Combined use of total fluorine and oxidative fingerprinting for quantitative determination of side-chain fluorinated polymers in textiles

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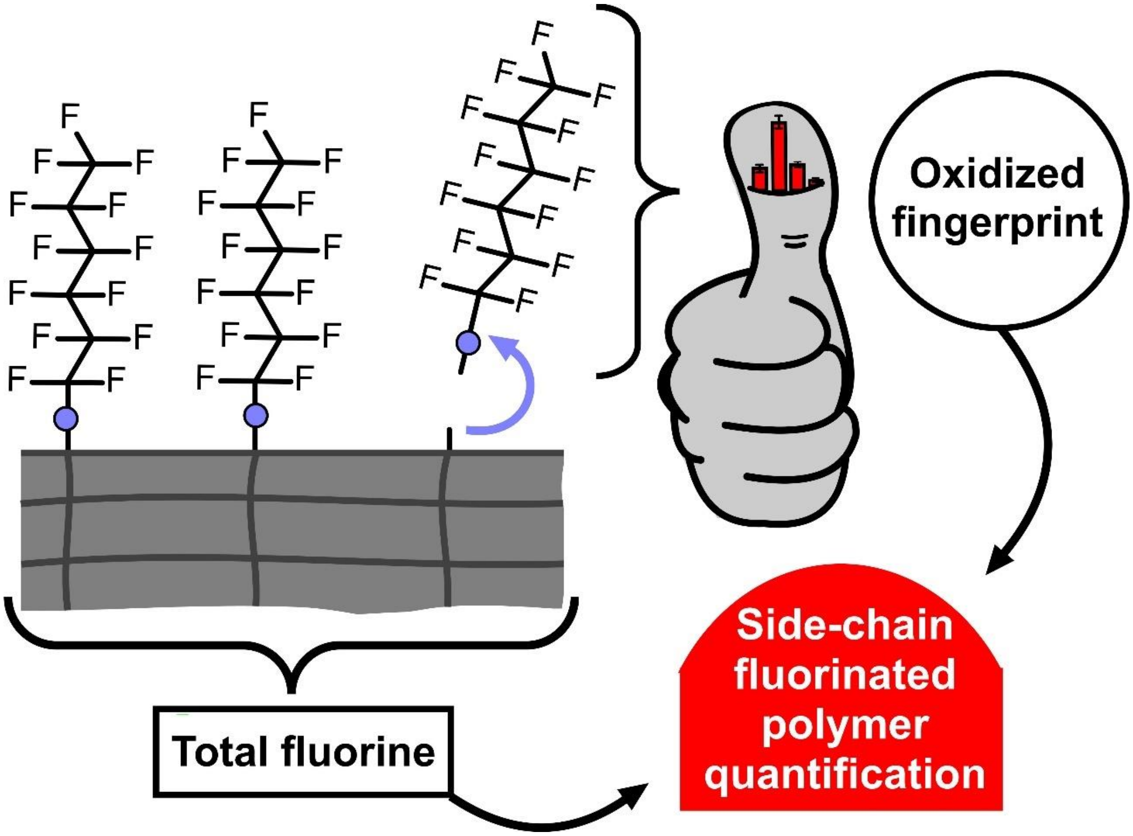
Graphical Abstract



Abstract

Given their extensive production volumes and potential to form persistent perfluoroalkyl acids (PFAAs), there is concern surrounding the ongoing use of side-chain fluorinated polymers (SFPs) in consumer products. Targeted SFP quantification relies on matrix assisted laser desorption ionization-time-of-flight mass spectrometry, which suffers from poor accuracy and high detection limits. Alternatively, total fluorine (TF)-based methods can be used, but these approaches report concentrations on a "fluorine equivalent" basis (e.g. F/m^2 in the case of textiles) and are incapable of elucidating structure/chain length, which is critical for predicting the identity and quantity of degradation products. Here a new method for comprehensive characterization of SFPs is presented, which makes use of the total oxidizable precursors assay for fingerprint-based structural elucidation, and combustion ion chromatography for TF quantification. When used in parallel, quantitative determination of SFPs (in units of mass of C_nF_{2n+1}/m^2 textile) is achieved. Expressing SFP concentrations in terms of mass of side-chain (as opposed to fluorine equivalents) facilitates estimation of both the structure and quantity of PFAA degradation products. As a proof-of-principle, the method was applied to six unknown SFP-coated medical textiles from Sweden. Four products contained C6-fluorotelomer-based SFPs (concentration range 36-188 mg C_6F_{13}/m^2), one contained a C4-sulfonamide-based SFP (718 mg C_4F_9/m^2), and one contained a C8-fluorotelomer-based SFP (249 mg C_8F_{17}/m^2).

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large and diverse group of mostly anthropogenic compounds that have been synthesized since the 1940s.[1] The unique properties of perfluoroalkyl chains, including combined lipophobicity and hydrophobicity, has led to the extensive use of PFAS in industrial and consumer applications.[2] However, the vast majority of PFAS are extremely persistent or degrade to highly persistent end products,[3] which has contributed to the near ubiquitous occurrence of PFAS in the environment, including in humans and wildlife.[4]

Several PFAS, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have already been added to the United Nations Stockholm Convention on Persistent Organic Pollutants[5] while others have been restricted in the European Union (i.e. C_9 - C_{14} perfluoroalkyl carboxylic acids)[6] or are under consideration for inclusion in the Stockholm Convention (i.e. perfluorohexane sulfonate; PFHxS).[7] However, novel, replacement PFAS continue to be produced, often with unknown hazards.[8] Several of these replacement PFAS, including perfluorobutane sulfonate (PFBS), perfluorohexanoic acid (PFHxA) and hexafluoropropylene oxide dimer acid (HFPO-DA; trade name GenX) have already been listed as substances of very high concern under REACH regulation,[9] and a restriction proposal for PFHxA is currently under consideration.

Polymeric PFAS comprise the largest share of PFAS on the global market.[2] These include fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers (SFPs).[1] SFPs can be based on either fluorotelomer- or perfluoroalkane sulfonyl fluoride-based chemistries, and are widely used as anti-wetting and anti-stain surface protecting agents in the carpet, textile and paper industry.[10] As a result, they can migrate and accumulate in the environment during a product's use or disposal phase where they may undergo degradation to ultimately form highly persistent perfluoroalkyl acids (PFAAs).[11,12] Early assessments have downplayed the role of SFP degradation as a contributor to historical PFAA emissions mainly due to reported millennia-scale degradation half-lives but also owing to critical data gaps regarding PFAS-related production, use and disposal.[13–15] However, in light of experimental studies suggesting much lower SFP degradation timescales of decades[16–19] there is renewed interest in the significance of SFP degradation as a potential PFAA source.

The rate of SFP degradation in the environment, and ultimately the contribution of SFPs to environmental PFAA levels remains highly uncertain.[20,21] Part of the challenge in characterizing SFPs is an absence of methods for quantifying these substances in consumer products. One approach developed by Rankin and Mabury[22] for quantification of SFPs utilized matrix assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry, but this technique is hampered by the use of highly persistent fluorinated solvents during sample preparation.[22] Moreover, MALDI-TOF is not as accurate as other analytical methods and suffers from poor detection limits.[22] Alternatively, total fluorine (TF)-based approaches have been applied to quantify fluorinated polymers.[11,23–27] These techniques are typically rapid, but do not provide structural information; consequently, concentrations can only be reported in terms of fluorine equivalents (i.e. mass of C_nF_{2n+1}/m^2 in the case of textiles), which hinders estimates of both the identity and quantity of PFAA-emission.

This paper presents a methodological framework for SFP determination in textiles. The approach uses the total oxidizable precursors (TOP) assay[28] for fingerprint-based structural elucidation, and TF measurements for quantification, which when used in conjunction produces concentrations in units of mass of C_nF_{2n+1}/m^2 textile. As a proof-of-principle, the method was applied to six unknown SFP-coated medical textiles from Sweden.

Experimental Methods

Standards and Reagents

A full list of standards and reagents is provided in this section and Table S1 of the Supporting Information (SI).

Textiles

Three polyamide (PA) textiles treated with C4-sulfonamide ($C_4F_9SO_2N$-; “FC4S”), 6:2-fluotoelomer ($C_6F_{13}CH_2CH_2$-; “FC6”), or 8:2 fluorotelomer ($C_8F_{17}CH_2CH_2$-; “FC8”) -based SFP coatings were used as reference materials for TOP-based fingerprinting. A fourth (uncoated) textile was used as a blank. Further details on preparation of these fabrics can be found elsewhere.[29] Briefly, an untreated (i.e. SFP-free) PA fabric (PA 6,6 made from hexamethylenediamine and adipic acid monomers each containing 6 carbons) with durable rip-stop pattern with 115 ± 5 g/m2 (60 ± 1 threads per cm warp and 33 ± 1 threads per cm weft) fabric surface density (FOV AB Sweden) was used for the in-house DWR pad-dry-cure finishing process[10] similar to industrial production processes. Waterborne SFP emulsions containing the different side-chain modifications for coating the textiles were supplied by major raw materials manufacturers.

In addition to the three reference textiles, 7 medical textiles were obtained from Stockholm Healthcare (Region Stockholm). These included 1 surgical drape (6A), 4 surgical gowns (12, 17A, 21 and R10), and 1 ambulance jacket (35A) all determined to contain an unknown fluoropolymer coating during initial screening experiments as well as a fluorine-free surgical drape (1A), which was used as a control. Further information on each textile is provided in Table S2 of the SI.

Total fluorine determination by combustion ion chromatography

TF determination represents the combined concentration of all fluorine-containing organic and inorganic substances. In the present work, TF measurements were performed directly on the textiles, and inorganic fluorine was assumed negligible relative to fluorine from SFPs (an assumption made by others as well[23]). TF determination was carried out using an AQF-2100H combustion unit (Mitsubishi) which was coupled to a Dionex™ ICS-2100 Integrion IC (Thermo Scientific). In brief, textile samples (0.3-0.8 mg each, depending on textile density) were cut using methanol pre-rinsed scissors, placed into a pre-baked ceramic sample boat and inserted into the combustion unit where it was heated gradually up to 1100 ^{o}C under an oxygen and argon flow. Combustion gases were absorbed in Milli-Q water, which was then injected into an ion exchange column (AS19 Dionex IonPac, Thermo Scientific), which was operated with a gradient elution program (Table S3). A linear calibration curve of NaF (5-point, 1-50 ppm, 1/x weighting was used to quantify the total amount of fluorine of textile samples. TF measurements using this approach have previously shown good comparability between labs.[25]

TOP Assay

The TOP assay[28] employs reactions with hydroxyl radicals generated by thermolysis of persulfate in basic solution to oxidize precursors to their related/terminal degradation PFAAs. Prior studies involving application of the TOP assay on textiles have utilized textile extracts[26,27,30,31] which will only oxidize low molecular weight residuals that are extractable from the fabric. To the best of our knowledge, no attempts have been made to elucidate the structure of SFPs based on their oxidation products; however, a recent study used a similar conceptual approach in order to reconstruct the main ingredients in aqueous film forming foams, using a combination of Bayesian inference, extractable organic fluorine, and the TOP assay.[32] Here we build on these initial studies by applying the TOP assay directly to SFP-treated textiles in order to account for non-extractable precursors (both non-polymeric and polymeric), and ultimately predict the structure of the SFP based on the pattern of oxidation products. Briefly, a 30 mg (2.7 cm^2) piece of textile was cut using methanol-rinsed scissors and placed in a 50 mL polypropylene (PP) tube together with Milli-Q water (30mL). Potassium persulfate (0.48g) and NaOH (0.456 mL of 10 N) were then added and the solution was vortexed and placed in the oven at 85 ^{o}C for 6 hours. Thereafter, the samples were allowed to cool and the pH was adjusted using concentrated HCl. Individual isotopically labeled internal standards (ISTDs; 4 ng each) were added and the samples were extracted by solid phase extraction (SPE). Oasis WAX SPE cartridges (6cc, 150 mg, 30 μm) were pre-conditioned with 0.1% NH_4OH in methanol (4mL), then methanol (4mL), then Milli-Q water (4mL). Samples were loaded at 1 drop per second, after which the cartridges were rinsed with Milli-Q water (4mL) and dried under vacuum. Targets were eluted into 13 mL PP tubes using 0.1% NH_4OH in methanol (8mL). The extract was concentrated to approximately 0.5 mL under nitrogen, then transferred to an Eppendorf tube where the recovery standard (RSTD) was added.

Extracts were stored at -4 ^{o}C until the day of analysis, where they were centrifuged and transferred into micro-vial for analysis by LC-MS/MS.

LC-MS/MS analysis

Details of target PFAS analysis are provided in the SI. Briefly, extracts were analyzed on a Waters ultra-performance liquid chromatograph (UPLC) equipped with a BEH C18 analytical column (2.1×50 mm, 1.7 µm particle size, Waters; see Table S4 for LC gradient) and coupled via an electrospray ionization source to a Xevo TQ-S triple quadrupole mass spectrometer (Waters). The mass spectrometer was operated in negative ion electrospray ionization selected reaction monitoring mode, with two precursor/product ion transitions monitored for most targets (Table S1).

Quality Control

Laboratory background contamination was monitored by including procedural blanks (30 mL Milli-Q water, n = 3) with every TOP assay batch. A triplicate control of textile in Milli-Q water without addition of oxidant was also performed with every TOP batch. Finally, to ensure the efficacy of the TOP assay when processing unknown textiles, we spiked samples of the non-fluorinated textile (1A) with 30 ng of individual PFAA-precursors (6:2 and 8:2 fluorotelomer sulfonates, both *n*=3). Results of these experiments are provided in Figure S1 of the supporting information. TF measurements were analyzed together with a certified reference material (BCR-461, fluorine in clay), which showed good agreement with reference values (average of n=3 replicates = 552±7.3[stdev] mg F/kg vs reference of 568±60 mg F/kg).

Data handling

Conversion between PFAS concentrations (C_{PFAS}; μg PFAS/m^2) and fluorine equivalent concentrations ($C_{\mathrm{F\_PFAS}}$; μg F /m^2) was achieved using Equation 1, where n_{F} is the number of fluorine atoms in the molecule, A_{F} is the atomic weight of fluorine (g/mol), and MW_{PFAS} is the molecular weight of the individual PFAS (g/mol).

$$\textbf{Equation 1. } C_{\mathrm{F\_PFAS}} = C_{\mathrm{PFAS}} \times n_{\mathrm{F}} \times A_{\mathrm{F}} / MW_{\mathrm{PFAS}}$$

Results and Discussion

Characterization of reference materials

TF concentrations were similar in all three reference materials (663, 554, and 592 mg F /m^2 textile for the FC4S, FC6, and FC8-coated textiles, respectively). Knowledge of the SFP structure enabled conversion of

TF concentrations to side-chain equivalents, resulting in values of 849 mg C_4F_9/m^2, 715 mg C_6F_{13}/m^2, and 768 mg C_8F_{17}/m^2 for the FC4S, FC6, and FC8-coated textiles, respectively. Presenting SFP concentrations as side-chain equivalents (e.g. mg C_4F_9/m^2 textile), as opposed to simply fluorine equivalents (i.e. mg F/m^2 textile) facilitates predictions of both the identity and quantity of PFAAs emitted from degradation of the SFP during a product's lifespan and disposal. However, because the structure of the SFP is usually unknown, TF concentrations alone cannot be used to predict the concentration of specific PFAAs emitted from these products. While we considered the possibility that extractable residuals might display fingerprint-like profiles (i.e. without requiring the TOP assay), existing data indicate that such profiles are often ambiguous,[33] a finding that was corroborated in the present study (see below). Moreover, modern products have been shown to contain lower residuals[31,34] which can hamper characterization, in particular considering potential confounders such as dust or sorption of PFAS from air. To address these problems, we hypothesized that application of the TOP assay to textiles coated with SFPs would reveal fingerprint-like profiles that could be used to identify the structure of the side-chain used in the coating. To test this hypothesis, we started by subjecting each of our reference materials to a modified version of the TOP assay, in which the oxidant is added directly to the textile, as opposed to textile extracts.

Application of the TOP assay directly to the FC4S-, FC6- and FC8-coated reference textiles revealed fingerprint-like PFAA profiles (Figure 1). The FC4S-coated textile produced almost exclusively perfluorobutanoic acid (PFBA; accounting for >90% of measured PFAS on a fluorine weight basis) and was the only reference material to produce PFBS following oxidation. While perfluoroalkyl sulfonamides typically form PFCAs post-oxidation,[28] a recent interlaboratory comparison reported that high concentrations of oxidant could favor base-catalyzed hydrolysis of sulfonamides, leading to formation of perfluoroalkyl sulfonates (PFSAs).[35] This was considered an advantage in the present work, because PFSA oxidation products are specific to sulfonamide-containing SFPs, which allows them to be further distinguished from telomer-based SFPs. In comparison, the PFAS profile from oxidation of the C6 fluorotelomer SFP was dominated by perfluoropentanoic acid (PFPeA; 63% of total PFAAs), followed by PFHxA, PFBA and perfluoroheptanoic acid (PFHpA) (18, 17 and 1.5%, respectively), while the C8 fluorotelomer SFP produced a much broader range of PFCAs (C4 to C14) of which PFHpA and PFOA were the most abundant products (27 and 18% of total PFAS yield, respectively). For both fluorotelomer-based SFPs, PFSAs were not observed following oxidation.

TF characterization pre- and post-TOP provided evidence of side-chain cleavage for the FC4S SFP ($p<0.05$; Figure 1), but statistically significant differences were not observed for C6 and C8 side-chains, indicating that TOP was, overall, inefficient at degrading the SFP to PFAAs. However, in all but the FC4 SFP, PFCA formation following TOP was greater when applying the assay directly to the textiles, compared to on extracts (see Figure S2 of the SI), indicating that the observed profiles were not simply a function of low molecular weight residuals. Overall, these results indicate that the TOP assay alone cannot be used for quantitative determination of SFPs without considerable improvements in efficiency of oxidation for SFPs. Nevertheless, for the purpose of qualitative identification of SFP-structure, the TOP assay successfully produced strong and highly specific profiles suitable for distinguishing SFPs from one another.

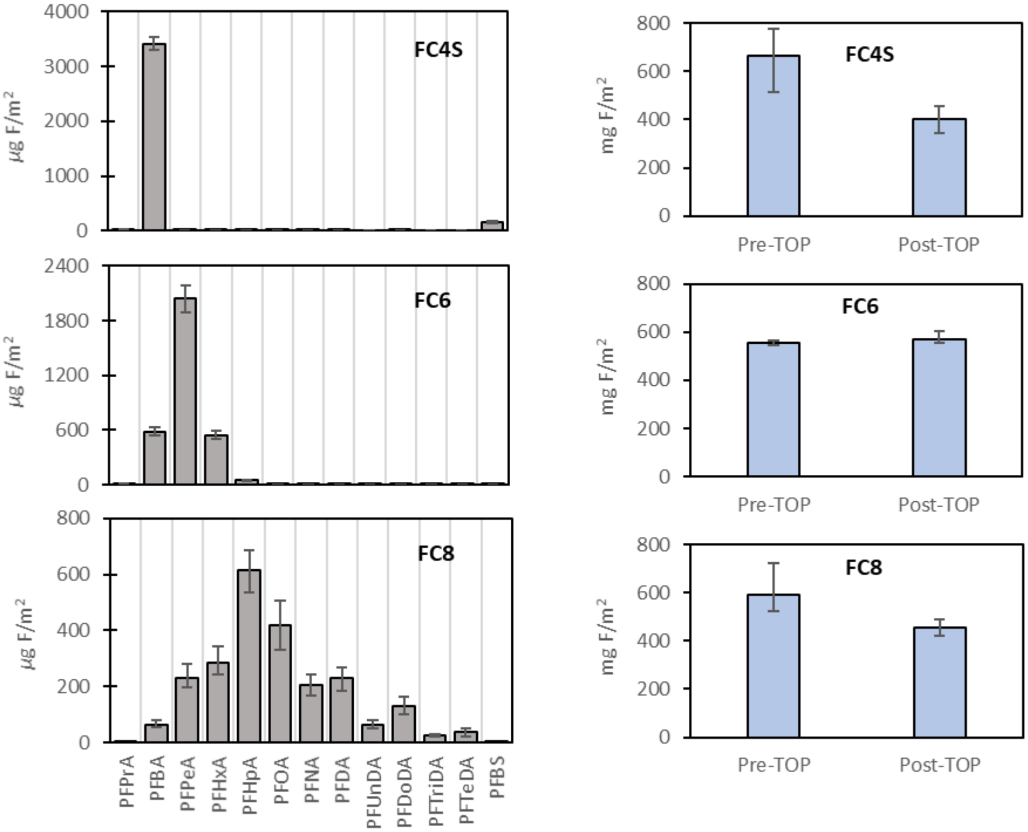


Figure 1. Profiles of detectable PFAAs in textile reference materials following TOP (left) and corresponding TF measurements (right) on reference materials performed before and after TOP. Error bar represents min and max values from n=3 replicates. Reference materials showed strong fingerprint-like profiles following TOP despite that most of the SFP appeared to remain intact, based on TF measurements before and after TOP.

Application of method to commercial textiles

Application of the TOP assay to the 6 unknown SFP-coated medical textiles produced a series of C4-C12 PFAAs, the profiles of which were easily matched by visual inspection to profiles produced by the 3 reference materials (Figure 2). In contrast, the fluorine-free surgical drape (1A) did not produce PFAAs following oxidation. Among the SFP-coated textiles, 6A, 12, 17A, and 21 exhibited PFAA profiles post-TOP which matched the FC6 reference textile, R10 matched the FC8 reference textile and 35A matched the FC4S reference textile (Figure 2). Moreover, the oxidation profile of 35A contained PFBS, consistent with the reference material and further confirming it as a sulfonamide-based SFP. In comparison to the

PFAA profiles generated by the TOP assay, an analysis of extractable residuals for each of the textiles displayed low and inconsistent profiles amongst the FC6 products (Figure S3), further highlighting the necessity of the TOP assay in order to elucidate SFP structure.

The fluorine-free surgical drape (1A) did not contain detectable levels of fluorine, while concentrations in the remaining products ranged from 28 mg F/m^2 (803 μg F/g, textile 21) to 560 mg F/m^2 (6560 μg F/g textile 35A) (Figure 2, Table S5), which is comparable to TF concentrations in other textiles.[23,26,27] Combining these concentrations with structures obtained from TOP-based fingerprinting produced concentrations of 36-188 mg C_6F_{13}/m^2 for samples 6A, 12, 17A, and 21, respectively, 249 mg C_8F_{17}/m^2 for sample R10, and 718 mg C_4F_{13}/m^2 for sample 35A. Assuming an arbitrary surface area of 2 m^2 for all products (a reasonable estimate for most products), and 100% conversion to their respective PFAA equivalents, the aforementioned SFPs could be expected to form 82-429 mg of PFHpA for products 6A, 12, 17A, and 21, 551 mg of perfluorononanoic acid (PFNA) for R10, and 1400 mg of PFBS. These quantities should be considered upper bound limits; in reality the yields are expected to be much lower than 100% and the products will include a suite of chain lengths, based on the mechanism of degradation. Nevertheless, this calculation clearly demonstrates the benefits of chain-length-based SFP concentrations as opposed to fluorine equivalents for estimating PFAA emissions from SFP-containing consumer products.

Advantages and limitations of the current methodology

To the best of our knowledge, this is the first time the TOP assay has been used together with TF measurements to both quantify and structurally elucidate SFPs in textiles. This method improves upon exclusively TF-based quantification methods by reporting concentrations in terms of side-chains (as opposed to fluorine equivalents), which improves predictions of PFAA degradation products. Future work should apply this methodology on a wider range of products (e.g. papers, carpets, etc) with known SFPs to further confirm the specificity of the PFAA oxidation profiles. The inefficiency of the TOP assay on the oxidation of SFPs is also a notable area for improvement, but since we relied on TF measurements for quantification, this is not considered a limitation of the current methodology. It is important to note that the recalcitrance of SFPs to the TOP assay observed here does not necessarily mean that SFPs will be stable in the environment, where both physical and chemical weathering will be relevant. Overall, the present work provides a first proof-of-principle for combined application of the TOP assay with TF measurements, for quantitative determination of SFPs in consumer products.

Acknowledgements

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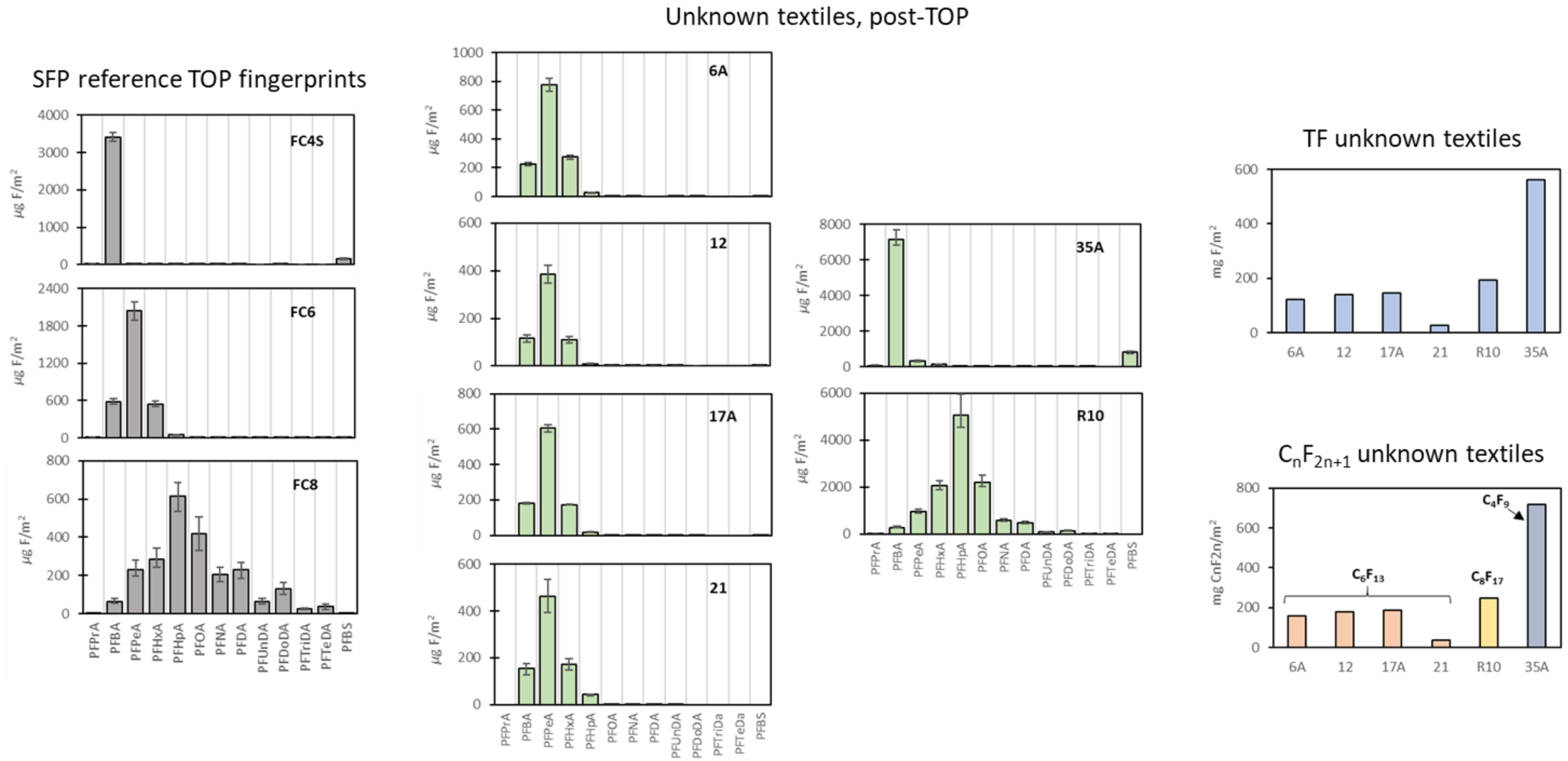

Figure 2. Fingerprint PFAA profiles following application of TOP to reference textiles (left) and unknown textiles (middle left and middle right). Top right shows TF levels before and after oxidation, and bottom right the resulting side-chain concentrations (converted from TF concentrations) after identifying the side-chain. Error bar represents min and max values from n=3 replicates.

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