Closing the Mass Balance on Fluorine on Papers and Textiles

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Experimental

Reagents

For LC-MS/MS analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (regent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Sodium hydroxide (98%, reagent grade), ethyl acetate (99.9%, reagent grade), potassium persulfate (>99%, ACS reagent), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH). For GC-MS analysis Ethyl acetate (HLPC grade) was purchased from EMD Millipore Corp (Bilerica, MA).

Volatile Analysis by GC-MS

Instrumental Analysis

Extracts were analyzed for volatile PFASs using positive chemical ionization mode gas chromatography mass spectrometry (GC-MS) operated in single ion monitoring mode (SIM), with SIM ions given in Table S1. The calibration range for all analytes was from 10-200 ng. Analytes were separated using a DB-WAX column (30 m x 0.250 mm, 0.25 µm film thickness, Agilent, Santa Clara, CA). The carrier gas was helium and the injection volume was 2 µl. The initial oven temperature was 60 ^{o}C, held 1 min, increased at 5 ^{o}C/min to 75 ^{o}C, increased at 10 ^{o}C/min to 130 ^{o}C, and then 50 ^{o}C/min to 240 ^{o}C. Analyte responses were normalized to internal standards as indicated in Table S1. If values were outside of the calibration range further dilutions were performed and the extract was re-analyzed.

Whole method performance for volatile PFASs by GC-MS

Spike and recovery experiments were conducted using a 2x2 cm^2 of "pre-cleaned" cotton twill fabric that served as a surrogate matrix. The cotton twill fabric was pre-cleaned with 1:1 hexane:acetone using a Soxhlet overnight and then air dried in a fume hood. The sample was then spiked with 20 ng (n=3) to give an equivalent of 50 $\mu g/m^2$ of each analyte (6:2, 8:2, 10:2 FTOH and N-EtFOSE) or 120 ng (n=3) to give an equivalent of 300 $\mu g/m^2$ of each analyte and allowed to dry for 10 min. Isotopically-labeled internal standards were added and each sample was then extracted as described in the main manuscript. Accuracy, determined by % recovery, was calculated by dividing the concentration analytically determined after extraction by the expected (spiked) concentration for each analyte and then multiplying by 100. Precision was determined by an n=5 analysis at a 120 ng using the spiking and extraction procedures described above. The instrumental limit of detection (LOD) was determined to be three times the standard error of the calibration curve slope and the limit of quantification (LOQ) was determined as ten times the standard error of the slope of the calibration curve.[1] Each batch of samples contained three solvent blanks that consisted of solvent and isotopically-labeled standards spiked in pre-cleaned glass vials containing no sample matrix. Separate spike and recovery experiments were not performed for papers, but the performance parameters of the method were assumed to apply equally to both papers and textiles.

Ionic PFASs by LC-MS/MS

Extraction efficiency of Individual Ionic PFASs- An experiment was done to determine the number of necessary extraction cycles to remove >90% of methanol extractable mass of individual PFASs similar to van der Veen et al..[2] A single representative paper and textile was selected based on the presence of the greatest range of individual PFASs present. Two replicates of each paper and textile were cut from the sample (0.3±0.01g) and placed in 15mL centrifuge tubes. One of the two was spiked with 0.72 ng of all isotopically-labeled standards and allowed to dry, the other was not spiked. Both sets were then extracted in methanol as described above, but four individual rounds of extraction were performed. Rather than collecting all supernatant in one centrifuge tube, each round of extraction was collected individually. For the samples with mass labeled internal standards added before extraction, each round of extraction was diluted 1:5 in methanol and analyzed. For samples without isotopically-labelled standard present, each round of extraction was diluted 1:5, 0.72 ng of mass isotopically-labeled standard was added, and then analyzed.

Preliminary experiments performed on the extracts of select papers and textiles (e.g. Textile 9) were performed under the same liquid chromatography-quadrupole time of flight instrumentation and parameters described in Barzen-Hanson et al.,[3] but with a 4.6x50mm Zorbax Eclipse Plus C18 (Santa Clara, CA, Agilent) guard column attached to the same Zorbax Eclipse Plus C18 (Agilent). The same XIC list described in Barzen-Hanson et al. was used[3] and positive controls (i.e. PFOA known to be present by LC-MS/MS analysis) were identified. However, no obvious groups of unknown perfluorinated substances were identified. It was therefore outside of the scope of this paper to identify unknown precursors.

TOP Assay by LC-MS/MS

The recovery of individual polyfluorinated precursors (no paper or textile present) was determined by adding 2.4 ng each of seven oxidizable polyfluorinated precursors (57-74 nmol F to give 2,000ng/L) in into seven separate 1.2mL autosampler vials, each containing 60 µL of methanol. The methanol was then blown to dryness, after which 3 mL of the TOP assay reaction solution was added and the reaction was carried out as described in the main manuscript.

The second recovery experiments consisted of spiking 4 replicates of a blank paper (Paper 2) to give an equivalent of 8.3 ng/g (Σ68 nmol F) of each Qn and Sq analytes. The spike was allowed to dry for 48 hr, after which the vials were extracted with methanol as described above. The resulting extract was blown to dryness, reacted, spiked with internal standards, and reacted as described above. All extracts created for the recovery experiments were analyzed for PFCAs by LC-MS/MS as described above.

Concentrations of PFCAs formed after oxidation were converted to nmol F. Recovery was determined by dividing the summed nmol F formed after oxidation by the nmol F of each polyfluorinated precursor added prior to oxidation. Precision, described as % RSD, was computed from replicates (n=4) from the mixture recovery experiment.

Total Fluorine by PIGE-

The accuracy, represented as % recovery, about the total fluorine measured by PIGE was determined from existing data in Ritter et al..[4] A calibration curve with the equation seen below used to determine the concentration of three individual fluorinated standards. The standards were spiked onto the same paper matrix used to develop the calibration curve at 515nmol F/cm^2. Recovery was determined by dividing the concentration of the individual standards by the expected concentration.

$$\frac{nmol\ F}{cm^2} = 0.172\left(\frac{counts}{\mu C}\right) - 5.58$$

Results and Discussion

Ionic Individual PFASs –

Methanol was selected as the extraction solvent based on preliminary experiments, and on literature precedent.[2,5-13] Preliminary experiments indicated that the ratio of 0.3± 0.01g to 3.33mL methanol per round of extraction produced the lowest RSD across all analyte classes of interest for both papers and textiles (Table S4).

The extraction efficiency was consistent in comparison to experiments performed by van der Veen et al. and Zabaleta et al., 2016.[2,14] The extraction profiles (% mass of individual PFAS recovered in each extraction/total mass) were similar, indicating that spiked and PFASs associated with the material exhibit similar extraction behavior. Three rounds of extraction removed >90% of ionic PFASs, and were applied to all subsequent analysis and data collection. TOP assay extraction efficiency experiments were not performed because TOP assay was run on the extract resulting from the methanolic extraction, and it was assumed unknown precursors behaved somewhat similarly to known precursors (i.e. diPAPs) and would also be extracted to >90% efficiency.

PIGE-

Tables and Figures

Table S1. GC-MS target analyte full name, acronym, SIM ions (quantification ion is underlined), internal standard, and data quality tier.

Full Name	Acronym	SIM	Internal Standard	Data Quality*
6:2 fluorotelomer alcohol	6:2 FTOH	365, 327	$^{2}H_2$-,$^{13}C_2$-6:2 FTOH	Qn
8:2 fluorotelomer alcohol	8:2 FTOH	465, 427	$^{2}H_2$-,$^{13}C_2$-8:2 FTOH	Qn
10:2 fluorotelomer alcohol	10:2 FTOH	565, 527	$^{2}H_2$-,$^{13}C_2$-8:2 FTOH	Qn
N-ethyl perfluorooctane sulfonamidoethanol	N-EtFOSE	554, 572	$^{9}H_2$-N-EtFOSE	Qn

*Data quality follows the same criteria as established in the ionic PFASs section.

Individual Ionic PFASs by LC-MS/MS

Table S2. LC-MS/MS target analyte full name, acronym, acquisition masses and parameters, internal standard, calibration reference, and data quality.

Analyte	Acronym	PI* (m/z)	CV* (V)	FI-1* (m/z)	CE* (eV)	FI-2* (m/z)	CE* (eV)	Internal Standard	Calibration Reference	Data Quality*
Perfluorobutanoic acid	PFBA	213	20	169	8	n/a	n/a	[$^{13}C_4$]PFBA	PFBA	Qn
Perfluoropentanoic acid	PFPeA	263	20	219	8	n/a	n/a	[$^{13}C_3$]PFPeA	PFPeA	Qn
Perfluorohexanoic acid	PFHxA	313	20	269	8	119	22	[$^{13}C_2$]PFHxA	PFHxA	Qn
Perfluoroheptanoic acid	PFHpA	363	20	319	8	169	14	[$^{13}C_4$]PFOA	PFHpA	Ql
Perfluorooctanoic acid	PFOA	413	20	369	8	169	18	[$^{13}C_4$]PFOA	PFOA	Qn
Perfluorononaoic acid	PFNA	463	22	419	8	169	18	[$^{13}C_5$]PFNA	PFNA	Qn
Perfluorodecanoic acid	PFDA	513	22	469	10	269	18	[$^{13}C_2$]PFDA	PFDA	Qn
Perfluoroundecanoic acid	PFUnDA	563	22	519	10	169	22	[$^{13}C_2$]PFUnDA	PFUnDA	Qn
Perfluorododecanoic acid	PFDoDA	613	22	569	10	169	24	[$^{13}C_2$]PFDoDA	PFDoDA	Qn
Perfluorortridecanoic acid	PFTriDA	663	24	619	12	169	26	[$^{13}C_2$]PFDoDA	PFTriDA	Ql
Perfluorotetradecanoic acid	PFTeDA	713	24	669	12	169	26	[$^{13}C_2$]PFDoDA	PFTeDA	Ql
Perfluoropentadecanoic acid	PFPeDA	763	25	719	12	169	28	[$^{13}C_2$]PFDoDA	PFTeDA	Ql
Perfluorohexadecanoic acid	PFHxDA	813	25	769	12	169	30	[$^{13}C_2$]PFDoDA	PFHxDA	Ql
Perfluoroheptadecanoic acid	PFHpDA	863	25	819	13	169	30	[$^{13}C_2$]PFDoDA	PFHxDA	Ql
Perfluorooctadecanoic acid	PFOcDA	913	25	869	15	169	30	[$^{13}C_2$]PFDoDA	PFOcDA	Ql
2-perfluorobutylethanoic acid	FBEA	277	20	63	7	193	23	[$^{13}C_2$]FHEA	FHEA	Ql
2-perfluorohexylethanoic acid	FHEA	377	20	293	22	63	7	[$^{13}C_2$]FHEA	FHEA	Qn
2-perfluorooctylethanoic acid	FOEA	477	20	393	20	63	10	[$^{13}C_2$]FOEA	FOEA	Qn
2-perfluorodecylethanoic acid	FDEA	577	20	493	18	63	10	[$^{13}C_2$]FDEA	FDEA	Qn
2H-perfluoro-2-hexenoic acid	FBUEA	257	19	193	16	143	33	[$^{13}C_2$]FHUEA	FHUEA	Ql
2H-perfluoro-2-octenoic acid	FHUEA	357	18	293	17	243	34	[$^{13}C_2$]FHUEA	FHUEA	Qn
2H-perfluoro-2-decenoic acid	FOUEA	457	22	393	17	343	36	[$^{13}C_2$]FOEA	FOUEA	Qn
2H-perfluoro-2-dodecenoic acid	FDUEA	557	24	493	17	443	38	[$^{13}C_2$]FDEA	FOUEA	Ql
3-Perfluoropropyl propanoic acid *(3:3)*	FPrPA	241	19	177	7	117	24	[$^{13}C_2$]FHEA	FPrPA	Ql
3-Perfluoropentyl propanoic acid *(5:3)*	FPePA	341	19	237	14	217	24	[$^{13}C_2$]FHUEA	FPePA	Ql

3-Perfluoroheptyl propanoic acid *(7:3)*	FHpPA	441	19	337	13	317	23	[$^{13}C_2$]FOEA	FHpPA	Ql
3-Perfluorononyl propanoic acid *(9:3)*	FNPA	541	19	437	14	417	23	[$^{13}C_2$]FDEA	FHpPA	Ql
Perfluoroethane sulfonate	PFEtS	199	50	80	28	99	26	[$^{18}O_2$]PFBS	PFEtS	Ql
Perfluoropropane sulfonate	PFPrS	249	50	80	30	99	26	[$^{18}O_2$]PFBS	PFPrS	Ql
Perfluorobutane sulfonate	PFBS	299	50	80	32	99	26	[$^{18}O_2$]PFBS	PFBS	Qn
Perfluoropentane sulfonate	PFPeS	349	54	80	34	99	27	[$^{18}O_2$]PFHxS	PFHxS	Ql
Branched Perfluorohexane sulfonate	Br-PFHxS	399	58	80	36	99	28	[$^{18}O_2$]PFHxS	PFHxS	Qn
Perfluorheptane sulfonate	PFHpS	449	64	80	46	99	32	[$^{13}C_2$]PFOS	PFOS	Ql
Branched Perfluorooctanesulfonic acid	Br-PFOS	499	70	80	46	99	34	[$^{13}C_2$]PFOS	PFOS	Qn
Perfluorononane sulfonate	PFNS	549	73	80	49	99	35	[$^{13}C_2$]PFOS	PFDS	Ql
Perfluorodecane sulfonate	PFDS	599	76	80	52	99	36	[$^{13}C_2$]PFOS	PFDS	Ql
4:2 fluorotelomer sulfonate	4:2 FTS	327	42	307	19	81	26	[$^{13}C_2$] 4:2 FtS	4:2 FTS	Sq
6:2 fluorotelomer sulfonate	6:2 FTS	427	42	407	22	81	28	[$^{13}C_2$] 6:2 FtS	6:2 FTS	Sq
8:2 fluorotelomer sulfonate	8:2 FTS	527	48	507	24	81	33	[$^{13}C_2$] PFDA	8:2 FTS	Sq
10:2 fluorotelomer sulfonate	10:2 FTS	627	54	607	26	81	38	[$^{13}C_2$] 6:2 FtS	8:2 FTS	Ql
Perfluorobutane sulfonamido acetic acid	FBSAA	356	35	298	20	78	30	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Perfluoropentane sulfonamido acetic acid	FPeSAA	406	37	348	22	78	32	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Perfluorohexane sulfonamido acetic acid	FHxSAA	456	40	398	24	78	35	d_3-MeFOSAA	FOSAA	Ql
Perfluoroheptane sulfonamido acetic acid	FHpSAA	506	42	448	25	78	37	d_3-MeFOSAA	FOSAA	Ql
Perfluorooctane sulfonamido acetic acid	FOSAA	556	45	498	27	78	40	d_3-MeFOSAA	FOSAA	Sq
Methyl perfluorobutane sulfonamido acetic acid	MeFBSAA	370	28	219	18	283	13	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Methylperfluoropentane sulfonamido acetic acid	MeFPeSAA	420	29	269	18	333	24	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Methyl perfluorohexane sulfonamido acetic acid	MeFHxSAA	470	31	319	19	169	26	d_3-MeFOSAA	MeFOSAA	Ql
Methyl perfluoroheptane sulfonamido acetic acid	MeFHpSAA	520	32	369	19	169	28	d_3-MeFOSAA	MeFOSAA	Ql
Methylperfluorooctane sulfonamido acetic acid	MeFOSAA	570	34	419	20	169	30	d_3-MeFOSAA	MeFOSAA	Sq
Ethylperfluorobutane sulfonamido acetic acid	EtFBSAA	384	28	219	18	326	18	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Ethylperfluoropentane sulfonamido acetic acid	EtFPeSAA	434	29	269	18	376	18	[$^{13}C_2$]PFHxA	MeFBSAA	Ql
Ethylperfluorohexane sulfonamido acetic acid	EtFHxSAA	484	31	319	19	426	19	d_5-EtFOSAA	EtFOSAA	Ql
Ethylperfluoroheptane sulfonamido acetic acid	EtFHpSAA	534	32	369	19	476	19	d_5-EtFOSAA	EtFOSAA	Ql
Ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	584	34	419	20	526	20	d_5-EtFOSAA	EtFOSAA	Sq
Bis(perfluorobutyl) phosphinate	4:4 PFPIA	501	50	301	40	101	55	[$^{13}C_4$]-6:2DiPAP	6:6 PFPi	Ql

Perfluorobutyl perfluorohexyl phosphinate	4:6 PFPIA	601	60	301	42	401	43	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Ql
Bis(perfluorohexyl) phosphinate	6:6 PFPIA	701	72	401	43	101	62	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Qn
Perfluorohexylperfluorooctyl phosphinate	6:8 PFPIA	801	85	401	44	501	45	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Ql
Bis(perfluorooctyl) phosphinate	8:8 PFPIA	901	98	501	46	101	69	$[^{13}C_4]$-6:2DiPAP	8:8 PFPi	Qn
4:2 disubstituted polyfluoroalkyl phosphate	4:2 diPAP	589	36	97	27	343	16	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Ql
4:2/6:2 disubstituted polyfluoroalkyl phosphate	4:2/6:2 diPAP	689	37	97	29	343	17	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Ql
6:2 disubstituted polyfluoroalkyl phosphate	6:2 diPAP	789	38	97	30	443	18	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Sq
6:2/8:2 disubstituted polyfluoroalkyl phosphate	6:2/8:2 diPAP	889	39	97	33	443	19	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2 disubstituted polyfluoroalkyl phosphate	8:2 diPAP	989	40	97	35	543	20	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Sq
8:2/10:2 disubstituted polyfluoroalkyl phosphate	8:2/10:2 diPAP	1089	41	97	37	543	21	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
10:2 disubstituted polyfluoroalkyl phosphate	10:2 diPAP	1189	42	97	39	643	22	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
6:2 fluorotelomer mercaptoalkyl phosphate diester	6:2 FTMAP	921	70	79	50	575	30	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
6:2/8:2 fluorotelomer mercaptoalkyl phosphate diester	6:2/8:2 FTMAP	1021	75	79	50	575	30	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2 fluorotelomer mercaptoalkyl phosphate diester	8:2 FTMAP	1121	90	79	50	675	35	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2/10:2 fluorotelomer mercaptoalkyl phosphate diester	8:2/10:2 FTMAP	1221	90	79	50	675	40	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
10:2 fluorotelomer mercaptoalkyl phosphate diester	10:2 FTMAP	1321	90	79	50	775	40	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
N-ethyl perfluorooctanesulfonamidoethanol-based phosphate diester	SAmPAP	1203	75	526	40	169	65	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
Perfluoro[1,2,3,4-$^{13}C_4$]butanoic acid	$[^{13}C_4]$ PFBA	217	20	172	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[3,4,5-$^{13}C_3$]pentanoic acid	$[^{13}C_3]$ PFPeA	266	20	222	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]hexanoic acid	$[^{13}C_2]$ PFHxA	315	20	270	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid	$[^{13}C_4]$ PFOA	417	20	372	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$[^{13}C_5]$ PFNA	468	22	423	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]decanoic acid	$[^{13}C_2]$ PFDA	515	22	470	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]undecanoic acid	$[^{13}C_2]$ PFUnDA	565	22	520	10	n/a	n/a	n/a	n/a	n/a

Perfluoro[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$] PFDoDA	615	22	570	10	n/a	n/a	n/a	n/a	n/a
2-perfluorohexyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FHEA	379	20	294	22	n/a	n/a	n/a	n/a	n/a
2-perfluorooctyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FOEA	479	20	394	20	n/a	n/a	n/a	n/a	n/a
2-perfluorodecyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FDEA	579	20	494	18	n/a	n/a	n/a	n/a	n/a
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	[$^{13}C_2$] FHUEA	359	18	294	17	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[2,3,4-$^{13}C_3$]-butanesulfonate	[$^{13}C_2$] PFBS	302	50	99	26	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$] PFHxS	403	58	103	28	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octane sulfonate	[$^{13}C_2$] PFOS	503	70	99	34	n/a	n/a	n/a	n/a	n/a
4:2[1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 4:2 FTS	329	43	81	26	n/a	n/a	n/a	n/a	n/a
6:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 6:2 FTS	429	42	409	22	n/a	n/a	n/a	n/a	n/a
Methyl-d_3-perfluorooctane sulfonamido acetic acid	[$^{2}H_3$] MeFOSAA	573	34	419	20	n/a	n/a	n/a	n/a	n/a
Ethyl-d_5-perfluorooctane sulfonamido acetic acid	[$^{2}H_5$] EtFOSAA	589	34	419	20	n/a	n/a	n/a	n/a	n/a
6:2 disubstituted-[1,2-$^{13}C_2$]-polyfluoroalkyl phosphate	[$^{13}C_4$] 6:2 diPAP	794	38	97	30	n/a	n/a	n/a	n/a	n/a

*PI (precursor ion), CV (cone voltage), FI (fragmentation ion), CE (collision energy), Qn (quantitative), Sq (semiquantitative), Ql (qualitative), Sc (Screen)

Table S3. Analytical Validation Parameters for Recovery (Accuracy), RSD (Precision), Limit of Detection (LOD), and Limit of Quantification (LOQ) for volatile analytes.

	Recovery at 20ng (%)	Recovery at 120ng (%)	RSD (%)	LOD (μg/m^2)	LOQ (μg/m^2)
Analytes					
6:2 FTOH	87	100	2.3	0.37	1.2
8:2 FTOH	79	98	3.9	0.83	2.8
10:2 FTOH	94	92	2.7	2.4	8.1
N-EtFOSE	100	78	1.5	1.2	3.8

Table S4. Sample mass to methanol extraction ratio for determination of minimum material for maximum precision (RSD%) for papers and textiles.

	RSD (%) range across class											
	PFCAs		FTCAs		PFSAs		FtS		(Me,Et,)FXSAA		diPAPS	
Weight to methanol ratio	Papers	Textiles	Papers	Textiles	Papers	Textiles	Papers	Textiles	Papers	Textiles	Papers	Textiles
0.5g:8.33mL	2-25	6-29	5-10	<LOD	<LOQ	7-24	<LOD	14-174	<LOD	12-31	<LOD	23-43
0.3g:3.33mL	4-17	10-19	12-25	<LOD	19	5-16	<LOD	14-26	<LOD	7-24	<LOD	40-49
0.1g:1.67mL	4-16	10-29	30-40	<LOD	35	14-39	<LOD	41-131	<LOD	15-62	<LOD	30-62

Table S5. Analysis of individual extraction cycles for native (not spiked) ionic PFASs and isotopically-labeled ionic PFASs.

	Paper				**Paper + Internal Standard**				**Fabric**				**Fabric + Internal Standard**			
% mass recovered in each extraction/total mass	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
PFBA	65	29	5.7	<LOD	69	26	4.2	0.7	62	30	8.8	<LOD	76	19	4.1	1.5
PFPeA	73	27	<LOD	<LOD	68	27	3.8	0.7	55	28	12	5.2	77	17	4.5	1.6
PFHxA	61	31	6.3	1.5	61	36	3.7	<LOD	56	25	12	6.7	75	20	3.6	1.4
PFHpA	<LOD	<LOD	<LOD	<LOD	61	36	3.7	<LOD	65	22	8.5	4.1	75	20	3.6	1.4
PFOA	100	<LOD	<LOD	<LOD	61	34	4.9	<LOD	69	22	6.8	2.6	81	17	2.5	<LOD
PFNA	<LOD	<LOD	<LOD	<LOD	65	32	3.2	<LOD	72	21	4.4	2.9	80	17	2.1	0.4
PFDA	<LOD	<LOD	<LOD	<LOD	61	34	4.6	0.6	77	16	5.4	0.9	77	19	2.7	0.6
PFUnDA	<LOD	<LOD	<LOD	<LOD	69	26	4.9	<LOD	91	9	<LOD	<LOD	77	18	3.6	1.0
PFDoDA	<LOD	<LOD	<LOD	<LOD	65	30	3.3	0.9	83	17	<LOD	<LOD	83	14	2.8	<LOD
PFTrDA	48	44	8.0	<LOD	65	30	3.3	0.9	76	21	3.9	<LOD	83	14	2.8	<LOD

PFTeDA	<LOD	<LOD	<LOD	<LOD	65	30	3.3	0.9	61	29	6.0	4.3	83	14	2.8	<LOD
FHEA	59	33	7.6	<LOD	90	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	74	20	5.6	<LOD
FOEA	<LOD	<LOD	<LOD	<LOD	58	39	2.4	<LOD	<LOD	<LOD	<LOD	<LOD	82	11	5.1	1.1
FDEA	<LOD	<LOD	<LOD	<LOD	61	29	11	<LOD	<LOD	<LOD	<LOD	<LOD	83	17	<LOD	<LOD
FHUEA	57	34	6.1	2.5	67	28	4.4	1.0	<LOD	<LOD	<LOD	<LOD	70	25	4.6	0.6
FOUEA	<LOD	<LOD	<LOD	<LOD	58	39	2.4	<LOD	<LOD	<LOD	<LOD	<LOD	82	11	5.1	1.1
FPePA	58	35	6.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtS	67	33	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	41	33	15	11	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	72	19	4.9	3.9	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	70	29	1.6	<LOD	70	21	6.9	2.5	83	11	4.1	1.4
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	73	19	4.7	4.0	<LOD	<LOD	<LOD	<LOD
PFHxS	<LOD	<LOD	<LOD	<LOD	77	23	<LOD	<LOD	75	17	6.0	2.4	74	21	3.0	2.0
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	76	19	4.0	0.7	<LOD	<LOD	<LOD	<LOD
PFOS	<LOD	<LOD	<LOD	<LOD	75	25	<LOD	<LOD	77	18	4.5	1.3	80	16	4.0	0.4
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	79	18	3.5	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FtS	<LOD	<LOD	<LOD	<LOD	67	29	4.0	<LOD	<LOD	<LOD	<LOD	<LOD	68	26	4.9	1.0
6:2 FtS	<LOD	<LOD	<LOD	<LOD	65	32	3.7	<LOD	81	19	<LOD	<LOD	81	15	3.1	0.1
8:2 FtS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	76	18	3.6	2.6	<LOD	<LOD	<LOD	<LOD
10:2 FtS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	98	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	72	22	4.2	1.6	<LOD	<LOD	<LOD	<LOD
MeFBSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	75	20	5.1	<LOD	<LOD	<LOD	<LOD	<LOD
MeFHxSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	88	11	1.0	<LOD	80	15	5.2	<LOD
MeFHpSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	66	29	5.3	<LOD	80	17	2.6	<LOD
MeFOSAA	<LOD	<LOD	<LOD	<LOD	64	26	8.0	2.6	73	20	5.1	2.5	77	16	5.1	1.6
EtHxSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	63	30	5.0	2.2	66	23	7.4	3.5	77	18	4.1	0.4
6:2 DiPAP	<LOD	<LOD	<LOD	<LOD	59	35	5.0	1.3	81	15	2.9	0.6	84	13	2.2	0.7

Table S6. Accuracy (% Recovery), Precision (% RSD), and Limit of Detection and Quantification for Papers and Textiles

	Papers				Textiles			
	Recovery (%)	RSD (%)	LOD (μg/m^2)	LOQ (μg/m^2)	Recovery (%)	RSD (%)	LOD (μg/m^2)	LOQ (μg/m^2)
LC-MS/MS Analytes								
PFBA	74	5.9	0.056	0.18	87	4.2	0.066	0.21
PFPeA	110	8.4	0.052	0.17	90	5.8	0.066	0.22
PFHxA	78	12	0.059	0.20	89	4.1	0.029	0.091
PFHpA	97	11	0.039	0.13	87	7.8	0.081	0.26
PFOA	92	12	0.040	0.13	88	16	0.12	0.40
PFNA	92	4.8	0.028	0.089	88	4.4	0.081	0.26
PFDA	75	15	0.037	0.12	98	6.5	0.053	0.18
PFUdA	94	2.2	0.063	0.21	100	24	0.14	0.47
PFDoDA	79	6.5	0.024	0.076	93	5.1	0.029	0.096
PFTrDA	79	8.5	0.030	0.10	87	5.2	0.062	0.21
PFTeDA	73	12	0.035	0.11	85	7.1	0.066	0.21
FHEA	80	9.6	0.058	0.19	84	16	0.13	0.43
FOEA	120	9.1	0.052	0.17	96	6.8	0.12	0.38
FDEA	130	22	0.095	0.32	81	22	0.18	0.58
FHUEA	71	7.9	0.012	0.039	66	4.9	0.07	0.22
FOUEA	66	16.0	0.032	0.11	85	12	0.073	0.24
FPrPA	93	3.4	0.024	0.076	45	13	0.16	0.52
FPePA	70	6.5	0.03	0.11	54	2.4	0.086	0.28
FHpPa	69	11	0.034	0.11	80	3.4	0.093	0.31
PFBS	72	6.3	0.016	0.053	80	4.3	0.055	0.18
PFPeS	72	8.3	0.031	0.10	91	4.6	0.050	0.17
PFHxS	78	4.6	0.035	0.11	83	3.5	0.076	0.25
PFHpS	71	10	0.029	0.094	77	9.2	0.079	0.26
PFOS	90	15	0.038	0.12	92	3.0	0.15	0.48
PFNS	62	6.8	0.034	0.11	62	6.8	0.059	0.19
PFDS	72	6.2	0.027	0.090	68	9.1	0.054	0.17
4:2 FtS	71	4.8	0.028	0.092	90	3.8	0.048	0.16
6:2 FtS	76	2.9	0.019	0.063	94	5.6	0.044	0.14
8:2 FtS	120	6.5	0.016	0.055	86	4.8	0.039	0.13
FOSAA	36	5.3	0.023	0.077	170	5.9	0.029	0.096
MeFBSAA	74	8.4	0.021	0.069	87	4.3	0.082	0.27
MeFOSAA	78	5.5	0.025	0.084	100	1.6	0.047	0.15
EtFOSAA	77	6.0	0.010	0.034	87	2.3	0.045	0.15
6:6 PFPIA	42	3.1	0.016	0.053	76	4.4	0.044	0.15
8:8 PFPIA	46	11	0.022	0.070	54	12	0.080	0.26
6:2 diPAP	81	8.3	0.022	0.070	88	8.4	0.023	0.073
8:2 diPAP	120	17	0.070	0.23	110	15	0.056	0.18

Table S7. Known precursors % recovery (on a total nmole basis), number of perfluorinated carbons in chain, and distribution of carbon chain length after the TOP Assay (no paper or textile present).

Known Precursor	Mass recovered (%)	Number of perfluorinated carbons in precursor chain	Distribution of carbon PFCA chain length after oxidation
6:6PFPi	17	6	C5-C6
FOUEA	3.8	8	C5-C8
8:2 diPAP	45	8	C4-C9
FHUEA	41	6	C4-C7
6:2 FtS	36	6	C4-C7
6:2 diPAP	3.4	6	C5-C8
SAmPaP	0.0	8	none
mixture[a]	57	4-14	C4-C14

[a]For mixture composition see Table S2 (all Qn and Sq analytes)

Table S8. Concentrations (μg/m^2) of Individual Volatile and Ionic PFASs analyzed by GC-MS and LC-MS/MS.

		Individual Ionic PFASs in μg/m^2																
		Papers								Textiles								
	MW	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	9
Individual PFASs (Volatile)																		
6:2 FTOH	364.11	<LOD	<LOD	<LOD	<LOD	**18**	**14**	<LOD	<LOD	<LOD	**7.0**	**370**	<LOD	**2.1**	<LOD	**11**	**14000**	**130**
8:2 FTOH	464.12	**30**	**3.6**	<LOD	**9.1**	**16**	**12**	**25**	<LOD	**72**	**130**	**990**	**170**	**73**	**22**	**1300**	**340**	**170**
10:2 FTOH	564.13	**12**	<LOD	<LOD	<LOD	**15**	**3.0**	**10**	<LOD	**37**	**42**	**490**	**70**	**4.3**	<LOD	**330**	**140**	**110**
N-EtFOSE	571.25	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3100**
Individual Ionic PFASs (Non-Volatile)																		
PFBA	213.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**19**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.37**	**4.7**	**39**
PFPeA	263.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.25**	**7.0**	**14**
PFHxA	313.98	<LOD	<LOD	<LOD	<LOD	**0.27**	<LOQ	<LOD	**13**	<LOD	<LOD	**0.16**	<LOD	<LOQ	<LOD	**0.90**	**31**	**100**
PFHpA	363.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	**0.31**	**8.8**	**67**
PFOA	413.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	**0.45**	<LOD	**3.3**	<LOQ	**110**
PFNA	463.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	**0.23**	**0.93**	<LOQ	**0.17**	<LOQ	**0.24**	**7.5**
PFDA	513.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	**0.30**	**0.18**	**1.1**	<LOQ	**3.5**
PFUnDA	563.96	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.57**	<LOQ	<LOQ	<LOD	<LOD	**1.4**
PFDoDA	613.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.14**	<LOQ	**0.25**	<LOQ	**1.5**
PFTriDA	663.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	**1.8**
PFTeDA	713.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	**2.9**
PFPeDA	763.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	813.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.45**
PFHpDA	863.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOcDA	913.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.47**
FBEA	278.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHEA	377.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.8**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.82**	<LOD
FOEA	477.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.27**	**0.77**	<LOD	**0.32**	**0.59**	<LOQ	<LOQ
FDEA	577.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD
FBUEA	257.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

FHUEA	357.99	<LOD	<LOD	<LOD	<LOQ	**0.12**	<LOQ	<LOD	**4.1**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.2**	<LOD
FOUEA	457.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOD
FDUEA	557.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD
FPrPA	242.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FPePA	342.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHpPA	442.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FNPA	542.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtS	199.95	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	249.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.65**
PFBS	299.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**4.5**
PFPS	349.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.7**
PFHxS	399.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	**11**
PFHpS	449.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**6.3**
PFOS	499.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.69**	<LOD	<LOD	**190**
PFNS	549.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	599.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**4.2**
4:2 FtS	327.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
6:2 FtS	427.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**
8:2 FtS	527.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.49**
10:2 FtS	627.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
FBSAA	356.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FPeSAA	406.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHxSAA	456.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
FHpSAA	506.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	556.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**6.6**
MeFBSAA	370.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
MeFPeSAA	420.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFHxSAA	470.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.3**
MeFHpSAA	520.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.8**
MeFOSAA	570.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**17**

EtFBSAA	385.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFPeSAA	435.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFHxSAA	485.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFHpSAA	534.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	584.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.71**
4:4 PFPiA	501.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:6 PFPiA	601.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:6 PFPiA	701.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:8 PFPiA	801.92	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:8 PFPiA	901.92	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 diPAP	590.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2/6:2 diPAP	689.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	789.98	<LOD	<LOD	<LOD	<LOD	<LOD	**0.17**	<LOQ	<LOD	<LOD	<LOD	<LOD	**0.31**	<LOD	<LOQ	<LOD	<LOD	**8.8**
6:2/8:2 diPAP	889.98	<LOQ	<LOQ	<LOD	<LOQ	<LOQ	**0.73**	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	<LOD	**0.43**
8:2 diPAP	989.97	<LOD	<LOD	<LOD	<LOD	<LOD	**0.35**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.9**
8:2/10:2 diPAP	1089.96	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.31**	<LOQ	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**3.3**
10:2 diPAP	1189.96	<LOD	<LOQ	<LOD	<LOD	<LOD	**0.25**	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	**1.6**
6:2 FTMAP	921.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	**1.1**
6:2/8:2 FTMAP	1021.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
8:2 FTMAP	1121.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2/10:2 FTMAP	1221.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTMAP	1321.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
SAmPAP	1203.98	<LOQ	**0.39**	<LOD	<LOD	<LOD	<LOQ	**4.8**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ

<LOD=Less than limit of detection

<LOQ=Less than limit of quantification

Bolded number=above quantification

Table S9. Ionic PFASs after TOP assay, described as net production of PFCAs and PFSAs.

		Net Production (Δ) of ionic PFASs after TOP Assay in μg/m^2																
		Papers								Textiles								
	MW	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8[a]	9
PFBA	213.99	**0.81**	<LOD	**0.40**	<LOD	**42**	**29**	<LOD	**600**	<LOD	**6.8**	**40**	**2.5**	**2.8**	**1.8**	**6.1**	**16**	**780**
PFPeA	263.98	**2.2**	<LOD	**1.0**	<LOD	**100**	**70**	**1.8**	**1300**	**1.6**	**12**	**84**	**5.6**	**6.4**	**4.8**	**15**	**69**	**1200**
PFHxA	313.98	**0.23**	<LOQ	<LOQ	<LOD	**13**	**6.9**	**1.7**	**420**	**1.3**	**24**	**98**	**11**	**11**	**6.7**	**21**	**0.3**	**1900**
PFHpA	363.98	<LOQ	<LOD	<LOD	<LOD	**0.57**	**0.59**	<LOQ	**19**	**3.5**	**59**	**170**	**20**	**21**	**11**	**52**	**0.0**[b]	**1600**
PFOA	413.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	**1.9**	**17**	**43**	**6.9**	**7.8**	**5.9**	**22**	**0.54**	**15000**
PFNA	463.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**	<LOD	**1.5**	**22**	**41**	**4.1**	**11**	**6.1**	**20**	<LOD	**220**
PFDA	513.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	**0.88**	**8.8**	**6.8**	**1.2**	**6.3**	**2.7**	**13**	**0.0**[b]	**47**
PFUnDA	563.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**6.5**	**0.82**	<LOQ	**4.4**	**2.2**	**7.5**	<LOD	NC[c]
PFDoDA	613.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.40**	**3.9**	<LOQ	<LOD	**2.8**	**1.1**	**6.6**	<LOD	**25**
PFTriDA	663.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**1.8**	<LOD	<LOD	**1.4**	**0.48**	**1.8**	<LOD	NC[c]
PFTeDA	713.95	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	**0.90**	<LOQ	<LOQ	<LOQ	**0.22**	**0.89**	<LOD	NC[c]
PFPeDA	763.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	NC[c]
PFHxDA	813.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.61**	<LOD	<LOD	**0.73**	**0.20**	**0.67**	<LOD	NC[c]
PFHpDA	863.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.22**	<LOD	<LOD	<LOD	<LOQ
PFOcDA	913.94	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOQ	**0.41**	<LOD	**0.23**	<LOD	NC[c]
PFOS	499.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**160**
Σ PFASs nmol F/m^2		**0.011**	**<LOQ**	**0.0046**	**<LOQ**	**0.53**	**0.36**	**0.014**	**7.8**	**0.040**	**0.58**	**1.7**	**0.18**	**0.27**	**0.15**	**0.59**	**0.28**	**73**

[a]Textile 8 had 2.2% non-converted PFASs after TOP assay (not shown).

[b]The quantity of PFHpA and PFDA showed no net production (Δ), and remained the same.

[c]Due to larger dilutions done for the TOP assay analysis, these values fell below the LOQ and no net value could be computed (NC= not computed).

<LOD=less than the limit of detection

<LOQ=less than the limit of quantification

MW=Molecular weight

Total Fluorine by PIGE-

Table S10. Accuracy (% Recovery) for total fluorine on papers and textiles determined by PIGE.

Fluorinated Standards	PFBA	PFHxA	PFOA
Spiked concentration (nmol F/cm^2)	515	515	515
Counts/uC	3035 ± 71.0	3101 ± 104	2980 ± 64.3
Calculated concentration (nmol F/cm^2)	516	528	507
Recovery ± SD (%)	**100 ± 2**	**103 ± 3**	**98 ± 2**

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