Polyfluorinated Compounds in Serum Linked to Indoor Air in Office Environments

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Supplemental Material

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Air Sampling Procedures

We sampled air using a glass tube fitted with a glass fiber filter (GFF) followed by a 30 mm layer of pre-cleaned polyurethane foam (PUF), a layer of XAD-2 resin (1.5 g) and a second 30 mm layer of PUF (ORBO-1500, outside diameter 22 mm, Supelco, USA). Sampling media were connected to a stationary air pump using ¼-inch Tygon tubing and mounted approximately 1.2 m off the ground on a tripod located in a corner of the office. Pumps ran continuously for a total of 96 hours at 4 L/min; air flow was monitored at both the beginning and end of the four-day sampling period. We collected 3 field blanks and 3 pairs of duplicates. Field blanks were handled and treated the same as air sampling media except that they were not attached to pumps and were, instead, wrapped in foil and bubble wrap immediately after being exposed to the air. At the end of the 96 hour sampling period, sampling media were wrapped in foil and bubble wrap and stored at -20°C until shipped for analysis.

Analysis of Air Samples

Particulate and gaseous phase neutral PFCs were captured and extracted together to provide total air concentrations of the target analytes. Prior to extraction, air sampling media (PUF/XAD-2/PUF) were spiked with 100 µL (200 pg/µL) of standard solution containing the following isotopically labeled compounds: ^{13}C 6:2-FTOH, ^{13}C 8:2-FTOH, ^{13}C 10:2-FTOH, D_3-MeFOSA, D_5-EtFOSA, D_7-MeFOSE. Sample media were Soxhlet extracted together with GFFs in pre-cleaned cellulose thimbles (22 mm x 80 mm), with a 1:1 mixture of petroleum ether:acetone for 18-24 hours. Extracts were reduced to ~8 mL by rotary evaporation, then blown down to ~0.5 mL under nitrogen and solvent exchanged to ethyl acetate for gas chromatography–mass spectrometry (GC/MS) analysis of neutral PFCs. For the purpose of calculating sample recoveries, 10 µL of N,N-Me_2FOSA (10 ng/µL) was added prior to instrumental analysis.

Air sample extracts were measured for neutral PFCs (FTOHs, FOSAs and FOSEs) by GC-positive chemical ionization mass spectrometry (GC-PCIMS) using a Hewlett-Packard 6890 GC-5973 mass selective detector (MSD) in selective ion monitoring (SIM) mode. Methane was used as the reagent gas for PCI. Analytes were separated on a 30 m DB-wax column with 0.25 mm inside diameter and 0.25 µm film thickness. Additional analytical details are given elsewhere.[1] Quantification was based on peak areas of the mass-labeled compounds (spiked before extraction) and the corresponding native compound peak areas. For example, ^{13}C 6:2-FTOH was used to calibrate 6:2-FTOH. In this way, analyte concentrations were adjusted to losses during sample extraction and volume reduction, as well as to signal enhancement or suppression due to potential matrix effects.[2] Because deuterated EtFOSE was not available at the time of the study, D_7-MeFOSE was used to calibrate both MeFOSE and EtFOSE. The air samples were not extracted for ionic compounds during analysis, thus measurement of the less volatile, ionic PFCs such as PFOA and PFOS was not possible. Compound recoveries were as follows: 6:2-FTOH (83% +/- 27), 8:2-FTOH (84% +/- 25), 10:2-FTOH (107% +/- 20), EtFOSA (128% +/- 30), MeFOSA (128% +/- 32), and MeFOSE (189% +/- 35).

References

(1) Shoeib, M.; Harner, T.; Webster, G.; Lee, S.C. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: Implications for human exposure. *Environ. Sci. Technol.* In press DOI: 10.1021/es103562v.

(2) Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Berger, U.; Barber, J. L.; Temme, C. An improved method for

the analysis of volatile polyfluorinated alkyl substances in environmental air samples. *Anal. Bioanal. Chem.* **2007**, *387*, 965-975.

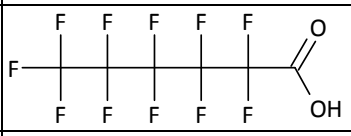
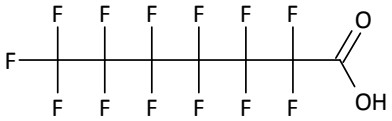
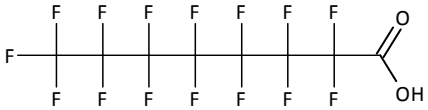
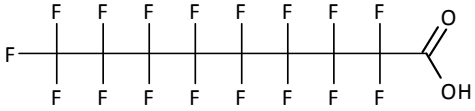
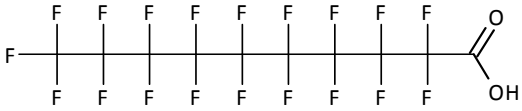
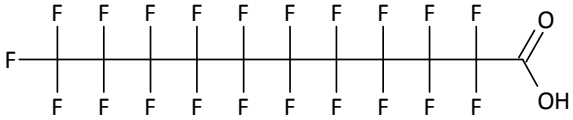
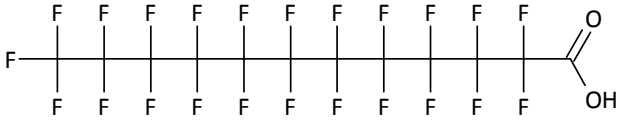
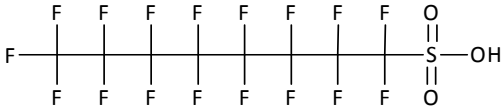
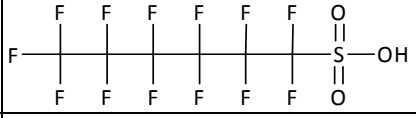
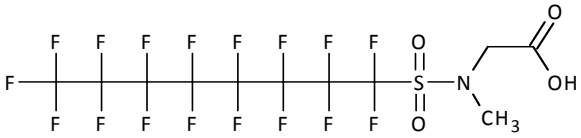
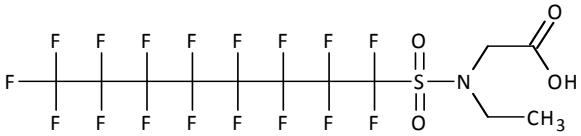
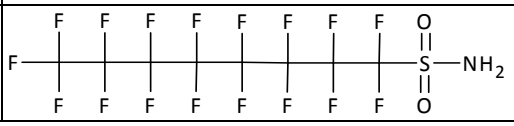
Analysis of Serum Samples

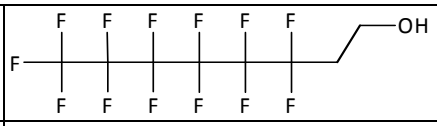
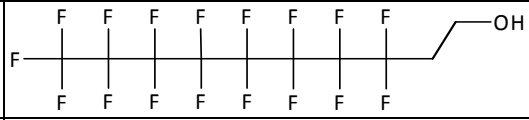
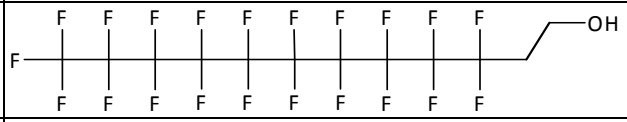
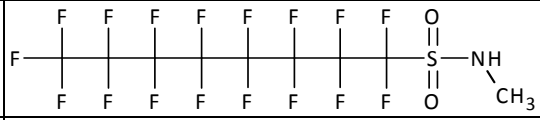
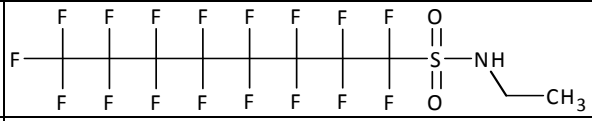
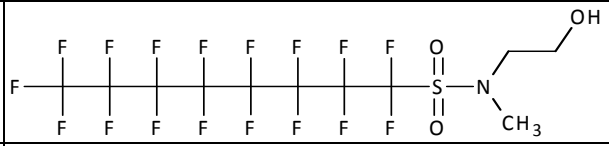
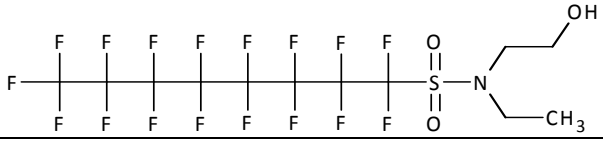
After clotting and centrifugation, serum was recovered from whole blood and stored in polypropylene criovials at -80 °C before being shipped on dry ice to CDC for analysis. PFCs were measured using a modification of a published method based on a solid phase extraction (SPE) system linked directly on-line with HPLC isotope dilution tandem mass spectrometry.[3] Internal standards ($^{13}C_2$-PFOA, $^{13}C_5$-perfluorononanoic acid [PFNA], $^{13}C_2$-perfluorodecanoic acid [PFDA], $^{18}O_2$-perfluorohexane sulfonic acid [PFHxS], $^{18}O_2$-PFOS, $^{18}O_2$-perfluorooctane sulfonamide [PFOSA], D_3- N-methyl perfluorooctane sulfonamidoacetate [N-MeFOSAA], and D_5-N-EtFOSAA) were added to 0.1 mL serum along with 0.1M formic acid. Spiked sera were placed on a Symbiosis on-line SPE system (Spark Holland, Plainsboro, NJ). The system loaded samples onto Polaris C18 SPE cartridges (Varian, Palo Alto, CA). PFCs were eluted off the cartridge directly into the Agilent 1100 HPLC (Agilent Technologies) with separation on a C8 column (Betasil C8, 50 mm x 3 mm, 5 μm; ThermoHypersil-Keystone, Bellefonte, PA) using a methanol-ammonium acetate in water gradient. An API 4000 (Applied Biosystems, Foster City, CA) mass spectrometer was equipped with a negative ion Turbo ion-spray source and one to three transitions per compound were monitored. All compounds were quantified using a relative response ratio to their isotopically-labeled internal standard. The calibration curve was created from standards purchased from Wellington Laboratories (except for N-MeFOSAA, N-EtFOSAA, and PFOS which were provided by 3M), spiked into bovine calf serum, and extracted alongside the samples.

References

(1) Kuklenyik, Z.; Needham, L. L.; Calafat, A. M. Measurement of 18 perfluorinated organic acids and amides in human serum using on-line solid-phase extraction. *Anal. Chem.* **2005**, *77*, 6085-6091.

Supplemental Material, Table 1. Polyfluorinated compound names, structures, and CAS numbers.

Acronym	Chemical Name	Structure	CAS#
PFHxA	Perfluorohexanoic acid		307-24-4
PFHpA	Perfluoroheptanoic acid		375-85-9
PFOA	Perfluorooctanoic acid		335-67-1
PFNA	Perfluorononanoic acid		375-95-1
PFDeA	Perfluorodecanoic acid		335-76-2
PFUA	Perfluoro-undecanoic acid		2058-94-8
PFDoA	Perfluoro-dodecanoic acid		307-55-1
PFOS	Perfluorooctane-sulfonic acid		1763-23-1
PFHxS	Perfluorohexane-sulfonic acid		355-46-4
N-MeFOSAA	N-methyl perfluorooctane sulfonamidoacetate		No CAS#
N-EtFOSAA	N-ethyl perfluorooctane sulfonamidoacetate		No CAS#
PFOSA	Perfluorooctane-sulfonamide		754-91-6

6:2 FTOH	6:2 fluorotelomer alcohol		647-42-7
8:2 FTOH	8:2 fluorotelomer alcohol		678-39-7
10:2 FTOH	10:2 fluorotelomer alcohol		865-86-1
MeFOSA	N-methyl perfluorooctane sulfonamide		31506-32-8
EtFOSA	N-ethyl perfluorooctane sulfonamide		4151-50-2
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol		24448-09-7
EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol		1691-99-2

Supplemental Material, Table 2. Pearson correlations (*r*) among log-transformed PFCs in office air.

	6:2 FTOH	8:2 FTOH	10:2 FTOH	Et FOSA	Me FOSA	Et FOSE	Me FOSE
6:2 FTOH	1	0.49*	0.55*	0.04	0.21	0.14	0.31
8:2 FTOH		1	0.98*	-0.36*	-0.06	0.01	0.22
10:2 FTOH			1	-0.27	-0.01	0.06	0.26
EtFOSA				1	0.61*	0.56*	0.40*
MeFOSA					1	0.55*	0.91*
EtFOSE						1	0.55*
MeFOSE							1

*signifies $p < 0.05$

Supplemental Material, Table 3. Pearson correlations (*r*) among log-transformed PFCs in serum.

	PFOA	PFNA	PFDeA	PFHxS	PFOS
PFOA	1	0.50*	0.25	0.55*	0.53*
PFNA		1	0.78*	0.46*	0.76*
PFDeA			1	0.26	0.73*
PFHxS				1	0.57*
PFOS					1

*signifies $p < 0.05$

Supplemental Material, Table 4. PFC concentrations in serum and office air for each subject by building.

	PFC concentrations in serum (ng/mL)[a]									PFC concentrations in office air (pg/m^3)						
	PFOA	PFNA	PFDeA	PFUA	PFDoA	PFHxS	PFOS	N-MeFOSAA	N-EtFOSAA	6:2-FTOH	8:2-FTOH	10:2-FTOH	EtFOSA	MeFOSA	EtFOSE	MeFOSE
LOD	0.1	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.2	19.5	84.7	24.5	1.26	0.40	0.03	12.6
Building A																
1	5.2	1.7	0.4	<LOD	< LOD	1.3	14.6	0.5	0.4	1790	38200	7810	17.2	9.7	98.6	160
2	4.3	2.6	0.3	0.4	< LOD	2.8	16.5	0.5	< LOD	2940	49200	9240	6.2	12.8	< LOD	176
3	4.1	1.6	0.5	0.3	< LOD	0.8	6.9	< LOD	< LOD	1830	41500	7910	6.7	25.7	20.4	301
4	3.9	2.9	2.5	2.8	1.1	1.7	66.8	< LOD	< LOD	< LOD	26700	4560	9.1	15.4	8.9	179
5	4.7	1.6	0.4	0.6	< LOD	2.1	8.6	< LOD	< LOD	4080	68300	12600	2.6	6.3	27.2	79.7
6	5.8	2.1	0.3	0.3	< LOD	3.3	22.4	< LOD	< LOD	2770	70600	12100	< LOD	5.9	< LOD	86.0
Building B																
1	4.4	1.8	0.3	0.2	< LOD	1.3	16.4	0.3	< LOD	10000	30000	7950	36.9	60.8	63.1	739
2	1.8	1.0	0.2	0.3	< LOD	0.3	4.8	0.3	< LOD	9010	18800	6010	23.2	82.6	100	1170
3	4.0	1.3	0.3	<LOD	< LOD	1.3	13.4	0.9	< LOD	2730	31500	7960	23.5	24.5	44.5	335
4[b]	4.0	1.6	0.3	0.2	< LOD	0.8	9.5	< LOD	< LOD	3520	8870	3610	19.3	67.9	50.6	630
5	8.9	1.1	0.2	<LOD	< LOD	2.2	9.8	0.9	< LOD	1260	23100	4590	13.7	11.3	22.4	151
6	8.1	2.8	0.5	<LOD	< LOD	2.6	14.7	0.3	< LOD	424	13600	2960	10.3	29.8	38.0	237
7	2.8	3.3	1.1	1.1	0.2	0.7	18.1	< LOD	< LOD	3640	13000	5400	20.1	27.9	31.1	302
8	2.2	1.4	0.3	<LOD	< LOD	0.5	6.3	< LOD	< LOD	1820	11800	3430	26.3	120	151	1560
9[c]	3.4	2.1	0.5	NA	< LOD	1.2	16.0	0.4	< LOD	NA	NA	NA	NA	NA	NA	NA
10	8.3	2.4	0.3	0.3	< LOD	1.1	9.4	1.9	0.8	5130	25700	6700	23.3	39.5	50.3	459
11[b]	8.8	1.9	0.4	0.2	< LOD	2.8	19.2	0.9	< LOD	11000	20800	5820	25.6	33.2	68.2	481
12	3.6	1.3	0.3	0.2	< LOD	1.1	5.5	< LOD	< LOD	9100	44700	9490	40.7	162	216	2480
13	3.8	1.6	0.3	0.4	< LOD	2.6	9.0	< LOD	< LOD	429	22300	4470	15.9	29.7	31.1	309
14	3.9	2.6	0.7	0.7	< LOD	2.4	9.7	0.4	< LOD	1860	8670	2580	42.7	41.9	84.0	419
15	5.1	2.1	0.5	0.4	< LOD	7.8	16.2	< LOD	< LOD	3890	10300	3290	7.4	23.2	26.3	134
16	4.1	1.2	0.2	<LOD	< LOD	1.8	10.5	0.4	< LOD	1690	16500	7650	51.2	109	82.8	1300
17	4.6	1.6	0.4	0.2	< LOD	3.1	8.8	0.2	< LOD	1610	11700	2460	13.3	32.0	22.8	298
Other[d]																
1	1.7	1.7	0.4	0.6	< LOD	0.7	9.2	< LOD	< LOD	286	283	138	8.3	11.7	19.6	86.9
2	4.7	1.3	0.3	0.2	< LOD	0.8	10.9	< LOD	< LOD	431	2210	966	21.1	15.0	11.7	82.3
3	1.1	0.6	< LOD	<LOD	< LOD	0.4	2.8	< LOD	< LOD	< LOD	1300	646	26.3	32.5	24.2	237
4	1.5	0.7	< LOD	<LOD	< LOD	0.2	3.4	< LOD	< LOD	417	1010	355	13.5	16.8	< LOD	48.5
5	2.5	1.5	0.3	<LOD	< LOD	12.7	15.6	0.4	< LOD	609	1110	382	20.1	131	70.2	3880
6	4.8	2.2	0.4	0.3	< LOD	3.1	16.4	0.4	< LOD	2520	2090	1250	115	18.2	18.2	86.8
7	2.9	1.2	0.3	0.3	< LOD	2.2	7.6	0.3	< LOD	563	1410	410	47.3	59.0	26.2	364
8	1.8	1.8	0.3	0.2	< LOD	1.1	7.7	< LOD	< LOD	361	430	212	34.7	16.9	17.6	57.8

[a]PFHxA, PFHpA, and PFOSA were undetected in all samples and are not listed (LOD = 0.6, 0.4, and 0.1, respectively).

[b]Air concentrations are the average of duplicate samples.

[c]Air concentrations not available due to malfunctioning air pump.

[d]Includes samples from 5 different buildings