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## Supporting Information

### Human nails analysis as a biomarker of exposure to perfluoroalkyl compounds

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## Materials and Methods

**Reagents.** Potassium perfluorohexane sulfonate (PFHxS, 98%) was purchased from Interchim (Montlucon, France). Potassium perfluorooctane sulfonate (PFOS, 98%) was purchased from Fluka (Steinheim, Germany). Perfluorooctanoate (PFOA, 95%) was purchased from Wako Pure Chemical Industries (Osaka, Japan). Perfluorononanoate (PFNA, 95%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Perfluorodecanoate (PFDA, 96%) and perfluorododecanoate (PFDoA, 97%) were purchased from Acros Organics (Geel, Belgium). Perfluorotetradecanoate (PFTA, 97%) was purchased from Aldrich (Steinheim, Germany). Sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate and perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>]-octanoic acid were purchased from Wellington Laboratories Inc. (Canada). Tetrabutylammonium hydrogensulfate (TBAHS) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99%) were obtained from Acros Organics (Geel, Belgium). HPLC grade ammonium acetate was obtained from Dikma Technology (Richmond, VA). HPLC grade methyl tert-butyl ether (MTBE), methanol, and acetonitrile were purchased from Tedia (Fairfield, OH). Nitric acid (99.999%) and Triton X-100 were purchased from Sigma-aldrich. (St. Louis, MO), hydrogen peroxide and sodium hydroxide (99.999%) from Acros Organics (Geel, Belgium).

**Pretreatment of blood samples.** The blood samples were analyzed as serum after centrifugation and the serum was extracted by ion pair method described by Hansen et al (2001). Briefly, 1 mL of TBAHS (0.5 M) and 2 mL of Na<sub>2</sub>CO<sub>3</sub> buffer (0.25 M) were added into the polypropylene tube containing 0.5 mL of serum sample. The extraction was conducted twice by addition of 5 mL of MTBE and 5 min of shaking. The organic layers were evaporated at room temperature under a nitrogen gas flow. The analytes were redissolved in 1 mL acetonitrile. Then the insoluble impurity was removed by centrifugation (4 °C, 12000 rpm, 30 min). The supernatant was collected and evaporated under a nitrogen gas flow, and reconstituted in 500 µL mixture of acetonitrile and 10 mM ammonium acetate (2:3, v/v). Bovine serum was used as surrogate matrix for determining the recovery and constructing extracted calibration standards.

**Instrumental analysis of PFAA.** Chromatography was performed using an Agilent 1100 HPLC system (Agilent, Palo Alto, CA). A 25 µL aliquot of extract was injected

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onto an Agilent Eclipse Plus C18 column (2.1×100 mm, 3.5 μm, Agilent, Palo Alto, CA) with 10 mM ammonium acetate and acetonitrile as mobile phase initializing with 40% acetonitrile at a flow rate of 250 μL/min and column temperature of 40 °C. The gradient was increased to 90% acetonitrile at 9 min and then held for 2 min. A post time of 8 min was run for equilibration during injection interval. The HPLC system was interfaced to an Agilent 6410 Triple Quadrupole mass spectrometer (Agilent, Santa Clara, CA) operated with electrospray ionization (ESI) in negative mode. The gas temperature and ion spray voltage were maintained at 350 °C and 4000 V. Ions were monitored with a multiple reaction monitoring (MRM) mode, and the parameters involving parent and product ions, and collision energies of each target analyte were detailed in other study (Bao et al., 2009).

### **Literature cited**

Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ. Sci. Technol.* **2001**, 35(4), 766-770.

Bao, J.; Jin, Y. H.; Liu, W.; Ran, X. R.; Zhang, Z. X. Perfluorinated compounds in sediments from the Daliao River system of northeast China. *Chemosphere* **2009**, 77(5), 652-657.

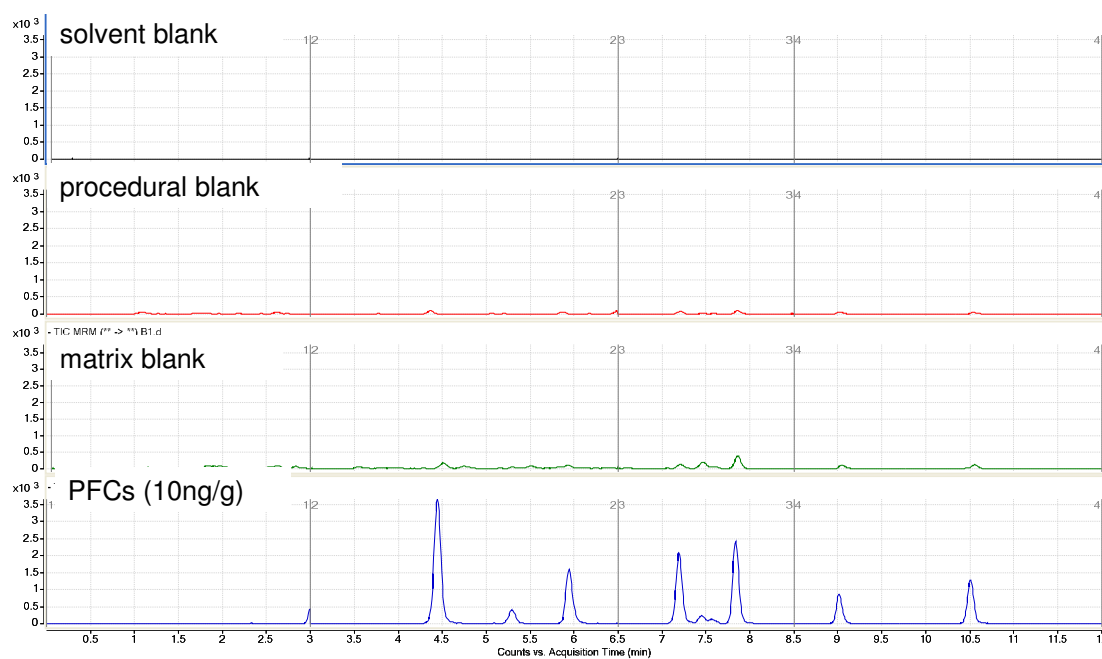


Figure S1 Chromatography of blanks and PFAA standard

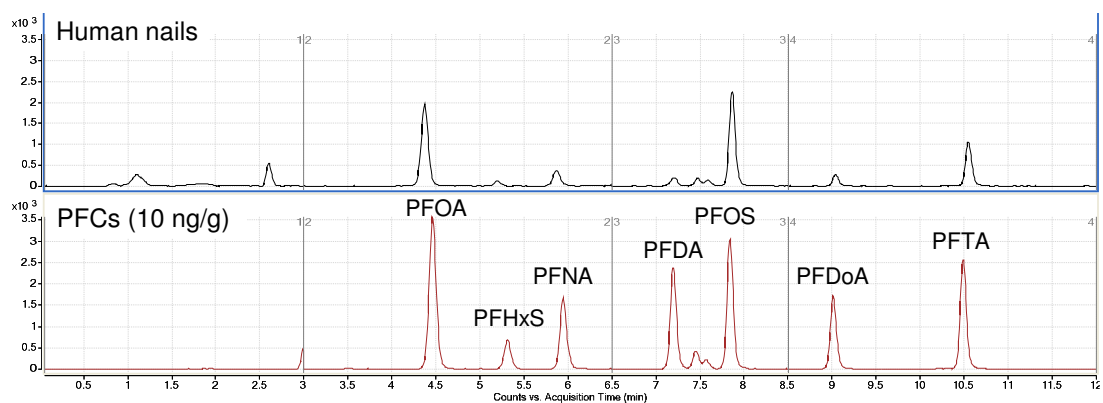


Figure S2 Chromatography of human nails and PFAA standard

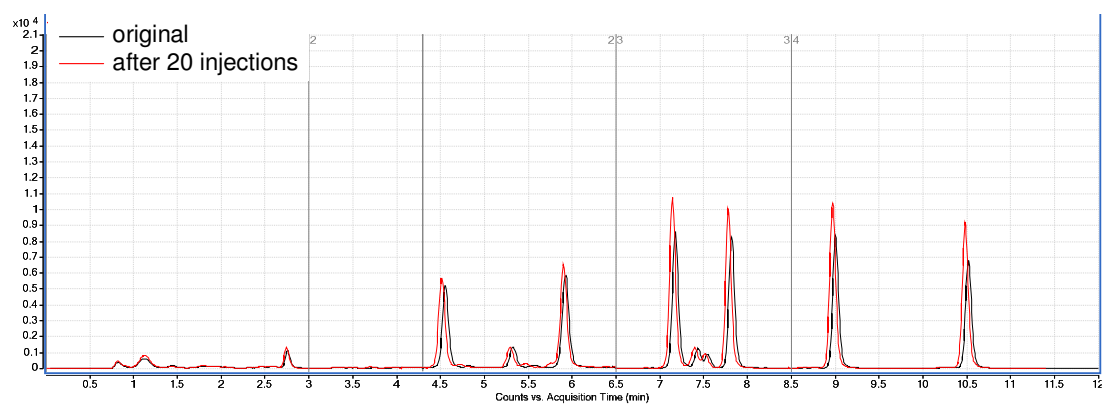


Figure S3 Chromatography of PFAA standard before and after 20 injections of human nails samples

Table S1 Replicate analysis of human nail samples

Subject	PFOS			PFNA			PFDoA			PFTA		
	Conc.(ng/g)		RSD	Conc.(ng/g)		RSD	Conc.(ng/g)		RSD	Conc.(ng/g)		RSD
	No.1	No.2	(%)	No.1	No.2	(%)	No.1	No.2	(%)	No.1	No.2	(%)
1	101	80.4	16.3	25.2	28.4	8.28	15.2	13.7	7.34	25.7	28.6	7.64
2	40.3	46.9	10.7	17.4	15.0	10.3	17.2	19.6	9.22	13.6	16.2	12.2
3	45.0	34.8	18.2	10.7	9.03	12.1	8.47	10.4	14.5	6.28	4.94	16.9
4	34.0	30.1	8.50	8.90	7.31	13.9	9.58	8.38	9.45	8.83	10.9	14.9
5	63.6	48.7	18.9	9.84	11.3	9.88	18.4	21.7	11.6	12.6	11.7	5.79
6	56.2	56.5	0.43	7.62	8.77	9.95	13.4	15.6	10.7	7.80	8.81	8.57

Table S2 PFOS concentrations measured in paired fingernail samples without, with once or multiple washing

Pair	Unwash vs. Once wash			Once wash vs. Twice wash			Twice wash vs. Thrice wash		
	unwash	Once wash	% diff	Once wash	Twice wash	% diff	Twice wash	Thrice wash	% diff
	(ng/g)	(ng/g)	(%)	(ng/g)	(ng/g)	(%)	(ng/g)	(ng/g)	(%)
1	47.2	37.9	20	55.9	44.2	21	9.05	8.86	2
2	56.6	25.9	54	37.2	32.8	12	40.0	45.1	-13
3	70.7	34.7	51	57.2	20.9	63	25.5	34.0	-33
4	14.5	11.2	23	13.4	10.5	22	31.4	28.5	9
5	39.2	14.2	64	9.82	7.83	20	17.8	15.6	12
6	106	31.9	70	6.33	5.87	7	5.62	6.53	-16

Table S3 Correlation between PFAA concentrations in serum, fingernail, and toenail samples collected concurrently or with an interval

	Sampling interval (month)	PFOS	PFNA	PFDA	PFDoA	PFTA
Fingernail/toenail	0	0.54**	0.32*	0.47**	0.42**	0.61**
	2	0.63**	0.16 <sup>-</sup>	0.23 <sup>-</sup>	0.28*	0.29*
	4	0.70**	0.17 <sup>-</sup>	0.20 <sup>-</sup>	0.23 <sup>-</sup>	0.02 <sup>-</sup>
Fingernail/serum	0	0.00 <sup>-</sup>	0.38**	-0.11 <sup>-</sup>		
	2	0.07 <sup>-</sup>	0.14 <sup>-</sup>	-0.03 <sup>-</sup>		
	4	0.09 <sup>-</sup>	0.12 <sup>-</sup>	-0.01 <sup>-</sup>		
Toenail/serum	0	0.05 <sup>-</sup>	0.05 <sup>-</sup>	0.02 <sup>-</sup>		
	4	0.12 <sup>-</sup>	0.12 <sup>-</sup>	0.03 <sup>-</sup>		
	6	0.39*	0.14 <sup>-</sup>	0.30 <sup>-</sup>		

Correlation coefficient donated as  $p < 0.05$  (\*),  $p < 0.01$  (\*\*),  $p > 0.05$  (°), analyzed by Spearman analysis