Supporting Information for:

Another Pathway for Firefighter Exposure to Per- and Polyfluoroalkyl Substances: Firefighter Textiles

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MATERIALS AND METHODS

Sample Collection:

The samples collected ranged in manufacturing age between 2002 and 2017, and several unused (never-worn) samples were obtained from 2007, 2008 and 2017. The remainder were out-of-service (used) turnout gear from 2002 - 2014. In addition, 11 material swatches were obtained from textile manufacturers that represented new (in 2018) thermal liners used in the fabrication of turnout gear. After collection, active-duty PPE specialists with three different fire departments in California, Georgia and Indiana were able to assist with the identification of fabrics used in the donated samples. All materials were designated specialty fabrics produced from four of the major specialty textile manufacturers in the US: Gore (Newark, DE), Milliken and Company (Spartanburg, SC), TenCate Fabrics (Union City, GA), and Tyndale USA (Pipersville, PA).

PPE gear manufacturers sampled:	**# samples**
Globe Manufacturing (Pittsfield MA),	11
Lion Group (Dayton OH),	12
Honeywell First Responder (Dayton, OH),	2
Lakeland Fire (Decatur, AL)	2
Quest Fire Apparel (Saratoga Springs, NY)	1
Quaker Safety (Quakertown, PA)	2

Table S1. The type and number of turnout gear samples used in this study.

Total fluorine measurements:

Textile preparation was performed as in Ritter *et al.*[26] Briefly, each textile sample was cut into replicate targets for PIGE analysis using HPLC-grade methanol-washed scissors. Each textile target was cut to approximately 2 cm × 2 cm in size and mounted to a stainless-steel target frame with a 1 cm diameter hole in the middle. A beam of 4.0 MeV protons was extracted through a thin (8 μm) Kaptan® foil into air and was used to irradiate each replicate sample for approximately 180 seconds, with a beam intensity between 40 – 60 nA. Resultant gamma-rays were detected by a 20% High-Purity Germanium detector (Canberra) placed at approximately 70 degrees to the incident beam and less than 3 cm from the target. Replicate samples were measured from two to five locations on each textile. The dust sample was coarse-sieved (2-mm stainless steel mesh) to remove hair, leaves, food remnants and trash from the dust. The dust sample was put into thin-walled (0.002”) resealable bag (Uline) of approximately 2.5 cm × 2.5 cm and mounted on the same target frames for PIGE analysis. Total fluorine concentrations were obtained by using spectral data for the ^{19}F(p,pγ) reaction, which were analyzed by integrating the background-subtracted peaks at 110 keV and 197 keV, and the beam intensity was monitored periodically with a faraday cup measurement and normalized to on-target intensity by using the 770 keV background-subtracted peak from the ^{40}Ar(p,nγ) reaction in air for each run.

The minimum detection limits for total fluorine by PIGE in textiles were determined from external calibration curves created by coating textiles in a PFOA stock solution[26]. The accuracy of PIGE, as indicated by % recovery ± standard deviation, ranged from 98 ± 2−103 ± 3%. The precision of

PIGE for a set of replicate measurements shown in Table S4 as indicated by RSD, is ±5.4% with an MDL of 16.2 ppm F for these fabrics. While the analytical precision of measurements from the same target was 5.4%, the variation between spots close by each other from a single fabric ranged from 2% - 9.5% for the samples tested, as can be seen in Table S4. This indicates that there is additional variability of total fluorine on used materials beyond that of the measurement technique.

Total fluorine measurements by PIGE are impossible to quantify for textiles that exceeded 30% by weight of fluorine. The gamma-ray detector and acquisition system experiences more than 50% dead time on such samples, making quantification unreliable. This has only affected measurements on pure PFTE to date, but since the moisture barrier is comprised of a PFTE liner, total fluorine measurements of the moisture barriers were not valid and are excluded from the data presented here. Typical concentrations below 1% total fluorine were quantitative and reproducible.

Textile Extractions:

To further screen for the degradation of PFAS from the turnout gear, selected samples were subject to two types of extraction protocols: a base-assisted extraction and a methanol extraction. The base extraction was performed by placing approximately 250 mg of textile or dust sample into a 15 mL conical HDPE tube (VWR) and sonicating overnight with approximately 10 mL of 2.0 M NaOH solution. This solution was filtered through a HPLC-grade-methanol-washed qualitative filter (Whatman) to remove solids and sent for commercial LC-MS/MS analysis in a clean, parafilmed conical HDPE tube. The Australian samples were extracted similarly, except that 0.1 M ammonia was used. The methanol extractions were also performed by placing approximately 250 mg of dust sample into a 15 mL conical HDPE tube, and sonicating overnight with approximately 10 mL of HPLC-grade methanol. This solution was similarly filtered and sent for commercial LC-MS/MS analysis. All solvents used were tested in advance to be fluorine-free by solid-phase extraction (Waters WAX cartridges) and subsequent PIGE analysis. Undoubtedly, some PFAS were lost to the filtration step in these procedures, but significant quantities were recovered in the extractant in all cases, and the separation of solids from the extractant was essential for the subsequent LC-MS/MS analysis.

LC-MS/MS Analysis:

Selected sample extractions were sent for LC-MS/MS analysis at a certified testing laboratory (Vista Analytical). 24 common PFAS analytes were measured and calibrated against standards purchased mainly from Wellington and some from CIL. All standard solutions, isotope dilution standards and spike recovery solutions were formulated at Vista Analytical. Isotope dilution was used for the quantification of 19 of the 24 native compounds. A complete list of LC-MS/MS analytes is included in Table S2, and those with isotope dilution quantification have the specific species listed. Sample clean-up was performed using a weak-anion SPE cartridge. Separation is on an iClass Acquity UPLC using a Waters BEH C18 1.7um column. This is paired with a Waters TQS-micro MS system in negative-ESI mode with sMRM acquisition. Two MRMs are monitored for each unknown with a minimum of 14 scans per peak. Data are processed with TargetLynx XS software. Calibration ranges are typically from 0.5 ng/g – 500 ng/g and process blanks were analyzed for each matrix, and 10 ng/g spike recovery measurement was performed for each analyte every eight samples.

Analyte (isotope label)	**MDL (ng/g)**	**Analyte (isotope label)**	**MDL (ng/g)**
PFBA (^{13}C3-PFBA)	1.29	PFPeS	4.52
PFPeA (^{13}C3-PFPeA)	1.86	PFHxS (^{18}O2-PFHxS)	2.86
PFHxA (^{13}C2-PFHxA)	1.87	PFHpS	1.57
PFHpA (^{13}C4-PFHpA)	1.89	PFOS (^{13}C8-PFOS)	7.79
PFOA (^{13}C2-PFOA)	2.18	PFNS	13.2
PFNA (^{13}C5-PFNA)	1.64	PFDS	1.85
PFDA (^{13}C2-PFDA)	2.36	4:2 FTS (^{13}C2-4:2 FTS)	4.55
PFUnA (^{13}C2-PFUnA)	3.26	6:2 FTS (^{13}C2-6:2 FTS)	2.11
PFDoA (^{13}C2-PFDoA)	2.54	8:2 FTS (^{13}C2-8:2 FTS)	2.63
PFTrDA	1.12	PFOSA (^{13}C8-PFOSA)	2.09
PFTeDA (^{13}C2-PFTeDA)	1.82	MeFOSAA (d3-MeFOSAA)	2.78
PFBS (^{13}C3-PFBS)	3.35	EtFOSAA (d5-EtFOSAA)	2.96

Table S2: The specific 24 PFAS analytes measured in this study. The 19 that include stable isotope dilution standards have the labeled species listed in parentheses. The minimum detection limit (MDL) is listed in ng/g for each analyte.

TOP assay:

The three Australian samples were also tested by the Total Oxidizable Precursor Assay (TOPA)[31] to provide a different assessment of total fluorine. In this analysis the pre-TOPA results were from textiles that were extracted with 0.1 M ammonia in methanol, and a portion of the same extract was then carefully evaporated and reconstituted in the alkali persulphate media prior to digestion (TOPA). The digestate was then analyzed for PFAS as described above and named as “post-TOPA”

RESULTS AND DISCUSSION

All the individual PIGE measurements for the thermal liners and the outer shells used in table 1 are listed in Tables S2 and S3 below. There is roughly a thousand-fold more fluorine in the moisture barrier and the outer shell than used thermal liners, so only negligible fluorine is lost presumably between the moisture barrier and the thermal liner – yet it results in a significant source of PFAS in the thermal liner at the ppm level.

Thermal liner - Exterior (facing MB and Outer Shell)					
Sample	**ppm F**	**error**	**Sample**	**ppm F**	**error**
new1-B	66	10	Used1-A	121	14
new1-C	45	8	Used1-B	210	18
new2-A	251	21	Used1-C	177	17
new2-C	151	15	Used1-E	95	12
new2-E	152	15	Used1-N	157	16
new2-N	109	13	Used2-G	178	17
new2-B	77	11	Used2-K	157	16
new3-E	87	15	Used2-L	115	14
new4-B	120	14	Used3-B	97	12
new4-G	170	16			
new4-K	141	15			
new4-L	91	12			
new5-B	50	10			
new5-G	107	20			
new5-L	72	14			
new5-K	108	20			
new6-B	52	8			
new6-B2	47	8			

Thermal liner - Interior (facing skin)					
Sample	**ppm F**	**error**	**Sample**	**ppm F**	**error**
new1-B	20	7	Used1-A	139	15
new1-C	27	7	Used1-B	130	14
new2-A	58	10	Used1-C	57	11
new2-C	66	11	Used1-E	25	9
new2-E	62	10	Used1-N	43	10
new2-B	39	9	Used1-W	95	13
new3-E	62	12	Used2-G	58	11
new4-G	105	13	Used2-K	45	10
new4-K	67	11	Used2-L	89	13
new4-L	71	11	Used3-B	43	8
new5-B	41	8			
new5-G	45	9			
new5-L	42	8			
new5-K	50	9			
new6-B	18	6			
new6-B2	31	7			

Table S3: The individual PIGE measurements (converted to ppm) for the thermal liner averages used in table 1.

Outer layer					
Sample	**ppm F**	**error**	**Sample**	**ppm F**	**error**
new1-B	21049	1287	used1-B	15797	955
new1-G	23232	1428	used1-G	13821	780
new1-K	29900	1895	used1-K	14882	837
new1-L	29518	1840	used1-L	22816	1308
new2-A	15085	929	used1-A	12818	723
new2-B	21652	1362	used1-B	16379	924
new2-C	16758	1029	used1-C	15950	904
new2-E	17179	1050	used1-E	20910	1182
new2-N	20613	1278	used1-N	11040	618
new2-W	20002	1228	used1-W	12437	701

Table S4: The individual PIGE measurements (converted to ppm) for the outer shell averages used in table 1.

These data represent an average of many sets of turnout gear, and for a subset of 4 samples where we have identified the same brand and same textile used, we did 6 replicate measurements of each garment's outer shell. The degradation of the outer shell is broken down by years since manufacture in Figure S1 and the data are provided in Table S4. Although some of the gear was older than 12 years, none of textiles used in service for longer than 10 years, which may explain why the loss of fluorine ceases for the oldest samples. Again, even for matched brand samples at different ages, statistically significant total fluorine is lost from the garment.

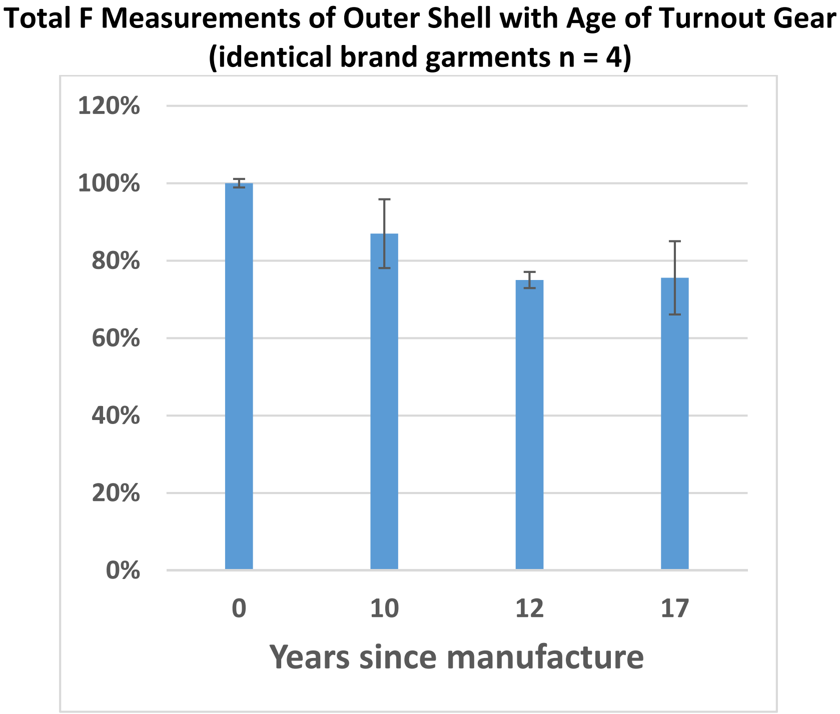

Figure S1: Total fluorine on the surface of the outer layer goes down significantly with age of gear. There is discoloration and wear with age as well. We do not have a record of sunlight exposure, nor wash history. The error bars represent one standard deviation of the ~6 measurements per sample. The statistical significance of reduction between 0 – 10 years is *t*(9)=4.12 *p*=0.001, and between 10 and 12 years is *t*(9)=3.74 *p*=0.002, while there is no statistically significant difference between the samples that were 12 and 17 years past manufacture: *t*(10)=0.19 *p*=0.43). It is important to note that most gear is only in service for <10 years before routine replacement, but significant quantities of fluorine are lost from the outer shell during this time.

Sample	ppm F	error	Sample	ppm F	error
New - rep 1	7251	391	Used - 2006 rep 1	5341	289
New - rep 2	7322	396	Used - 2006 rep 2	5614	303
New - rep 3	7203	388	Used - 2006 rep 3	5468	296
New - rep 4	7148	386	Used - 2006 rep 4	5322	288
New - rep 5	7245	390	Used - 2006 rep 5	5338	290
New - rep 6	7101	383	Used - 2006 rep 6	5375	292
Used - 2008 rep 1	6918	374	Used - 2001 rep 1	5654	305
Used - 2008 rep 2	6367	342	Used - 2001 rep 2	4634	251
Used - 2008 rep 3	6212	334	Used - 2001 rep 3	5765	311
Used - 2008 rep 4	6477	350	Used - 2001 rep 4	5672	306
Used - 2008 rep 5	5393	292	Used - 2001 rep 5	5975	323
			Used - 2001 rep 6	5000	270

Table S4: The individual PIGE measurements for the data presented in Figure S1. These errors are the statistical errors of the measurements. In some cases the variation between replicate pieces of the textile varied significantly more than the measurement precision, so the standard deviation of the measurements is used in Figure S1 to represent the error bars.

Also, different areas of the garments that experience high wear are shown to lose fluorine at a higher rate, as are the exterior layers of the outer layer (exposed to sunlight and water) compared to the inner layers. The degradation of the outer shell seems to significantly increase with age of the garment, while the presence of a significant fluorine signature in the thermal liners of unused turnout gear suggests that the PFAS shed from the moisture barrier has already largely occurred by the time the garment has been manufactured, although degradation continues with time.

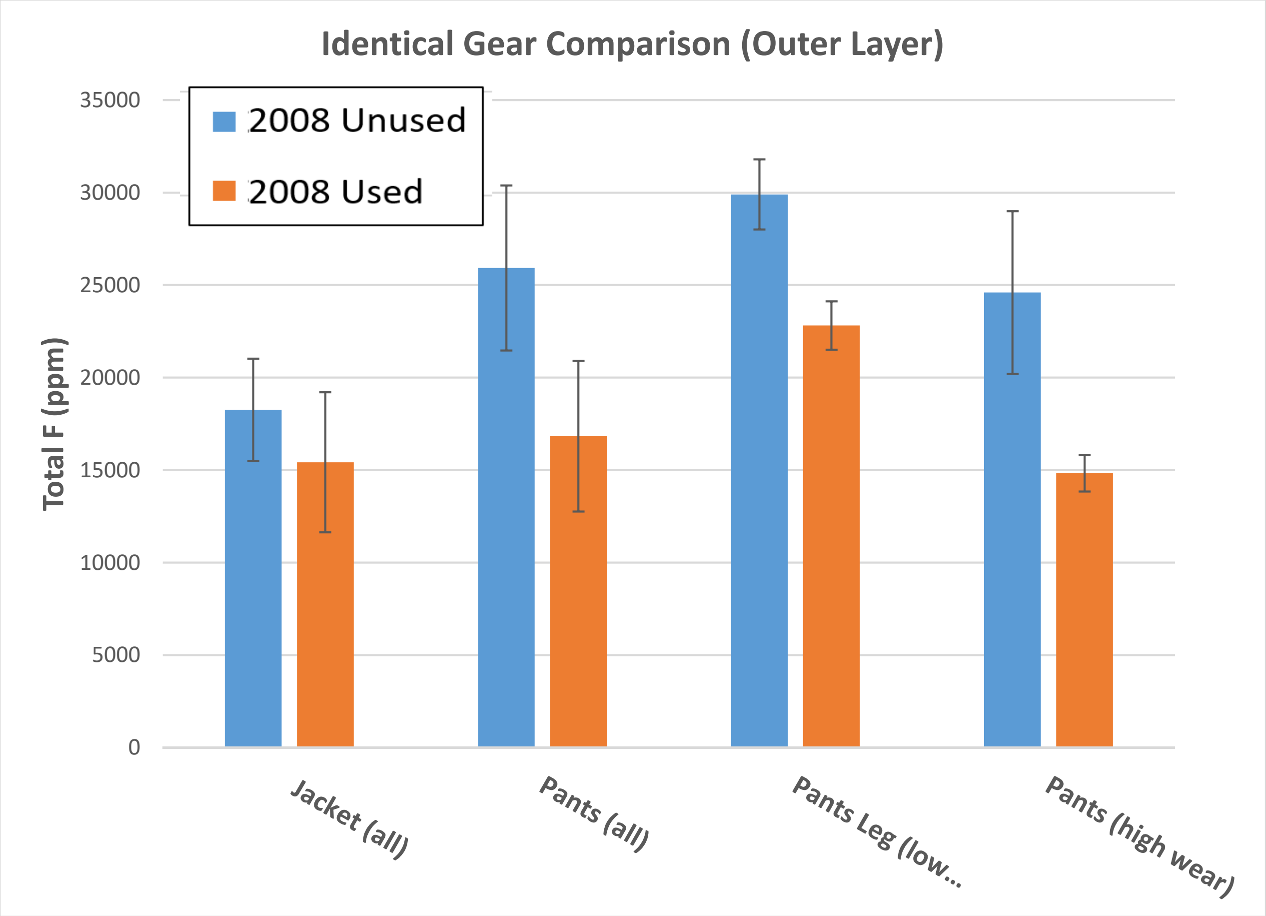

Figure S2: For one set of gear, identical garments were found used and unused from the same date of manufacture (2008) from the same manufacturer, from the same textile. Different areas of the garments with obviously different amounts of wear were observed to have different amounts of total fluorine. The error bars on the plot represent the standard deviation of the measurements.

One set was still in original packaging, other was taken out of service after 10 years of service in a major metropolitan FD. In each case the used gear was lower in total fluorine on the surface of the outer layer. While the jacket showed no statistically significant dependence on location sampled, the pants showed more wear on the groin, seat and knee sampling locations (high wear locations) and the total fluorine loss was higher in these areas than the location in mid-calf (pants leg location).

The comparison of a base extraction vs methanolic extraction for the dust collected at a representative fire department PPE handling facility is shown in table S5.

values in ppb	PPE facility Base extraction	PPE facility Methanol extraction
PFBA	94	80
PFPeA	41	45
PFHxA	44	40
PFHpA	17	26
PFOA	31	50
PFNA	7	18
PFDA	<MDL	25
PFUnA	<MDL	17
PFDoA	<MDL	10
PFBS	3110	13
PFPeS	<MDL	<MDL
PFHxS	<MDL	<MDL
PFOS	<MDL	26
6:2 FTS	25	34
8:2 FTS	<MDL	23
n-Et-FOSAA	<MDL	10

Table S5: The average PFAS concentrations (in ppb) found in a fire department PPE handling facility by LC-MS/MS analysis, extracted by the same base extraction used for textiles and a pure methanolic extraction designed to keep the fluoroamidosulfonates intact.

The raw data from the LC-MS/MS analysis of Vista Labs are shown in Table S6 in ng/g (ppb). Even when multiplied by their stoichiometric ratios of fluorine atoms per molecule and summed represent only about 1% of the total fluorine measurements found by PIGE, consistent with previous measurements of textiles[28]. Despite the exquisite sensitivity and specificity of LC-MS/MS, the abundance of PFAS found in environmental samples are limited by the analytes in the library of calibrated standards. There are literally 100-fold more PFAS present in the material that represent pre-cursor material, polymeric fluorine that remains in the gear, unidentified congeners, and intermediate oxidation products that are not identified nor captured in routine LC-MS/MS analysis.

Analyte	**Thermal Layer 2008 (New)**	**Thermal Layer 2014 (Used)**	**Moisture Barrier 2008 (New)**	**Moisture Barrier 2008 (Used)**	**Moisture Barrier 2014 (Used)**	**Moisture Barrier 2017 (New)**	**Outer Shell 2008 (New)**	**Outer Shell 2014 (Used)**
PFBA	<MDL	139	12.8	20.5	615	991	10.6	21.5
PFPeA	<MDL	228	12.6	18.1	104	2.49	17.8	164
PFHxA	<MDL	199	30.5	35.8	28.6	36.9	36.9	10.9
PFHpA	<MDL	105	12.4	14.3	5.82	25.4	25.4	2.23
PFOA	77.7	850	45.9	36.6	71.4	<MDL	182	97.3
PFNA	2.63	25.3	<MDL	2.76	1.95	<MDL	8.2	<MDL
PFDA	2.98	133	6.51	23.7	<MDL	<MDL	5.51	<MDL
PFUnA	<MDL	7.96	<MDL	2.51	<MDL	<MDL	<MDL	<MDL
PFDoA	<MDL	68.6	5.01	25.9	<MDL	<MDL	<MDL	<MDL
PFTrDA	<MDL	2.16	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFTeDA	<MDL	<MDL	24.3	<MDL	<MDL	<MDL	<MDL	<MDL
PFBS	283	53400	140	230	47900	90400	142	1050
PFPeS	<MDL	4.75	<MDL	<MDL	62	4.13	<MDL	<MDL
PFHxS	<MDL	7.58	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFOS	<MDL	6.93	<MDL	2.05	<MDL	<MDL	<MDL	<MDL
6:2 FTS	<MDL	25.9	<MDL	<MDL	12.9	<MDL	<MDL	<MDL
8:2 FTS	<MDL	11.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Table S6: The specific PFAS concentrations (in ppb) found in select firefighter textiles by LC-MS/MS analysis, following a base extraction. Only analytes with values above MDL are shown. The isotope-labeled spike recovery for all PFAS was in the range of 80 – 120% for all samples and analytes. The sample blanks were <MDL for all analytes.

The raw data from the LC-MS/MS analysis of EnviroLab (Australia) are shown in Table S7, shown for samples before and after TOPA in ng/g (ppb). The was significantly more PFAS observed post-TOPA than the targeted LC-MS/MS analytes on all layers. This supports the premise of additional PFAS precursors being present in the extracts from the gear.

Analyte	Thermal liner 2012 (used)	Thermal liner 2012 (used)	Moisture barrier 2012 (used)	Moisture barrier 2012 (used)	Outer shell 2012 (used)	Outer shell 2012 (used)
	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA
PFBA	<MDL	1100	<MDL	2000	<MDL	1860
PFPeA	<MDL	8	<MDL	560	6	23
PFHxA	<MDL	8	6	680	18	36
PFHpA	<MDL	11	6	1200	7	15
PFOA	<MDL	37	64	1300	24	38
PFNA	<MDL	10	8	690	<MDL	<MDL
PFDA	<MDL	10	45	440	<MDL	<MDL
PFUnA	<MDL	5	<MDL	80	<MDL	<MDL
PFDoA	<MDL	<MDL	14	56	<MDL	<MDL
PFBS	270	330	260	370	1200	1800
PFOS	6	7	96	99	6	8
Analyte	Thermal liner 2009 (used)	Thermal liner 2009 (used)	Moisture barrier 2009 (used)	Moisture barrier 2009 (used)	Outer shell 2009 (used)	Outer shell 2009 (used)
	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA
PFBA	<MDL	2500	<MDL	4000	<MDL	4490
PFPeA	<MDL	12	<MDL	54	11	35
PFHxA	<MDL	5	11	34	21	45
PFHpA	<MDL	6	8	42	10	22
PFOA	<MDL	16	22	48	42	60
PFNA	<MDL	4	<MDL	10	<MDL	3
PFDA	<MDL	3	<MDL	8	<MDL	<MDL
PFUnA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFDoA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFBS	1900	2400	5700	7600	2800	3900
PFOS	4	4	7	6	7	7
Analyte	Thermal liner 2005 (used)	Thermal liner 2005 (used)	Moisture barrier 2005 (used)	Moisture barrier 2005 (used)	Outer shell 2005 (used)	Outer shell 2005 (used)
	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA	Pre-TOPA	Post-TOPA
PFBA	<MDL	1500	<MDL	1600	<MDL	854
PFPeA	<MDL	8	<MDL	96	8	27
PFHxA	<MDL	5	7	94	18	40
PFHpA	<MDL	9	6	200	19	39
PFOA	3	17	45	180	190	237
PFNA	<MDL	<MDL	<MDL	35	7	13
PFDA	<MDL	<MDL	7	33	8	12
PFUnA	<MDL	<MDL	<MDL	4	<MDL	<MDL
PFDoA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFBS	620	1100	425	622	100	186
PFOS	11	12	17	19	9	11

Table S7: The specific PFAS concentrations (in ppb) found in select firefighter textiles by LC-MS/MS analysis, before and after a total oxidizable precursor assay (TOPA). Only analytes with values above MDL are shown. The isotope-labeled spike recovery for all PFAS was in the range of 98 – 108% for all samples and analytes. The sample blanks were < MDL for all analytes.

During the measurements made for this study, an additional feature was observed using PIGE to screen the hands of the laboratory workers engaged in measuring the textiles. On three separate days, for five separate textile outer shells, a new nitrile glove was measured to have no significant fluorine content. Then the same glove was put on a laboratory worker who rubbed it intentionally several times across the outer shell being studied. Two of the garments were unused turnout gear, and three of the garments were used turnout gear. The glove was then remeasured immediately by PIGE and in three of the five cases, a measurable transfer of more than 50 ppm total F to the gloved hand was observed. These data are shown in table S8. Obviously, the data are just suggestive at this point with an undeveloped rigorous method, but this observation strongly supports the premise that side-chain fluoropolymers and the PFAS they bind do release to the environment upon wear. A full study will be performed to confirm this observation.

Manual transfer study	Before rubbing		After rubbing	
	ppm F	error	ppm F	error
Used outer layer 1	0	5	18	6
New outer layer 2	1	5	75	5
Used outer layer 3	3	5	10	6
New outer layer 4	9	8	127	12
Used outer layer 5	11	6	64	9

Table S8: The total fluorine concentrations (in ppm) found on nitrile gloves before and after handling five different outer shell samples. The MDL for PIGE is 16 ppm, so only three measurements yielded statistically significant manual transfer of fluorine from garment to hand.