# **Supporting Information (SI)**

# Per- and polyfluoroalkyl substances (PFAS) in dust collected from residential homes and fire stations in North America

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#### **Additional Methods**

#### Dust sample preparation and extraction

Dust samples were prepared to extract the 17 PFAS analytes listed in **Table S1** and are grouped into classes following previously described nomenclature (Buck *et al.*, 2011; Wang *et al.*, 2017). In this present study, analytes are split into two large subgroups: legacy and precursor PFAAs. Legacy PFAAs refers to the PFAAs (PFCAs and PFSAs) which are more persistent in the environment. PFAA precursors refers to the shorter-lived PFAS that are potentially capable of transforming into PFAAs.

Dust extraction methods have previously been described in Phillips *et al.* (2018). In brief, dust samples from fire station samples (n=49) and residential homes (n=184) were sieved to  $<150 \mu$ m or  $<500 \mu$ m and extracted with a total 30 mL of 1:1 dicholoromethane:hexane (v/v) using sonication. Extracts were concentrated to approximately 1 mL using a SpeedVac vacuum concentrator (ThermoFisher Scientific). Extracts were fractionated using Florisil solid-phase extraction cartridges (Supel-clean ENVI-Florisil, 6 mL, 500 mg; Supelco), eluting three fractions with 6 mL hexane, 10 mL ethyl acetate, and 6 mL methanol. The F2 fraction eluted using 10 mL ethyl acetate was used for analysis of FTOHs and FOSEs, and the F3 fraction eluted using 6 mL methanol was used for analysis of PFAAs and diPAPs (the F1 and F2 fractions were prioritized for analysis of other compounds in other studies). F2 fractions were concentrated to approximately 1 mL using a SpeedVac concentrator and were reconstituted in hexane prior to GC/MS analysis. Samples were spiked with mass-labeled internal standards prior to extraction for fire station samples and prior to cleanup for house dust samples.

#### HPLC-MS/MS analysis

Twelve PFAS compounds were analyzed using an Agilent 1260 Infinity II highperformance liquid chromatograph (HPLC) instrument coupled to an Agilent 6460A triple quadrupole mass spectrometer. The mass spectrometer was operated in negative electrospray ionization mode (HPLC-ESI-MS/MS). Separation of analytes by LC was performed using a 4.6 mm (I.D.) x 50 mm Agilent ZORBAX Eclipse XDB-C18 reversed-phase HPLC column (1.8 µm particle size) preceded by a 4.6 mm x 5 mm XDB-C18 guard cartridge.

Mobile phases were 2 mM ammonium acetate in water (mobile phase A) and 2 mM ammonium acetate in methanol (mobile phase B) using a flow rate of 0.4 mL/min. Gradient conditions for chromatographic separation were as follows: initial condition (30% B) was increased to 60% B over 1.5 minutes; then increased to 95% B over 2 minutes and held for 5.5 minutes; then increased to 100% B over 3 minutes, returned to initial condition (30% B) over 0.5 minutes, and held for 5.5 minutes. The column temperature was 45°C and the injection volume was 20  $\mu$ L. Data were acquired under multiple reaction monitoring (MRM) transitions using optimized parameters. Additional methods information, including transitions, is included in **Table S2**.

#### GC-MS analysis

Five PFAS compounds were analyzed using gas chromatography (GC) with an Agilent 7890A gas chromatograph instrument coupled to an Agilent 5975C mass spectrometer operated in electron impact mode (GC/EI-MS). Methods were previously described in Hammel *et al.* (2019). In brief, pressurized temperature vaporization (PTV) injection was employed in the inlet, and a 0.25 mm (I.D.) x 30 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (J&W Scientific, 0.25 µm film thickness) was used in the GC for separation of analytes. Helium was used as carrier gas at a constant flow rate of 1.3 mL/min. The inlet was set to a temperature to 300°C for 0.3 minutes, and a 600°C/min ramp was employed to increase the inlet temperature to 300°C in order to efficiently transfer the samples to the head of the GC column. The GC oven was held at 80°C for 2 minutes followed by a temperature ramp of 20°C/min to 250°C, a ramp of 1.5°C/min to 260°C, and a ramp of 25°C/min to 300°C, and the ion source was held at 230°C. Additional methods information is available in **Table S2**.

Legacy PFA	As		PFAA Precursors				
PFCAs	Perfluoroalkyl carboxylic acids	CAS Number	diPAPs	Fluorotelomer phosphate diesters	CAS Number		
PFBA	Perfluorobutanoic acid	375-22-4	6:2 diPAP	6:2 fluorotelomer phosphate diester or sodium bis(1H,1H,2H,2H-perfluorooctyl) phosphate	57677-95-9		
PFPA	Perfluoropentanoic acid	2706-90-3	8:2 diPAP	8:2 fluorotelomer phosphate diester or sodium bis(1H,1H,2H,2H-perfluorodecyl) phosphate	678-41-1		
PFHxA	Perfluorohexanoic acid	307-24-4	FTOHs	Fluorotelomer alcohols	CAS Number		
PFHpA	Perfluoroheptanoic acid	375-85-9	6:2 FTOH	6:2 fluorotelomer alcohol or 2-Perfluorohexyl ethanol (FHET)	647-42-7		
PFOA	Perfluorooctanoic acid	335-67-1	8:2 FTOH	8:2 fluorotelomer alcohol or 2-Perfluorooctyl ethanol (FOET)	678-39-7		
PFNA	Perfluorononanoic acid	375-95-1	10:2 FTOH	10:2 fluorotelomer alcohol or 2-Perfluorodecyl ethanol (FDET)	865-86-1		
PFDA	Perfluorodecanoic acid	335-76-2					
PFSAs	Perfluoroalkyl sulfonic acids	CAS Number	PASF-based substances	Perfluoroalkane sulfonamido ethanols	CAS Number		
PFBS	Perfluorobutane sulfonic acid	375-73-5	MeFOSE	<i>N</i> -methyl perfluorooctane sulfonamido ethanol (N-MeFOSE)	24448-09-7		
PFHxS	Perfluorohexane sulfonic acid	355-46-4	EtFOSE	<i>N</i> -ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE)	1691-99-2		
PFOS	Perfluorooctane sulfonic acid	1763-23-1					

Table S1: List of PFAS analytes measured in dust

LC Compounds	Transition	Internal Standard	Transition
6:2 diPAP	789.0 > 96.9	M6:2 diPAP	793.0 > 96.9
8:2 diPAP	989.0 > 96.9	M8:2 diPAP	992.9 > 96.9
PFBA	213.0 > 168.9	MPFBA	217.0 > 172.0
PFBS	298.9 > 98.9	MPFHxS	402.9 > 83.9
PFPA	263.0 > 218.9	MPFHxA	315.0 > 269.9
PFHxA	313.0 > 268.9	MPFHxA	315.0 > 269.9
PFHxS	398.9 > 79.9	MPFHxS	402.9 > 83.9
PFHpA	363.0 > 318.9	MPFOA	417.0 > 371.9
PFOA	413.0 > 368.9	MPFOA	417.0 > 371.9
PFOS	498.9 > 79.9	MPFOS	502.9 > 80.0
PFNA	463.0 > 418.9	MPFNA	468.0 > 422.9
PFDA	513.0 > 468.9	MPFDA	515.0 > 470.0
GC Compounds	Quant / Qual Ions	Internal Standard	Quant / Qual Ions
6:2 FTOH	365 / 327	<sup>13</sup> C 6:2 FTOH	367 / 329
8:2 FTOH	465.2 / 427.2	<sup>13</sup> C 8:2 FTOH	467 / 429
10:2 FTOH	565 / 527	<sup>13</sup> C 8:2 FTOH	467 / 429
MeFOSE	558 / 540	dMeFoSE	547 / 565
EtFOSE	572 / 554	dEtFOSE	581 / 563

**Table S2:** MS conditions (m/z ions) for quantifying PFAS analytes in dust samples

		House Du	ist		Fire Station	SRM 2585	
Compound	MDL	SRM 2585 (n=5)	SRM 2585 RSD (%)	MDL	SRM 2585 (n=5)	SRM 2585 RSD (%)	Reference Values <sup>†</sup>
6:2 diPAP	0.48	299	25.6	2.54	698	2.6	$421 \pm 83^{*}$ $675 \pm 28.3^{**}$
8:2 diPAP	10.63	321	27.4	9.63	748	5.2	$868 \pm 30*$ 227 ± 27.3**
PFBA	1.72	54.7	31.4	1.03	104	9.7	$230 \pm 16^{\dagger}$ $249 \pm 25*$ $229 \pm 25.2**$
PFBS	22.28	23.8	14.8	8.56	13.8	20.9	$\begin{array}{c} 18.8 - 130 * \\ 21.3 \pm 2.87 * * \end{array}$
PFPA	0.14	67.1	27.2	1.2	139	14.5	$\begin{array}{c} 226 \pm 31 * \\ 235 \pm 24.4 * * \end{array}$
PFHxA	0.42	185	18.5	10.30	238	2.5	$260 \pm 25^{\dagger}$ 279* 349 ± 33.2**
PFHxS	0.25	1630	13.2	0.97	1300	7.4	$\begin{array}{c} 1440 \pm 250^{\dagger} \\ 1400 \pm 170^{**} \\ 1420 \pm 191^{**} \end{array}$
PFHpA	0.51	205	31.5	6.77	310	9.9	$249 \pm 32^{\dagger}$ $259^{*}$ $360 \pm 26.6^{**}$
PFOA	0.26	480	6.9	1.60	551	2.2	561* 747 ± 191**
PFOS	0.20	2420	8.8	1.44	2190	7.5	$2310 \pm 420^{\dagger}$ $2280 \pm 200^{**}$ $1860 \pm 256^{**}$
PFNA	0.15	76.7	10.1	0.47	65.4	31.7	$99.4 \pm 4.9^{\dagger}$ $101 \pm 5^{**}$ $90.1 \pm 12^{**}$
PFDA	0.06	55.6	10.8	1.49	51.4	5.4	$34.6 \pm 4.5^{\dagger}$ $38.6^{*}$ $66.9 \pm 10.7^{**}$
6:2 FTOH	6.44	4490	7.4	48.90	3450	101.8	$4560 \pm 868^{**}$
8:2 FTOH	15.80	5580	13.5	7.23	6940	57.3	$5220 \pm 850^{**}$
10:2 FTOH	N/A	N/A	N/A	5.00	3630	48.0	$3730 \pm 687^{**}$
MeFOSE	13.17	2250	23.8	5.00	2490	17.2	2790 ± 180**
EtFOSE	15.45	4500	8.5	5.00	3530	11.4	$4200 \pm 338^{**}$

Table S3: Average dust levels (ng/g dust) in house dust SRM 2585 and relative standard deviation (RSD)

<sup>†</sup>reference values as reported on the NIST Certificate of Analysis for SRM 2585 (NIST, 2018)

\*reference and information values as reported in Reiner et al. (2015)

\*\*reference values as reported in Winkens et al. (2018)

N/A: not applicable as this compound was not measured

	United States (2015,	Fire Stations n=25)	<b>Canadian Fire Stations</b> (2018, n=24)			
Compound	Median Concentration (ng/g dust)	Median oncentration (ng/g dust)Maximum Concentration (ng/g dust)		Maximum Concentration (ng/g dust)		
6:2 diPAP	291	5,770	243	6,270		
8:2 diPAP	95.9	1,460	105	2,250		
MeFOSE	32.0	627	28.5	1,110		
EtFOSE	19.8	17,540	<mdl< td=""><td>213</td></mdl<>	213		
6:2 FTOH	1,430	86,060	544	22,620		
8:2 FTOH	445	65,170	175	17,480		
10:2 FTOH	268	183,700	46.0	8,020		
PFBA	5.0	213	3.5	33.6		
PFOA	26.4	791	9.5	305		
PFNA	7.1	181	6.3	203		
PFDA	7.0	88.7	<mdl< td=""><td>137</td></mdl<>	137		
PFHxS	10.3	8,280	2.4	204		
PFOS	104	74,370	13.2	1,190		

\*only analytes detected in >50% of all 49 fire stations are reported here <MDL: below method detection limit

Characteristic		Sample Size
Country		
	United States	25
	Canada	24
Year of fire station construction		
	Pre-1970	22
	Post-1970	23
Square footage		
	Less than 3,500 square feet	21
	3,500 or greater square feet	19
Carpeting		
	Greater than 20% carpeting	20
	20% or less carpeting	19

**Table S5:** Characteristics of 49 fire stations included in this present study\*

\*sample size may not always sum to total due to incomplete survey information

Table S6: Ch	aracteristics of	184 residentia	l homes in	ncluded in	this p	present	study
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Characteristic		Sample Size		
Year of home construction				
	Pre-1970	34		
	Post-1970	86		
	No data	64		
Square footage				
	Less than 1,720 square feet	67		
	1,720 or greater square feet	67		
	No data	50		
Carpeting				
	Carpeted (any %)	124		
	Not carpeted	60		

Table S7: Summary of median PFAS dust concentrations (ng/g dust) in US house dust reported in the published literature and preserved in the published literature and published literature a
study

Reference	Year of Sample Collection	Sample Size (n)	PFOS	PFOA	PFHxS	PFHxA	PFBS	PFPA	РҒНрА	PFNA	PFDA
House dust SRM 2585 [NIST (2018) and Reiner <i>et al.</i> (2015)]	1993-1994	Unknown	2,310	561	1,440	260	19–130	226	249	99	35
Strynar and Lindstrom (2008)	2000-2001	102 homes	201	142	46	54	9	-	50	8	7
Kato <i>et al.</i> (2009) <sup>†</sup>	2004	10 homes	~95	~95	~100	-	-	-	-	-	-
Knobeloch et al. (2012)	2008	39 homes	47	44	16	0	2	5	17	12	6
Fraser et al. (2013)*	2009	30 homes	27	24	-	9	-	-	12	11	-
Karaskova et al. (2016)	2013	14 homes	14	9	9	6.5	1	3	4	4	1.8
Hall et al., present study	2014-2016	184 homes	4	8	2	9	-	-	9	3	6

<sup>†</sup>medians for US homes estimated from reference

\*geometric mean concentrations reported in lieu of median values

Blank values were either not reported or <MDL



# Figure S1: PFAS profiles in dust from homes and fire stations

Relative amounts of individual PFAS in dust from homes (n=184) and fire stations (n=49) based on the median concentrations and reported as percentage of dust composition. For homes, 10:2 FTOH was not measured.



#### Figure S2: ΣPFAS concentrations in dust samples by region

 $\Sigma$ PFAS in dust samples stratified by region and represented by scatterplots depicting individual samples, with lines at the minimum, median, and maximum concentrations.  $\Sigma$ PFAS refers to the sum of all PFAS analytes measured in the dust. In fire station dust, 17 analytes were measured, and 16 analytes were measured in house dust (10:2 FTOH was not measured in house dust). Fire station dust samples were collected from across the United States and Canada (n=4-9 per region, 49 total) while dust from residential homes was collected in North Carolina (n=184). Concentrations are reported on a log scale. Due to small sample sizes, no statistical tests were performed. Note: British Columbia fire stations collected dust from living quarters and fire truck interiors.

# Figure S3: ΣPFAS dust concentration and survey responses for residential homes

Differences in dust  $\Sigma PFAS$ concentrations in homes due to: a) year of construction, b) square footage of home, and c) carpeting. No significant differences in house dust  $\Sigma$ PFAS concentrations were seen based on year of construction, square footage, or carpeting. Significance determined by twotailed Mann-Whitney test. Sample sizes are variable due to missing survey data. Boxplots represent the minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup> percentile, and maximum concentrations. Concentrations are reported on a log scale. The  $\Sigma$ PFAS concentration represents the sum of all 16 PFAS analytes measured in a house dust sample.



# Figure S4: Square footage area of fire station living quarters and PFAS dust concentrations

Dust concentrations by individual analyte for a) legacy PFAAs and b) PFAA precursors. Significance determined by the two-tailed Mann-Whitney test. Boxplots represent the minimum, 25th percentile, median, 75th percentile, and maximum concentrations. Concentrations are reported on a log scale.





### Figure S5: Carpeting and FTOH dust concentrations in fire stations and homes

Dust concentrations by individual analyte for the FTOHs. Significance determined by the twotailed Mann-Whitney test. Boxplots represent the minimum, 25th percentile, median, 75th percentile, and maximum concentrations. Concentrations are reported on a log scale. For homes, 10:2 FTOH was not measured. Fire stations were stratified by greater than 20% carpeting (n=20) and 20% or less carpeting (n=19). Homes were stratified by carpeted (n=124) or not carpeted (n=60).



# Figure S6: PFAS concentrations in house dust in 2000-2001 and 2014-2016

Significance determined by the two-tailed Mann-Whitney test (p-values are all \*p<0.0001). Boxplots represent the minimum, 25th percentile, median, 75th percentile, and maximum concentrations. Concentrations are reported on a log scale. All analytes plotted were detected in >50% of dust samples in both studies.

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