighters could be exposed to from wearing unused firefighting gloves, hoods, and wildland gear. This report will also provide a baseline for future examinations of changes in PFAS concentrations in firefighter gloves, hoods, and wildland gear due to stresses related to firefighting activities.

 $2.$ **Materials and Methods**

Experimental chemicals and consumables were identical to those used in NIST TN 2248 [\[21\]](#page-69-7) and NIST TN 2260 [\[22\]](#page-69-8) and are detailed below (Section 3.1). Four firefighter glove textiles (Section 3.2), eight firefighter hood textiles (Section 3.3), and nine wildland firefighter textiles (Section 3.4) were obtained from several manufacturers of firefighter gear in 2021-2023. PFAS analytical standards (Sections 3.5 and A.1) and analytical techniques (Sections 3.6 and A.2) were also identical to those used in NIST TN 2248 [\[21\].](#page-69-7)

$2.1.$ **Materials**

Ammonium acetate (Optima LC-MS grade), ammonium hydroxide (Optima grade), ethyl acetate (Optima HPLC and GC grade), and water (Optima LC-MS grade) were obtained from Thermo Fisher Scientific (Waltham, MA). Methanol (OmniSolv LC-MS grade) for high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) mobile phase solutions were obtained from Supelco (Bellefonte, PA). In contrast, methanol (Optima LC-MS grade) was obtained from Thermo Fisher Scientific for all other purposes. Nitrogen gas (Ultra High Purity grade) and helium gas (Ultra High Purity grade) were obtained from Roberts Oxygen (Rockville, MD).

High-performance liquid chromatography (HPLC) vials (2 mL capacity, amber glass) and glass vial inserts (250 μL) were obtained from Agilent Technologies (Santa Clara, CA). Polyethylene 2 mL vial caps for nonvolatile and semivolatile analysis were obtained from Phenomenex (Torrence, CA). In contrast, 2 mL vial caps with polytetrafluoroethylene (PTFE)/silicone septa for volatile analysis were obtained from Agilent Technologies. HPLC vials, inserts, and caps were used as received from their vendors. Supelco Analytical (Bellefone, PA) Supelclean ENVI-Carb solid phase extraction (SPE) tubes (6 mL x 500 mg) were rinsed with 20 mL (2 x 10⁻⁵ m³) of 0.1 mol/L (10² mol/m³) ammonium hydroxide in methanol and dried before use. Glass 20 mL capacity scintillation vials, glass Pasteur pipettes, and polypropylene 15 mL centrifuge tubes (Cole-Parmer Instrument Company, Vernon Hills, IL) were used as received. Syringes (1 mL capacity) and syringe filters (0.22 μm, nylon) were obtained from Thermo Fisher Scientific and rinsed with 1 mL methanol before use.

$2.2.$ **Firefighter Gloves**

Structural firefighting gloves are required to meet NFPA 1971 [\[24\]](#page-70-1) requirements. They are a multilayer construction consisting of an outer leather protective layer and a moisture barrier and thermal liner inner layers. Some gloves have a separate inner liner, while others have a liner incorporated with the thermal layer. **Figure 1** shows a glove cut open to reveal the layers.

For this investigation, four different models of structural firefighter gloves were tested. All were commonly used brands commercially available in 2023. The four glove models were designated GL-A, GL-B, GL-C, and GL-D. Because each glove comprised multiple layers, PFAS concentrations were determined for individual layers after fabric swatches were cut from the assembled gloves. GL-A included a leather outer shell (GL-A-OS), expanded polytetrafluoroethylene (ePTFE) moisture barrier (GL-A-MB), and Nomex/Kevlar thermal liner/inner liner (GL-A-IL). Glove A was the only glove tested that only had three layers. GL-B included an outer shell of 100 % para-aramid knit fleece on the top of the glove's hand (GL-B-OS), while the outer layer on the glove's palm was leather (not tested). GL-B also included a moisture barrier of a proprietary material labeled 100 % waterproof (GL-B-MB). At the same time, the layer against the skin was a Nomex/Kevlar thermal liner on the top of the glove's hand (GL-B-TL) and a modacrylic inner liner facing the glove's palm (GL-B-IL). GL-C had a 100 % Kevlar outer shell on top of the glove's hand (GL-C-OS) and a leather outer shell on its palm (not tested). GL-C included an ePTFE moisture barrier (GL-C-MB), while the thermal liner (GL-C-TL) and inner liner (GL-C-IL) were Kevlar/Nomex fleece blends. GL-D had a leather outer shell (GL-D-OS), ePTFE moisture barrier (GL-D-MB), Kevlar/Nomex blend thermal liner (GL-D-TL), and 100 % modacrylic inner liner (GL-D-IL). **Table 1** lists values of area density and photos of each glove layer in all four gloves.

$2.3.$ **Firefighter Hoods**

Structural firefighters wear protective hoods made of heat-resistant knitted materials. They provide thermal protection and flame resistance to the head and neck. The hoods are worn

underneath the helmet, and if a self-contained breathing apparatus (SCBA) is worn, the hood is placed over the straps of the SCBA. The hoods have an opening in the front for a firefighter's face, or SCBA if worn, and have an extended bib area at the bottom of the hood that continues towards the shoulders so the hood can be tucked into the firefighter's coat. Hoods must meet the requirements of NFPA 1971 [\[24\].](#page-70-1) Only basic, knitted hoods designed for thermal protection were evaluated in this study. This study did not examine protective barrier hoods with extra particulate blocking features.

Eight models of hoods produced by three manufacturers were obtained from three vendors of firefighting gear in 2023. Hood samples were designated as HD-A through HD-H. The eight hoods comprised different types or combinations of materials and were obtained in various colors, while all were rib knit. HD-A was black and a mixture of carbon/aramid blend. HD-B was white and 100 % Nomex material. HD-C was black and a mixture of oxidized polyacrylonitrile and tri-blend carbon. HD-D was white and a mixture of Nomex and cellulose fibers made from wood. HD-E was tan and a mixture of polybenzimidazole (PBI) synthetic fiber and regenerated cellulose. HD-F was tan and a mixture of PBI synthetic fiber and cellulose fibers made from wood. HD-G was yellow and a mixture of polyimide derived from aromatic dianhydrides and aromatic diisocyanates, as well as cellulose fibers made from wood and heat-resistant, synthetic, lightweight fiber. HD-H has the same material composition as HD-G but was produced by a different manufacturer. **Table 1** lists values of area density and photos of each of the eight hoods.

$2.4.$ **Wildland Firefighter Gear Textiles**

Wildland firefighters wear different gear than those who typically fight structural fires. Unlike the turnout gear of structural firefighters, which is composed of three layers, including an outer shell, a moisture barrier, and a thermal liner, wildland garments typically only contain one layer of fabric, similar to the outer shell fabric of the structural turnout gear. Wildland gear fabric must meet the requirements for work in the wildland firefighting environment, as detailed in NFPA 1977 [\[26\].](#page-70-3)

For this investigation, nine commercially available wildland firefighter gear articles were manufactured by three common wildland firefighter gear manufacturers and then obtained by NIST from three different gear distributors in the form of fully assembled brush shirts, brush pants, or overcoats. Wildland firefighter gear samples were designated WL-A through WL-I and were all plain weave unless stated otherwise. WL-A was a coat made of meta-aramid, paraaramid, and anti-static to protect against electric arc. WL-B was a coat constructed of materials similar to WL-A but produced by a different manufacturer. WL-C was a coat labeled "nonfluorinated" and made of a cotton and nylon blend. WL-D was pants made of the same material as WL-A and obtained from the same manufacturer as WL-A. WL-E were pants made of heatresistant, synthetic, lightweight fiber and Nomex. WL-F were pants labeled as "non-fluorinated" and made of the same material as WL-D but obtained from a different manufacturer. WL-G were pants labeled as "non-fluorinated" and made of the same material as WL-C, obtained

from the same manufacturer as WL-C. WL-H was a shirt labeled "hypoallergenic due to the exclusion of chemical finishes and coatings." It was made of modacrylic, semi-synthetic lyocell fiber, and para-aramid fiber. WL-I was a shirt labeled as "not chemically treated" and made of the same material as WL-H but was obtained from a different manufacturer. **Table 1** shows the area density and photos of each wildland textile.

This NIST PFAS firefighter research is an anonymous study, meaning the researchers do not know the identity of the fabric manufacturer, and the fabric composition tables are not added until the report is complete. As obtained, the assembled wildland gear garments contained detailing such as stitching, buttons, reinforced areas, and reflective patches. For this evaluation, all the stitching or details were not included in the samples of wildland gear taken for PFAS analysis.

Table 1. Area densities (mean ± standard deviation of triplicate measurements; kg/m²) and images of structural firefighter gloves and hoods, as well as wildland firefighter gear textiles, were evaluated in this NIST TN.

Table 1. (Continued)

Table 1. (Continued)

Table 1. (Continued)

$2.5.$ **PFAS Analytical Standards**

This study uses the same 55 PFAS analyte list described in our previous reports [\[21\]-](#page-69-7)[\[22\].](#page-69-8) The selection of PFAS for inclusion in this study was based on earlier reports in the scientific literature, the professional experience of NIST researchers related to PFAS and firefighter gear, and conversations with subject matter experts outside NIST. Analytical standards were obtained for eleven perfluoroalkyl carboxylic acids (PFCA), eight perfluoroalkane sulfonic acids (PFSA), six perfluoroalkane sulfonamides (FASA), three per- and polyfluoroalkane sulfonamido acetic acids (FASAA), two perfluoroalkane sulfonamido ethanols (FASE), eight per- and polyfluoroalkyl ether acids (PPEA), two n:2 fluorotelomer acrylates (n:2 FTAcr), three n:2 fluorotelomer methacrylates (n:2 FTMAC), two n:2 fluorotelomer acetates (n:2 FTOAc), six n:2 fluorotelomer alcohols (n:2 FTOH), and four n:2 fluorotelomer sulfonates (n:2 FTS). Information for all PFAS and their associated reference standards are provided in **Table 2** and Appendix [A.1](#page-71-1) (**Table 35** – **Table 42**).

$2.6.$ **Chemical Analysis of PFAS in Firefighter Gear**

Three analytical procedures, referred to in this report as "nonvolatile," "semivolatile," and "volatile," were previously developed for the quantification of a chemically diverse set of PFAS in firefighter turnout gear textiles. The analytical methods used to quantify individual PFAS are shown in **Table 2**. Detailed descriptions of these methods were previously described in NIST TN 2248 [\[21\]](#page-69-7) and NIST TN 2260 [\[22\].](#page-69-8) Briefly, in the nonvolatile method, PFAS were extracted from stressed firefighter gear textiles by sonication in methanol at 25 °C with subsequent centrifugation, filtration through graphitized carbon (ENVI-Carb SPE tubes; 500 mg x 6 mL), and evaporation to dryness under nitrogen at 40 °C. Dried nonvolatile extracts were reconstituted in methanol and analyzed by LC-MS/MS. PFAS analyzed by the semivolatile and volatile analytical methods were extracted simultaneously by sonication in ethyl acetate at 25 °C and subsequent centrifugation, filtration through graphitized carbon (ENVI-Carb SPE tubes, 500 mg x 6 mL), and evaporation to 2 mL under nitrogen at 35 °C. Extracts were then analyzed by LC-MS/MS or GC-MS for semivolatile or volatile PFAS, respectively. PFAS concentrations below reporting limits or did not meet quality control standards were given a value and variance of zero for summed PFAS calculations. Reporting limits were PFAS and sample-specific. Most determined reporting limits were below 0.125 µg/kg for nonvolatile PFAS measurements (784 out of 1107) and below 0.625 µg/kg for semivolatile (102 out of 160) PFAS measurements. Reporting limits for volatile PFAS were 7.7 µg/kg or higher. More details on how reporting limits were calculated and specific reporting limits for each measurement are available in Appendix [A.3.1](#page-77-3) and **Table 3** – **Table 34**.

Table 2. Class names and abbreviations as well as individual compound names, abbreviations, analytical methods used for quantification (i.e., NV for nonvolatile, SV for semivolatile, and V for volatile) as well as Chemical Abstract Service Registry Numbers (CAS RN) of all PFAS analyzed in this technical note.

Table 2. (Continued)

3. **Results and Discussion**

$3.1.$ **Area Density of Gloves, Hoods, and Wildland Textiles**

Table 1 lists area densities for all firefighter glove layers, hood textiles, and wildland firefighter gear textiles examined here. The area densities were measured in triplicate as mass per unit area using approximately 2 cm x 2 cm cut squares of textiles. Gloves layer textile area densities varied from 0.078 kg/m² ± 0.001 kg/m² (GL-B-MB) to 1.15 kg/m² ± 0.03 kg/m² (GL-B-OS), hood area densities varied from 0.195 kg/m² \pm 0.005 kg/m² (HD-E) to 0.30 kg/m² \pm 0.01 kg/m² (HD-G), while wildland firefighter gear textiles had area densities from 0.179 kg/m² ± 0.003 kg/m² (WL-H) to 0.266 kg/m² ± 0.009 kg/m² (WL-C).

$3.2.$ **PFAS Occurrence and Concentrations in Firefighter Gloves Textiles**

Across 15 layers from four glove models, 12 individual PFAS were quantified above the analyteand sample-specific reporting limits, with between zero and seven PFAS quantified in each textile (**Fig. 2** and **Table 3** – **Table 17**). FASA was frequently quantified, with perfluorobutane sulfonamide (FBSA), *N*-methyl perfluorobutane sulfonamide (MeFBSA), and perfluorooctane sulfonamide (FOSA) being observed above reporting limits in 12, 7, and 2 textiles, respectively. Also widely detected, perfluorobutanoic acid (PFBA) was observed in 8 textiles, and perfluorobutane sulfonic acid (PFBS) was observed in 10 textiles.

Fig. 2. Average PFAS concentrations (µg PFAS/kg textile or ppb mass ratio) determined from triplicate analysis of individual firefighter glove layers (GL = glove, IL = inner liner, TL = thermal liner, MB = moisture barrier, OS = outer shell). Measurements that could not be reported due to unmet QC standards are in white.

The highest individual PFAS concentrations observed in any glove layer were the FASAs in the moisture barrier layers with MeFBSA present up to 117.2 μ g/kg ± 7.0 μ g/kg (mean ± standard deviation of triplicate measurements; GL-B-MB; **Table 7**), FBSA up to 51.2 µg/kg ± 6.7 µg/kg (GL-C-MB; **Table 11**), and FBSA up to 68 µg/kg ± 13 µg/kg (GL-D-MB; **Table 15**). Summed PFAS concentrations varied widely across glove layers from no PFAS detected in GL-A1-IL (**Fig. 3** and **Table 3**) to 118.9 µg/kg ± 7.1 µg/kg in GL-B-MB (**Fig. 3** and **Table 7**). The highest summed PFAS concentrations across all glove layers were also observed in the moisture barrier layers, with summed concentrations up to 118.9 µg/kg ± 7.1 µg/kg (GL-B-MD; **Fig. 3 and Table 7**). The wide range in summed PFAS concentrations across moisture barrier textiles derived from the variation in concentration of FASAs (**Fig. 3,** other category), with FBSA and MeFBSA concentrations contributing up to 100 % of PFAS observed in moisture barrier textiles.

Fig. 3. Summed PFAS concentrations in individual firefighter glove layers (GL = glove, IL = inner liner, TL = thermal liner, MB = moisture barrier, OS = outer shell). Error bars indicate the combined standard uncertainty of the summed PFAS concentrations. The bar color indicates the PFAS class.

$3.3.$ **PFAS Occurrence and Concentrations in Firefighter Hoods Textiles**

Across all eight firefighter hoods, only five individual PFAS were quantified above the analyteand sample-specific reporting limits, with between zero and three individual PFAS quantified in each hood textile (**Fig. 4** and **Table 18** -**Table 25**). PFOS was detected in three hoods at concentrations up to 0.15 μg/kg ± 0.07 μg/kg (HD-B; **Table 19)**, while FOSA, PFBS, PFOA, and perfluorotetradacanoic acid (PFTeDA) were each detected above reporting limits in one or two hood textiles. Summed PFAS concentrations were below 0.6 μg/kg in all hoods. PFSAs were most widely quantified; PFBS and PFOS were observed in one and three textiles, respectively. PFCAs were widely quantified, with PFOA and PFTeDA observed in one and two textiles, respectively. FOSA was also observed in one textile.

The highest individual concentrations observed for any hood were PFCAs, including PFOA (up to 0.3 μg/kg ± 0.1 μg/kg; HD-B; **Table 19**), PFTeDA (up to 0.10 μg/kg ± 0.05 μg/kg; HD-C; **Table 20**), and PFTeDA (up to 0.08 μg/kg ± 0.01 μg/kg; HD-H; **Table 25**). The other highest individual concentrations were PFSAs, including PFBS (up to 0.13 μg/kg ± 0.07 μg/kg; HD-A; **Table 18**) and PFOS (up to 0.15 μg/kg ± 0.07 μg/kg; HD-B; **Table 19)**. Summed PFAS concentrations varied across hoods from no PFAS detected in hoods HD-D, HD-E, HD-F, and HD-G (**Fig. 5** and **Table 21** to **Table 24**), to 0.6 μg/kg ± 0.1 μg/kg in HD-B (**Fig. 5** and **Table 19**). Compared to the glove layers, the PFAS concentrations were low in the hoods, and no volatile PFAS was detected above reporting limits. The range in summed PFAS concentrations derived from the variation in the PFCA or PFSA classes, with 100 % of the PFAS detected above reporting limits occurring from these two PFAS classes, except HD-B, in which FOSA was also detected.

Fig. 4. Average PFAS concentrations (µg PFAS/kg textile or ppb mass ratio) determined from triplicate analysis of individual firefighter hood textiles. The average concentration is indicated by shade (legend at right). Measurements that could not be reported due to unmet QC standards are in white.

Fig. 5. Summed PFAS concentrations in individual firefighter hoods (HD = hood). Error bars indicate the combined standard uncertainty of the summed PFAS concentrations. The bar color indicates the PFAS class.

$3.4.$ **PFAS Occurrence and Concentrations in Wildland Gear Textiles**

Across all nine wildland gear textiles, 11 individual PFAS were quantified above the analyte and sample-specific reporting limits, between zero and nine PFAS, quantified in each (**Fig. 6** and **Table 26** – **Table 33**). PFCAs, especially those with short perfluorinated chains (i.e., containing seven or fewer perfluorinated carbons) were frequently quantified, with PFBA, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) observed in 3, 6, 6, and 4 textiles, respectively. Also detected were 6:2 FTMAC and 6:2 FTOH; both were detected in 5 textiles, as well as 6:2 fluorotelomer sulfonic acid (6:2 FTS; 2 textiles), PFBS; 1 textile, perfluoropentane sulfonic acid (PFPeS; 1 textile), PFOS; 1 textile, and perfluorononane sulfonic acid (PFNS; 1 textile).

Fig. 6. Average PFAS concentrations (µg PFAS/kg textile or ppb mass ratio) determined from triplicate analysis of individual wildland firefighter gear textiles. The average concentration is indicated by shade (legend at right). Measurements that could not be reported due to unmet QC standards are in white.

The highest individual concentrations observed for any of the wildland gear textiles were in the fluorotelomerization (FT)-derived PFAS in WL-F, with 6:2 FTMAC concentration up to 2980 μg/kg ± 820 μg/kg (**Table 31**) and 6:2 FTOH concentration up to 1250 μg/kg ± 330 μg/kg (**Table 31**). Summed PFAS concentrations varied across wildland textiles from no PFAS detected in WL-B (**Fig. 7** and **Table 27**) to 4240 μg/kg ± 890 μg/kg in WL-F (**Fig. 7** and **Table 31**). Compared to the glove layers and hood textiles, summed PFAS concentrations were much higher in the wildland firefighter gear textiles. The range in summed PFAS concentrations derived from the variation in the FT-derived classes, with 6:2 FTMAC and 6:2 FTOH concentrations contributing over 95 % of the total summed PFAS in seven of the nine wildland firefighter gear textiles.

Fig. 7. Summed PFAS concentrations in individual wildland textiles (WL = wildland). Error bars indicate the combined standard uncertainty of the summed PFAS concentrations. The bar color indicates the PFAS class.

$3.5.$ **Summed PFAS Occurrence and Concentration Comparisons**

In this report, PFAS concentrations in gloves, hoods, and wildland textiles are similar to PFAS concentrations previously reported in turnout gear jackets and pants textiles in a recent NIST report (**Fig. 8**) [\[21\].](#page-69-7) The highest summed PFAS concentrations Maizel et al. [\[21\]](#page-69-7) reported in firefighter turnout gear outer shell and moisture barrier textiles were 1890 μ g/kg \pm 180 μ g/kg and 1865 μ g/kg \pm 88 μ g/kg, respectively. These measurements are lower than the summed PFAS concentrations reported here in wildland firefighter gear, with summed PFAS concentrations up to 4240 μg/kg ± 890 μg/kg, while the summed PFAS concentrations reported here in textiles present in gloves and hoods are much lower, with concentrations up to 118.9 μ g/kg \pm 7.1 μ g/kg and 0.6 μ g/kg \pm 0.1 μ g/kg, respectively. The highest concentration of individual PFAS in firefighter turnout gear textiles reported by Maizel et al. [\[21\]](#page-69-7) was 6:2 FTMAC, present at concentrations up to 1520 μ g/kg \pm 130 μ g/kg in an outer shell textile. While 6:2 FTMAC was not observed above reporting limits in firefighter gloves or hoods examined here, 6:2 FTMAC was observed in wildland firefighter gear at concentrations up to 2980 μ g/kg \pm 820 μ g/kg. Similarly, the second highest concentration of individual PFAS in turnout gear Maizel et al. [\[21\]](#page-69-7) reported was 6:2 FTOH, present in the outer shells up to 393 μ g/kg ± 98 μ g/kg. These measurements are lower than the 6:2 FTOH concentrations reported here in wildland firefighter gear, where 6:2 FTOH was present at concentrations up to $1250 \mu g/kg \pm 330 \mu g/kg$.

Fig. 8. Summed PFAS concentrations in individual firefighter gloves, hoods, and wildland textiles and from a previous report on structural firefighter jackets and pants [\[21\].](#page-69-7) Each report's measurements are ordered from left to right in increasing summed concentrations. The marker shade indicates the textile type (GL = glove, HD = hood, WL = wildland, MB = moisture barrier, OS = outer shell, TL = thermal liner).

6:2 FTMAC and 6:2 FTOH are intermediates in the production of side-chain fluorinated acrylate polymers [\[27\]-](#page-70-4)[\[28\]](#page-70-5) and have been previously identified in turnout gear textiles [\[18\]-](#page-69-4)[\[19\],](#page-69-5) [\[21\]](#page-69-7)[\[22\].](#page-69-8) 6:2 FTOH is also found in fast food packaging and stain- and water-resistant textiles

[\[29\].](#page-70-6) Anand et al. [\[30\]](#page-70-7) performed a toxicological assessment of 6:2 FTMAC and found that, overall, 6:2 FTMAC is considered to have low toxicity potential. Rice et al. [\[29\]](#page-70-6) compared the toxicological databases for 6:2 FTOH and PFHxA. They found that 6:2 FTOH is significantly more toxic than PFHxA, and 6:2 FTOH may be significantly underestimated as a human health risk. 6:2 FTMAC or 6:2 FTOH were detected above reporting limits in seven of the nine wildland firefighter textiles, but none in the hoods or gloves. These FT-derived PFAS in wildland textiles may indicate that these textiles were treated with side-chain fluorinated polymers. Fluorotelomerization-derived PFAS with more or less than six perfluorinated carbons were not detected in any other textile tested in this report, with only 6:2 FTS quantified in WL-E, WL-F, and GL-A-MB at concentrations up to 6.02 μ g/kg ± 0.19 μ g/kg.

PFBS, FBSA, and MeFBSA are all electrochemical fluorination-derived PFAS [\[27\]](#page-70-4)[,\[31\]](#page-70-8) with four perfluorinated carbons. Rericha et al. [\[32\]](#page-70-9) studied zebrafish to compare the toxicity of PFBS, PFPeA, FBSA, and 4:2 FTS (all containing four perfluorinated carbons). They concluded that FBSA was the most developmentally toxic and bioaccumulative, as well as inducing transcriptional changes that preceded morphological effects. In this report, PFBS, FBSA, and MeFBSA were each present above the reporting limits in 10, 12, and 7 glove layers, respectively, and were observed in the highest concentrations in the moisture barrier layers of gloves (i.e., 51.2 μ g/kg \pm 6.7 μ g/kg, 68 μ g/kg \pm 13 μ g/kg and 117.2 μ g/kg \pm 7.0 μ g/kg in GL-B-MB, GL-C-MB, and GL-D-MB), which may indicate that these glove layers are treated with similar durable water repellents treatments. Short-chain PFSAs are also used in water and stainrepellent treatments; for example, PFBS replaced PFOS as the active ingredient in a leading durable water-repellent fabric treatment in 2003 [\[28\],](#page-70-5) but there are current efforts to discontinue the use of PFAS in manufacturing across products [\[33\].](#page-70-10) FASAs are raw materials for various fluorochemical products, including surface protection products [\[27\].](#page-70-4) PFBS and MeFBSE gave the highest observed PFAS concentrations in two recent investigations of PFAS in firefighter turnout gear [\[2\]](#page-68-2)[,\[18\].](#page-69-4)

While no individual PFCA was identified in this NIST TN above 10 μg/kg in any textile, PFCAs were widely detected, with at least one quantified above the reporting limit in 17 textiles tested in this study. This agrees with two previous studies of PFCA concentrations in firefighter turnout gear that reported the near-universal quantification of short-chain PFCAs and occasional detection of PFCAs with up to 13 perfluorinated carbons, though all at individual concentrations below 40 μg/kg [\[2\],](#page-68-2)[\[18\],](#page-69-4)[\[21\].](#page-69-7) The omnipresence of low concentrations of PFCAs may reflect their use as fluoropolymer processing aids [\[27\].](#page-70-4) PFBA was the most widely observed PFCA and was present in 11 of the 17 textiles where PFCAs were identified. Weatherly et al. [\[34\]](#page-70-11) analyzed serum chemistries, histology, immune phenotyping, and gene expression to evaluate the systemic toxicity of sub-chronic dermal PFBA, and results showed sustained dermal exposure to PFBA induces liver toxicity and alterations of PPAR target genes. PPEAs, replacement polymer processing aids for PFCAs, were not present above reporting limits in any textile (**Figs. 2, 4, and 6**), which agrees with another recent examination of PFAS in firefighter

gear that measured none of the four PPEAs above reporting limits in any examined turnout gear layer [\[18\],](#page-69-4)[\[21\].](#page-69-7)

The significant variation in summed PFAS concentrations among gloves, hoods, and wildland textiles suggests that the amount of PFAS in unused gear varies according to the textiles used in manufacturing that gear (**Figs. 3, 5, and 7**). For example, a glove that contained the same mass of each textile layer would have almost ten times as much summed mass of the PFAS reported here if it were constructed of GL-B-MB, GL-B-OS, GL-D-TL, and GL-D-IL compared with a similar glove constructed of GL-A-MB, GL-A-OS, GL-B-TL, and GL-A-IL. As all gloves, hoods, and wildland textiles examined here met NPFA standards, this finding suggests that the amount of PFAS present in unused gear might, in some cases, be lowered through the choice of commercially available textiles. While the summed PFAS concentrations in some moisture barriers in gloves approached 200 μg/kg, all thermal and inner liners textiles in the gloves had summed PFAS concentrations under 5 μg/kg. The low summed PFAS concentrations likely reflect the lack of fluorinated polymer treatments in thermal and inner liners in gloves that are not subject to moisture-repellency standards. The fact that thermal and inner liners are the closest layers to firefighter skin in finished structural firefighter gloves could imply lower dermal PFAS exposure to firefighters than would be assumed by summing the PFAS present in all layers. However, other studies have found similar PFAS concentrations in structural firefighter turnout gear thermal liners as in other turnout gear textiles [\[2\],](#page-68-2) and the results presented here may be specific to the PFAS and textiles examined in this study.

4. **Summary**

This study utilized a targeted analytical approach to quantify 55 nonvolatile, semivolatile, and volatile PFAS across 15 individual layers from four unused firefighter glove models, eight unused firefighter hoods, and nine unused articles of wildland firefighting gear. Two extraction protocols were applied to maximize the recovery of targeted PFAS while minimizing the potential degradation of other polymer and non-polymer PFAS. Nonvolatile and semivolatile PFAS were quantified with separate HPLC-MS/MS methods, while volatile PFAS were quantified with GC-MS.

Of the 55 PFAS examined, 36 were quantified below reporting limits in all analyzed textiles, while the remaining 19 were each quantified in between 1 and 25 textiles. 6:2 FTMAC and 6:2 FTOH were present in the highest observed PFAS concentrations, though they were only present above reporting limits in 7 of the wildland gear textiles and none of the hood textiles or glove layers. Summed PFAS concentrations were highest in wildland gear textiles, followed by the moisture barrier layers in the gloves, and lowest in the hoods. Additionally, PFAS concentrations were higher in the moisture barrier layers of the gloves than in any of the other glove layers (outer shell, thermal liner, or inner liner).

This study adds to a growing body of literature examining PFAS concentrations in structural firefighting turnout gear, including textiles in gloves, hoods, and wildland gear. While this and other studies examined different textiles and utilized dissimilar analytical methods, each provided unique insight into the occurrence of PFAS in turnout gear. However, since this study used the same analytical methods outlined in NIST TN 2248 [\[21\]](#page-69-7) and NIST TN 2260 [\[22\],](#page-69-8) direct comparisons of PFAS concentrations can be concluded. Additional research on PFAS in used turnout gear, PFAS transport between gear layers or into firefighters, and the occupational hazards firefighters face are critical to understanding the potential PFAS exposure firefighters face.

5. **Future Work**

Future work will examine the effect of typical use on the types and concentrations of PFAS in stressed textiles present in structural firefighter gloves, hoods, and wildland gear, as higher PFAS concentrations have been observed in stressed textiles present in firefighter gear compared with unused firefighter gear textiles [\[22\].](#page-69-8) Stressing of the gear will include elevated temperatures, abrasion, and accelerated weathering. Additionally, future efforts will use highresolution mass spectrometry to identify a broader swath of PFAS than the 55 compounds quantified here, including screening for previously identified compounds and searching for novel non-targeted PFAS. Other potential sources of PFAS exposure to firefighters will also be evaluated, including multiple stressing of unused firefighter gear and dust or soot collected from fire stations. Finally, to better relate the measurements made here with the actual PFAS exposure to firefighters, the capacity of simulated sweat to extract PFAS from firefighter turnout gear will be evaluated.
Table 3. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-A-IL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 4. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-A-MB. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 5. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-A-OS. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 6. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-B-IL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 7. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-B-MB. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 8. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-B-TL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 9. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-B-OS. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 10. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-C-IL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile..

Table 11. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-C-MB. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 12. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-C-TL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

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Table 13. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-C-OS. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 14. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-D-IL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

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Table 15. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-D-MB. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 16. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-D-TL. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

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Table 17. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter glove textile GL-D-OS. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 18. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-A. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 19. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-B. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 20. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-C. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 21. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-D. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 22. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-E. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 23. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-F. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 24. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-G. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

Table 25. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in firefighter hood textile HD-H. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

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Table 34. PFAS concentrations and reporting limits (RL; µg PFAS/kg textile) in wildand textile WL-I. NV indicates the analytical method for nonvolatile, SV for semivolatile, or V for volatile.

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Appendix A. Experimental Details

A.1. PFAS Analytical Standards and NIST Reference Materials

Analytical standards (**Table 35**) and isotopically labeled standards (**Table 36**) for nonvolatile PFAS as well as semivolatile PFAS (**Table 37** and **Table 38**) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Analytical standards and isotopically labeled standards for volatile PFAS (**Table 39** and **Table 40**) were obtained from Wellington Laboratories and Synquest Laboratories (Alachua, FL).

NIST Reference Materials (RMs) 8446 Perfluorinated Carboxylic Acids and Perfluorooctane Sulfonamide in Methanol (8446) and 8447 Perfluorinated Sulfonic Acids in Methanol (8447) were obtained for use as quality control samples (**Table 41** and **Table 42**).
Table 35. Nonvolatile PFAS analytical standards obtained from Wellington Laboratories, with full analyte names, CAS RN, and abbreviations (bold), and analyte concentrations with expanded maximum combined percent relative uncertainty. PFHxS, PFOS, MeFOSAA, and EtFOSAA in PFAC30PAR were present as a mixture of structural isomers.

Table 36. Nonvolatile isotopically labeled PFAS internal and injection standards obtained from Wellington Laboratories, with full analyte names, and analyte concentrations with expanded maximum combined percent relative uncertainty where provided.

Table 37. Semivolatile PFAS analytical standards purchased from Wellington Laboratories including full analyte names, CAS RN, abbreviations (bold), and analyte concentrations with expanded maximum combined percent relative uncertainty where provided.

Table 38. Semivolatile isotopically labeled PFAS internal standards obtained from Wellington Laboratories, with full analyte names, and analyte concentrations with expanded maximum combined percent relative uncertainty where provided.

Table 39. Volatile target PFAS analytical standards, supplier, full analyte names, CAS RN, abbreviations (bold), and analyte concentrations with expanded maximum combined percent relative uncertainty where provided.

Table 40. Volatile internal standard PFAS purchased from Wellington Laboratories, including full analyte names, and analyte concentrations with expanded maximum combined percent relative uncertainty where provided.

Table 41. Reference mass fractions for NIST Reference Material 8446 including mean value and expanded uncertainty with 95 % confidence.

Table 42. Reference mass fractions NIST Reference Material 8447 including mean value and expanded uncertainty with 95 % confidence.

A.2. PFAS Analysis

PFAS analytical methods and quality control processes and limits were performed in an identical manner as reported in a previous NIST TN 2248 [\[21\].](#page-69-0)

A.3. Quality Control Results

Each analytical sequence resulted in a range of quality control (QC) results. Reporting limits determined for each measurement (Section A.5.1), NIST RM 8446 and 8447 recoveries (Section A.5.2), as well as OS-FRM recovery (Section A.5.3) are detailed below.

A.3.1. Reporting Limits

Reporting limits determined for each PFAS measurement in structural firefighter gloves, hoods, and wildland firefighter gear textiles are listed above in **Table 3** – **Table 34**. Histograms of the reporting limits for measurements made with each of the three analytical methods are shown in **Fig. 9**. Most determined reporting limits were below 0.125 µg/kg for nonvolatile PFAS measurements (784 out of 1107) and below 0.625 µg/kg for semivolatile (102 out of 160) PFAS measurements. Reporting limits for volatile PFAS were much higher; out of 410 reported volatile GC measurements, no reporting limit was under 7.7 µg/kg, and 132 were over 100 µg/kg.

Fig. 9. Histograms of reporting limits for individual measurements of nonvolatile (NV; bin width = 0.125 µg/kg), semivolatile (SV; bin width = 0.125 μ g/kg), and volatile PFAS (V; bin width = 50 μ g/kg).

A.3.2. NIST Reference Materials 8446 and 8447

Nonvolatile PFAS concentrations in firefighter turnout gear textile extracts were determined across four analytical sequences. Gravimetric dilutions of NIST RMs 8446 Perfluorinated Carboxylic Acids and Perfluorooctane Sulfonamide in Methanol as well as 8447 Perfluorinated Sulfonic Acids in Methanol were prepared and analyzed with each sequence and measured concentrations were between 80.4 % - 119% of the reference values for all analytes (**Fig. 10).**

The recovery of all NIST RM 8446 and 8447 analytes suggests that calibration regressions determined with each nonvolatile analytical sequence were consistent and accurate.

Fig. 10. Recovery of reference PFAS in NIST reference materials 8446 and 8447 across four analytical nonvolatile PFAS analytical sequences. 100 % recovery is indicated with a solid line while 70 % and 130 % recoveries are indicated with dashed lines.

A.3.3. Method Reproducibility Material OS-FRM

As described in NIST TN 2248 [\[21\]](#page-69-0) and NIST TN 2260 [\[22\],](#page-69-1) 400 firefighter gear outer shell textile OS-F samples were cut, weighed, and stored in 15 mL polypropylene centrifuge tubes as OS-FRM. Twelve were randomly selected and analyzed for nonvolatile, semivolatile, and volatile PFAS to determine baseline values. Each extraction batch of 11 firefighter gear samples was extracted with an additional single cutting of OS-FRM to demonstrate extraction consistency and calibration accuracy. Recoveries are shown in **Fig. 11**. Some recoveries are not shown because the measured concentration was below the sample and analyte specific reporting limit.

Fig. 11. Recovery PFAS with previously measured concentration over 0.5 µg/kg in OS-FRM across four analytical nonvolatile extraction batches, five semivolatile extraction batches, and six volatile extraction batches. Some recoveries are not shown because the measured concentration was below the sample and analyte specific reporting limit.

Appendix B. List of Symbols, Abbreviations, and Acronyms

10:2 FTAcr 10:2 fluorotelomer acrylate

4:2 FTS 4:2 fluorotelomer sulfonate

6:2 FTMAC 6:2 fluorotelomer methacrylate

6:2 FTOH 6:2 fluorotelomer alcohol

6:2 FTS 6:2 fluorotelomer sulfonate

8:2 FTAcr 8:2 fluorotelomer acrylate

ADONA 4,8-Dioxa-3H-perfluorononanoate

AFFF Aqueous film-forming foams

CAS RN Chemical Abstract Service Registry Number

9Cl-**PF3ONS** 9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid

11Cl-**PF3OUdS** 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid

DWR Durable water repellent

ePTFE Expanded polytetrafluoroethylene

EtFOSA N-Ethyl perfluorooctane sulfonamide

EtFOSAA N-Ethyl perfluorooctane sulfonamido acetic acid

EtFOSE N-Ethyl perfluorooctane sulfonamido ethanol

FASA Perfluoroalkane sulfonamide

FASAA Per- and polyfluoroalkane sulfonamido acetic acid

FASE Perfluoroalkane sulfonamido ethanol

FBSA Perfluorobutane sulfonamide

FHxSA Perfluorohexane sulfonamide

FOSA Perfluorooctane sulfonamide

FOSAA Perfluorooctane sulfonamido acetic acid

FT Fluorotelomerization

GC-MS Gas chromatography-mass spectrometry

HFPO-DA Hexafluoropropylene oxide dimer acid

HPLC High-performance liquid chromatography

INJ Injection standard

IS Internal standard

LC Liquid chromatography

MB Moisture barrier

MeFBSA N-Methyl perfluorobutane sulfonamide

MeFBSE N-Methyl perfluorobutane sulfonamidoethanol

MeFOSA N-Methyl perfluorooctane sulfonamide

MeFOSAA

N-Methyl perfluorooctane sulfonamido acetic acid

MeFOSE N-Methyl perfluorooctane sulfonamido ethanol

MS Mass spectrometry

MS/MS Tandem mass spectrometry

n:2 FTAcr n:2 fluorotelomer acrylate

n:2 FTOAc n:2 fluorotelomer acetate

n:2 FTOH n:2 fluorotelomer alcohol

n:2 FTMAC n:2 fluorotelomer methacrylate

n:2 FTS n:2 fluorotelomer sulfonate

NFPA National Fire Protection Association

NIST National Institute of Standards and Technology

NIST TN National Institute of Standards and Technology Technical Note

3-6-OPFHpA Perfluoro-3,6-dioxaheptanoic acid

OS Outer shell

PBI Polybenzimidazole

PF4OPeA Perfluoro-3-methoxypropanoic acid

PF5OHxA Perfluoro-4-methoxybutanoic acid

PFAS Per- and polyfluoroalkyl substances

PFBA Perfluorobutanoic acid

PFBS Perfluorobutane sulfonic acid

PFCA Perfluorocarboxylic acid

PFDA Perfluorodecanoic acid

PFDoDA Perfluorododecanoic acid

PFDS Perfluorodecane sulfonic acid

PFEESA Perfluoro-2-ethoxyethane sulfonic acid

PFHpA Perfluoroheptanoic acid

PFHpS Perfluoroheptane sulfonic acid

PFHxA Perfluorohexanoic acid

PFHxS Perfluoro hexane sulfonic acid

PFNA Perfluorononanoic acid

PFNS Perfluorononane sulfonic acid

PFOA Perfluorooctanoic acid

PFOS Perfluorooctane sulfonic acid

PFPeA Perfluoropentanoic acid

PFPeS Perfluoropentane sulfonic acid

PFPrS Perfluoropropane sulfonic acid

PFSA Perfluoroalkane sulfonic acid

PFTeDA Perfluorotetradacanoic acid

PFTrDA Perfluorotridecanoic acid

PFUnDA Perfluoroundecanoic acid

PPEA Per- and polyfluoroalkyl ether acid

PTFE Polytetrafluoroethylene

QC Quality control

RL Reporting limit

RM Reference material

SCBA Self-contained breathing apparatus

SPE Solid phase extraction

TL Thermal liner