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Supplemental Material

Erratum: “Measurement of Novel, Drinking Water-Associated PFAS in Blood from Adults and Children in Wilmington, North Carolina”

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References

Table S1 Mass-labeled analytical standards used for per- and polyfluoroalkyl substances (PFAS) analysis.

Analyte	Formula	Source of native standard ^a	Mass-labeled standard used
Fluoroethers			
HFPO-DA (“GenX”)	C ₆ HF ₁₁ O ₃	1	¹³ C ₃ -HFPO-DA
PMPA	C ₄ HF ₇ O ₃	2	¹³ C ₃ -HFPO-DA
PEPA	C ₅ HF ₉ O ₃	2	¹³ C ₃ -HFPO-DA
PFO2HxA	C ₄ HF ₇ O ₄	2	¹³ C ₃ -HFPO-DA
PFO3OA	C ₅ HF ₉ O ₅	2	¹³ C ₄ -PFOA
PFO4DA	C ₆ HF ₁₁ O ₆	2	¹³ C ₄ -PFOA
PFO5DoA	C ₇ HF ₁₃ O ₇	2	¹³ C ₄ -PFOA
NVHOS	C ₄ H ₂ F ₈ O ₄ S	2	¹³ C ₄ -PFOS
Nafion byproduct 1	C ₇ HF ₁₃ SO ₅	2	¹³ C ₄ -PFOS
Nafion byproduct 2	C ₇ HF ₁₄ SO ₅	2	¹³ C ₄ -PFOS
Legacy PFAS			
PFBA	C ₄ HF ₇ O ₂	1	¹³ C ₄ -PFBA
PFPeA	C ₅ HF ₉ O ₂	1	¹³ C ₂ -PFHxA
PFHxA	C ₆ HF ₁₁ O ₂	1	¹³ C ₂ -PFHxA
PFHpA	C ₇ HF ₁₃ O ₂	1	¹³ C ₄ -PFOA
PFOA	C ₈ HF ₁₅ O ₂	1	¹³ C ₄ -PFOA
PFNA	C ₉ HF ₁₇ O ₂	1	¹³ C ₅ -PFNA
PFBS	C ₄ HF ₉ SO ₃	1	¹⁸ O ₂ -PFHxS
PFHxS	C ₆ HF ₁₃ SO ₃	1	¹⁸ O ₂ -PFHxS
PFOS	C ₈ HF ₁₇ SO ₃	1	¹³ C ₄ -PFOS
6:2 FTS	C ₈ H ₅ F ₁₃ SO ₃	1	¹³ C ₂ -6:2FTS

^a Source: 1 Wellington Laboratories (Guelph, ON, Canada) or 2 The Chemours Company (Wilmington, DE)

Table S2 Method Performance and Quality Assurance. Mean, standard deviation (SD) and coefficient of variation (CV) for calf serum blanks and spikes at 1 ng/mL and 5 ng/mL. Mean and SD for legacy PFAS present in human serum Standard Reference Material (SRM) 1957 are shown for comparison with reference values determined by an interlaboratory comparison among six laboratories [1].

PFAS	Calf serum blanks		Calf serum spikes				SRM 1957		
	blank mean ± SD (ng/mL) (n=12)	blank CV (%) (n=12)	1 ng/mL mean ± SD (n=16)	1 ng/mL CV (%) (n=16)	5 ng/mL mean ± SD (n=15)	5 ng/mL CV (%) (n=15)	Mean (SD) (n=24)	CV (%)	Reference value (Expanded uncertainty) [1]
Fluoroethers									
GenX	0.3 ± 0.5	155	1.2 ± 0.7	56	5.5 ± 1.4	25			
PMPA	0.2 ± 0.1	67	0.9 ± 0.2	26	5.2 ± 0.8	16			
PEPA	0.0 ± 0.0	207	1.2 ± 0.2	13	5.4 ± 0.9	16			
PFO2HxA	0.4 ± 0.6	132	0.7 ± 0.5	76	4.2 ± 1.5	35			
PFO3OA	0.1 ± 0.1	185	0.9 ± 0.3	35	5.1 ± 0.9	18			
PFO4DA	0.0 ± 0.0	244	0.9 ± 0.1	11	4.9 ± 0.6	11			
PFO5DoA	0.0 ± 0.0	361	1.2 ± 0.1	6	5.6 ± 0.4	8.0			
NVHOS	0.0 ± 0.0	178	1.1 ± 0.1	11	5.1 ± 0.7	14			
Nafion byproduct 1	0.0 ± 0.0	361	1.2 ± 0.2	13	5.4 ± 0.8	14			
Nafion byproduct 2	0.0 ± 0.0	167	1.0 ± 0.1	10	4.9 ± 0.6	11			
Legacy PFAS									
PFBA	0.1 ± 0.1	109.5	1.1 ± 0.2	16.3	5.3 ± 0.3	5.5	0.21 (0.17)	77	
PFPeA	0.6 ± 1.6	269.8	1.4 ± 1.4	96.3	5.8 ± 3.5	61	0.97 (1.88)	194	
PFHxA	0 ± 0	211.6	1.1 ± 0.2	18.1	5.1 ± 0.2	4.2	< 0.1		
PFHpA	0 ± 0	117.7	1.1 ± 0.2	14.7	5.3 ± 0.4	8.2	0.28 (0.12)	44	0.305 (0.036)
PFOA	0 ± 0	192.7	1.1 ± 0.1	7.5	5.1 ± 0.2	5	4.93 (0.42)	9	5.00 (0.40)
PFNA	0 ± 0.1	301.5	1 ± 0.1	7.7	5.1 ± 0.3	6.2	0.78 (0.09)	12	0.880 (0.068)
PFBS	0 ± 0	261.1	1.2 ± 0.4	35.2	5.5 ± 1.6	29.2	0.14 (0.31)	225	
PFHxS	0 ± 0.2	311.9	1.1 ± 0.1	6.6	5.1 ± 0.2	4.6	3.96 (0.29)	7	4.00 (0.75)
PFOS	0 ± 0	196	1.2 ± 0.6	50.3	5 ± 0.5	9.6	20.86 (1.95)	9	21.1 (1.2)
6:2 FTS	0 ± 0	308.9	1 ± 0.1	11	5.1 ± 0.3	6	0.15 (0.57)	392	

^a Hydro-EVE is not included because an analytical standard was not available for Hydro-EVE at the time of the analysis

Table S3 Within run and between run precision for GenX Exposure Study serum samples analyzed in duplicate

PFAS	Within run duplicates (n = 41)		Across run duplicates (n = 7)	
	Mean ± SD Percent difference between duplicates	Mean ± SD (ng/mL)	Mean ± SD Percent difference between duplicates	Mean ± SD (ng/mL)
Fluoroethers				
PFO3OA	10.1 ± 17.8	0.16 ± 0.17	41.0 ± 58.1	0.79 ± 1.5
NVHOS	3.9 ± 10.6	0.10 ± 0.08	3.9 ± 5.5	0.77 ± 1.6
PFO5DoA	8.8 ± 7.8	0.41 ± 0.32	32.7 ± 17.8	0.58 ± 0.54
Nafion byproduct 2	5.7 ± 3.9	3.7 ± 2.6	11.3 ± 8.2	4.7 ± 5.4
PFO4DA	25.8 ± 43	4.6 ± 4.9	24.6 ± 15.5	11.6 ± 17.6
Legacy PFAS				
PFHpA	34.2 ± 44.5	0.54 ± 0.49	69.6 ± 63.8	1.40 ± 1.71
PFNA	10.1 ± 23.9	1.5 ± 1.0	6.0 ± 4.4	2.1 ± 1.1
PFHxS	5.1 ± 13.1	4.0 ± 2.3	3.5 ± 5.1	7.4 ± 4.5
PFOA	5.8 ± 12.1	5.7 ± 3.6	10.4 ± 17.9	8.9 ± 6.0
PFOS	8.2 ± 20.2	10.0 ± 6.1	8.3 ± 3.4	14.0 ± 6.0

Table S4 Lowest, median, and highest method reporting limit (MRL) for PFAS across eight analytical runs

PFAS	Lowest MRL (ng/mL)	Median MRL (ng/mL)	Highest MRL (ng/mL)
Fluoroethers			
GenX	0.1	0.3	2
PMPA	0.4	0.6	1.5
PEPA	0.1	0.1	0.5
PFO2HxA	0.5	2.1	5.8
PFO3OA	0.1	0.1	1.3
PFO4DA	0.1	0.1	0.1
PFO5DoA	0.1	0.1	0.1
NVHOS	0.1	0.1	0.2
Nafion byproduct 1	0.1	0.1	0.1
Nafion byproduct 2	0.1	0.1	0.1
Legacy PFAS			
PFBA	0.2	0.4	0.8
PFPeA	0.1	0.5	3.9
PFHxA	0.1	0.1	0.5
PFHpA	0.1	0.2	0.3
PFOA	0.1	0.1	0.5
PFNA	0.1	0.1	0.9
PFBS	0.1	0.5	1.5
PFHxS	0.1	0.1	1.8
PFOS	0.1	0.2	0.5
6:2 FTS	0.1	0.1	0.3

Table S5 Concentrations of PFAS in 20 stored serum samples collected in 2008-2009 from 30-44 year old women participating in an unrelated research study, living in the Raleigh, Durham, and Chapel Hill, NC area [2]

PFAS	MRL (ng/mL)	n > MRL (%)	Concentration (ng/mL)				
			5th percentile	25th percentile	Median	75th percentile	95th percentile
Nafion byproduct 2	0.1	0	< MRL	< MRL	< MRL	< MRL	< MRL
PFO4DA	0.1	0	< MRL	< MRL	< MRL	< MRL	< MRL
PFO5DoA	0.1	0	< MRL	< MRL	< MRL	< MRL	< MRL
PFOS	0.5	20 (100)	7.4	8.5	13.4	15.6	19.8
PFOA	0.5	20 (100)	1.6	2.4	4.2	5.0	5.6
PFHxS	1.8	13 (65)	< MRL	< MRL	2.1	2.8	4.9
PFNA	0.9	15 (75)	< MRL	0.9	1.3	1.6	2.0
PFHpA	0.3	0	< MRL	< MRL	< MRL	< MRL	< MRL

Table S6 Spearman's correlation coefficients between PFAS in serum

A. 310 participants in Nov 2017

	Nafion Byproduct 2	PFHpA	PFHxS	PFNA	PFO4DA	PFOA	PFOS
Nafion Byproduct 2	1.00	0.42	0.69	0.68	0.58	0.74	0.52
PFHpA	0.42	1.00	0.29	0.31	0.76	0.46	0.19
PFHxS	0.69	0.29	1.00	0.78	0.41	0.86	0.73
PFNA	0.68	0.31	0.78	1.00	0.42	0.87	0.84
PFO4DA	0.58	0.76	0.41	0.42	1.00	0.56	0.27
PFOA	0.74	0.46	0.86	0.87	0.56	1.00	0.70
PFOS	0.52	0.19	0.73	0.84	0.27	0.70	1.00

B. 78 participants in May 2018

	Nafion byproduct 2	PFHpA	PFHxS	PFNA	PFO4DA	PFOA	PFOS
Nafion byproduct 2	1.00	0.34	0.65	0.63	0.64	0.76	0.54
PFHpA	0.34	1.00	0.26	0.35	0.58	0.47	0.19
PFHxS	0.65	0.26	1.00	0.75	0.52	0.80	0.73
PFNA	0.63	0.35	0.75	1.00	0.45	0.84	0.85
PFO4DA	0.64	0.58	0.52	0.45	1.00	0.62	0.39
PFOA	0.76	0.47	0.80	0.84	0.62	1.00	0.67
PFOS	0.54	0.19	0.73	0.85	0.39	0.67	1.00

Table S7 Serum concentrations of fluoroethers and legacy PFAS in 44 Wilmington, NC residents (42 adults and 2 children) who provided samples in November 2017 and May 2018

PFAS	n > MRL ^a (%)	Concentration (ng/mL)				
		5 th percentile	25 th percentile	Median	75 th percentile	95 th percentile
Nafion byproduct 2						
November 2017	44 (100)	1.1	2.4	4.1	6.1	8.6
May 2018	44 (100)	0.8	1.6	2.5	4.5	7.1
PFO4DA						
November 2017	43 (98)	0.3	2.0	4.8	9.1	14.8
May 2018	41 (93)	0.1	0.7	1.1	3.0	6.5
PFHxS						
November 2017	44 (100)	1.1	2.4	3.8	5.4	8.4
May 2018	38 (86)	1.3	2.0	3.6	5.2	7.3
PFOA						
November 2017	44 (100)	1.7	3.5	5.9	8.8	12.4
May 2018	43 (98)	1.5	3.1	5.2	7.6	11.2
PFNA						
November 2017	44 (100)	0.6	1.0	1.5	2.3	3.2
May 2018	36 (82)	0.6	0.8	1.4	1.9	3.0
PFOS						
November 2017	44 (100)	3.9	7.2	9.7	15.7	23.5
May 2018	44 (100)	3.3	7.1	9.9	14.0	23.9
PFHpA						
November 2017	31 (70)	0.1	0.2	0.5	0.8	1.8
May 2018	23 (52)	0.2	0.2	0.3	0.8	1.5

^a The Method Reporting Limit (MRL) was 0.1 ng/mL for Nafion byproduct 2 and PFO4DA, ranged 0.1-0.5 ng/mL for PFOS, ranged 0.1-0.5 ng/mL for PFOA, ranged 0.1-1.8 ng/mL for PFHxS, ranged 0.1-0.9 ng/mL for PFNA, and 0.1-0.3 ng/mL for PFHpA

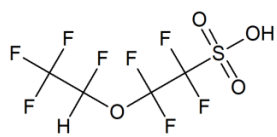
Table S8 Serum concentrations of legacy PFAS in 344 Wilmington, NC residents and the US population based on NHANES data from 2015-2016 survey year.

PFAS	Detection frequency (%)	Concentration (ng/mL)				
		5 th percentile	25 th percentile	Median	75 th percentile	95 th percentile
PFHxS						
US population, 2015-2016	99	0.3	0.7	1.2	2.1	4.9
GenX Exposure Study, 2017-2018	98	0.9	1.8	3.2	5.2	8.5
PFOA						
US population, 2015-2016	99	0.4	1.0	1.5	2.4	4.1
GenX Exposure Study, 2017-2018	99.7	1.5	2.7	4.3	6.9	11.0
PFNA						
US population, 2015-2016	98	0.2	0.4	0.6	0.9	1.9
GenX Exposure Study, 2017-2018	97	0.4	0.8	1.2	2.0	3.3
PFOS						
US population, 2015-2016	99	0.8	1.9	3.2	5.6	12.8
GenX Exposure Study, 2017-2018	99	2.7	5.0	8.6	13.6	26.8

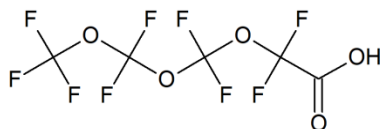
Table S9 Erroneous concentrations of PFO5DoA reported for first serum sample collected from 344 Wilmington, North Carolina, residents.

	MRL (ng/mL)	n>MRL (%)	Erroneous PFO5DoA concentration (ng/mL)				
			10 th percentile	25 th percentile	Median	75 th percentile	95 th percentile
Adults	0.1	256 (89)	0.1	0.2	0.3	0.6	1.0
Children	0.1	46 (84)	0.1	0.1	0.2	0.3	0.4
Overall	0.1	302 (88)	0.1	0.2	0.3	0.5	1.0

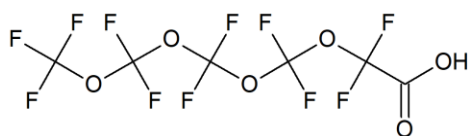
Note: These concentrations were substantially underestimated due to a mass interference in PFO5DoA calibration standards. Note: MRL, method reporting limit; PFO5DoA, perfluoro-3,5,7,9,11-pentaoxadecanoic acid.



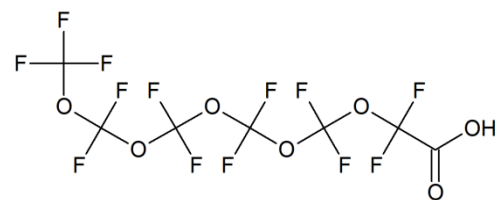
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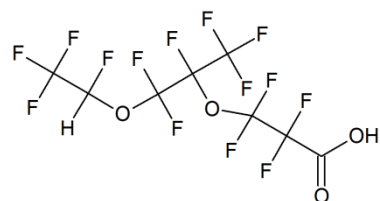
PFO3OA



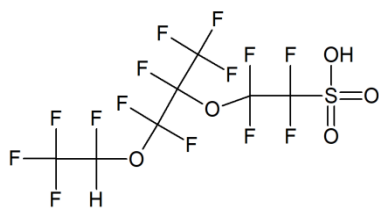
PFO4DA



PFO5DoA



Hydro-EVE



Nafion byproduct 2

Figure S1 Molecular structures of the six fluoroethers detected in serum samples from Wilmington, NC

References

1. Keller JM, Calafat AM, Kato K, Ellefson ME, Reagen WK, Strynar M, O'Connell S, Butt CM, Mabury SA, Small J. 2010. Determination of perfluorinated alkyl acid concentrations in human serum and milk standard reference materials. *Anal Bioanal Chem* 397:439-451.
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