Supplementary information

Characterization and dermal bioaccessibility of residual- and listed PFAS ingredients in cosmetic products

Shahla Namazkar,[1*] Oddny Ragnarsdottir,[2] Anton Josefsson,[1] Felice Branzell,[1] Sebastian Abel,[1] Mohamed Abou-Elwafa Abdallah,[2] Stuart Harrad[2] and Jonathan P. Benskin[1*]

1 Department of Environmental Science, Stockholm University, Stockholm, Sweden,
2 School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, UK

*Corresponding authors: Shahla.Namazkar@aces.su.se, Jon.Benskin@aces.su.se

Table S1. Chemical composition of synthetic human sweat applied in this study (1).

Sweat Ingredients	Measured Conc.	Company
Electrolytes and Ionic Constituents	(g/L)	
Sodium Sulfate	5.83×10^{-2}	Sigma Aldrich
Copper Chloride anhydrous	1.60×10^{-4}	Merck
Ammonium Hydroxide	1.82×10^{-1}	Fisher
Iron Sulfate Heptahydrate	2.72×10^{-3}	Fisher
Lead- Reference Solution 1000 ppm	2.49 x 10-5	Sigma Aldrich
Manganese- Reference Solution 1000 ppm	1.38×10^{-4}	Sigma Aldrich
Nickel- Reference Solution 1000 ppm	2.46×10^{-5}	Sigma Aldrich
Zinc - Reference Solution 1000 ppm	8.5×10^{-4}	Sigma Aldrich
Sodium Bicarbonate	2.52×10^{-1}	FSA
Potassium Chloride	4.55×10^{-1}	VWR
Magnesium Chloride Hexahydrate	1.67×10^{-2}	Sigma Aldrich
Sodium Phosphate Anhydrous Monobasic	4.84×10^{-2}	Sigma Aldrich
Calcium Chloride Dihydrate	7.65×10^{-1}	Fisher
Sodium Chloride	5.84×10^{-2}	Fisher
Organic Acids and Carbohydrates		
Acetic Acid	7.81×10^{-3}	Sigma Aldrich
Butyric Acid	2.11×10^{-4}	Sigma Aldrich
D (+) –Glucose	3.06×10^{-2}	Sigma Aldrich
Lactic Acid	1.57×10^{0}	Sigma Aldrich
Essential Amino Acid Mix	2.5 mM each: 17 AA	Sigma Aldrich
Nitrogenous Substances		
Ammonium Chloride	9.92 x 10-3	Fisher
Urea	6.01×10^{-1}	Sigma Aldrich
Creatinine	9.50×10^{-3}	Sigma Aldrich

15

16 **Table S2.** Mobile phase gradient program for mono- and diPAPs analysis.

LC Gradient Program			LC Flow Rate
Time (min)	Mobile phase A (%)[1]	Mobile Phase B (%)[2]	(mL/min)
0	80	20	0.3
4	0	100	0.3
6	0	100	0.3
7.5	80	20	0.3
9	80	20	0.3

17 [1] Mobile phase A: 95 % water and 5 % methanol containing 2 mM ammonium acetate and 5
18 mM 1-methyl piperidine (1-MP).

19 [2] Mobile phase B: 75 % methanol, 20 % acetonitrile, and 5 % water containing 2 mM
20 ammonium acetate and 5 mM 1-methyl piperidine (1-MP).

21

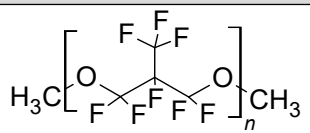
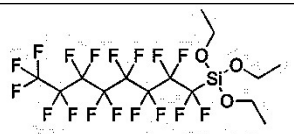
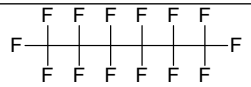
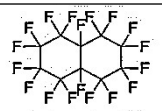
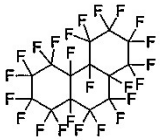
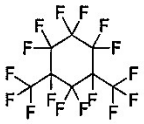
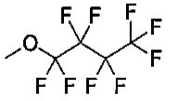
Table S3. The target analytes, their precursors, quantitative and qualitative ions, and the internal and native standards that were used to quantify the target analytes (2).

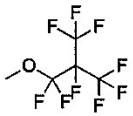
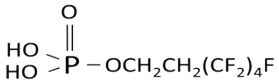
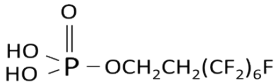
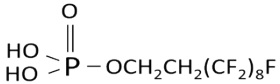
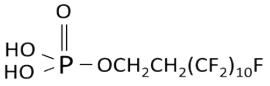
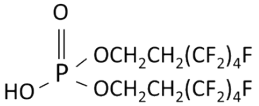
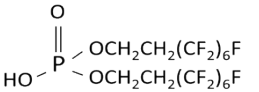
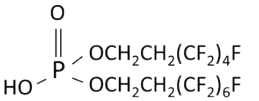
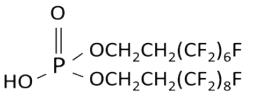
Target analytes	Precursor ion (m/z)	Quantitative ion (m/z)	Qualitative ion (m/z)	Internal standard	Transition of internal standard	Native standard
PFBA	213	169	149	$^{13}C_4$-PFBA	217>172	PFBA
PFPeA	263	219	169	$^{13}C_5$-PFPeA	266>223	PFPeA
PFHxA	313	269	119	$^{13}C_2$-PFHxA	315>270	PFHxA
PFHpA	363	319	169	$^{13}C_4$-PFHpA	367>322	PFHpA
PFOA	413	169	369	$^{13}C_4$-PFOA	417>372	PFOA
PFNA	463	419	219	$^{13}C_5$-PFNA	468>423	PFNA
PFDA	513	469	269	$^{13}C_2$-PFDA	515>470	PFDA
PFUnDA	563	519	269	$^{13}C_2$-PFUnDA	565>520	PFUnDA
PFDoDA	613	569	169	$^{13}C_2$-PFDoDA	615>570	PFDoDA
PFTriDA	663	619	169	$^{13}C_2$-PFDoDA	615>570	PFDoDA
PFTeDA	713	669	169	$^{13}C_2$-PFDoDA	615>570	PFTeDA
PFBS	299	80	99	$^{18}O_2$-PFHxS	403>84	PFBS
PFHxS	399	80	99	$^{18}O_2$-PFHxS	403>84	PFHxS
PFOS	499	80	99	$^{13}C_4$-PFOS	503>80	PFOS
PFDS	599	80	99	$^{13}C_4$-PFOS	503>80	PFDS
4:2 monoPAP	343	97	323	$^{13}C_2$-6:2 monoPAP	445>97	4:2 monoPAP
6:2 monoPAP	443	97	423	$^{13}C_2$-6:2 monoPAP	445>97	6:2 monoPAP
8:2 monoPAP	543	97	523	$^{13}C_2$-8:2 monoPAP	545>97	8:2 monoPAP
10:2 monoPAP	643	97	623	$^{13}C_2$-8:2 monoPAP	545>97	10:2 monoPAP
4:2/4:2 diPAP	589	343	97	$^{13}C_4$-6:2/6:2 diPAP	793>445	4:2/4:2 diPAP
4:2/6:2 diPAP	689	443	343	$^{13}C_4$-6:2/6:2 diPAP	793>445	6:2/6:2 diPAP
6:2/6:2 diPAP	789	443	97	$^{13}C_4$-6:2/6:2 diPAP	793>445	6:2/6:2 diPAP
6:2/8:2 diPAP	889	443	543	$^{13}C_4$-6:2/6:2 diPAP	793>445	6:2/8:2 diPAP
8:2/8:2 diPAP	989	543	97	$^{13}C_4$-8:2/8:2 diPAP	993>545	8:2/8:2 diPAP
6:2/10:2 diPAP	989	443	643	$^{13}C_4$-8:2/8:2 diPAP	993>545	8:2/8:2 diPAP

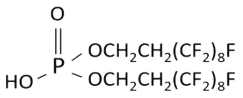
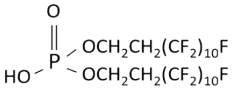
Table S4. Oven temperature program of used method in GC-ECD.

No	Run time [min]	Rate [°C/min]	Target value [°C]	Hold time [min]
1	0.000	Run		
2	5.000	0.00	70	5.00
3	11.000	4.00	90	1.00
4	31.003	15.00	290	6.67
5	31.003	Stop Run		

Table S5. Physicochemical properties of PFAS ingredients and mono- and diPAPs. All properties are "predicted median" and provided by CompTox Chemistry Dashboard (https://comptox.epa.gov/dashboard).

Perfluorinated Compounds	Structure	Molecular Formula	Molecular Mass (g/mol)	Henry's Law (atm-m^3/mole)	Boiling Point (°C)	Vapor Pressure (mmHg)	Water Solubility (mol/L)	LogKoa	LogKow
Polyperfluoromethyl-isopropyl ether		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Perfluorooctyl triethoxysilane		C14H19F13O3Si	510.4	5.6E-06	209	1.2E-01	2.3E-07	5.69	6.57
Perfluorohexane		C6F14	338.0	1.3E-02	53.7	2.2E+02	2.3E-05	0.959	5.22
Perfluorodecalin		C10F18	462.1	1.5E-02	143	6.8E+00	7.0E-06	3.26	6.91
Perfluoroperhydro-phenanthrene		C12F24	624.1	5.9E-06	208	4.2E-02	7.6E-07	3.93	8.47
Perfluoro-1,3-dimethylcyclohexane		C8F16	400.1	1.2E-02	96.1	8.9E+01	2.0E-06	2.28	6.23
Methyl perfluorobutyl ether		C5H3F9O	250.1	1.0E-02	46.2	3.8E+02	2.7E-04	1.59	3.74

Methyl perfluoroisobutyl ether		C5H3F9O	250.1	1.0E-02	37.9	6.3E+02	6.6E-04	1.6	3.68
4:2 monoPAP		C6H6F9O4P	344.1	4.9E-09	295.9	3.9E-05	3.1E-04	9.688	2.99
6:2 monoPAP		C8H6F13O4P	444.1	1.4E-11	244	5.2E-04	5.7E-03	7.84	3.46
8:2 monoPAP		C10H6F17O4P	544.1	1.5E-11	257	1.6E-04	1.9E+00	7.93	5.0
10:2 monoPAP		C12H6F21O4P	644.1	1.6E-11	313	8.0E-05	5.8E-05	7.96	6.47
4:2 diPAP		C12H9F18O4P	590.2	1.5E-11	261	1.3E-04	1.6E+00	8.48	5.2
6:2 diPAP		C16H9F26O4P	790.2	1.4E-11	286	1.9E-05	2.2E+00	9.08	8.13
4:2/6:2 diPAP		C14H9F22O4P1	690.2	1.6E-11	271	3.5E-05	5.1E-06	8.75	6.75
6:2/8:2 diPAP		C18H9F30O4P	890.2	1.6E-11	310	4.0E-05	2.6E+00	9.06	9.39

8:2 diPAP		C20H9F34O4P	990.2	1.1E-10	311	1.6E-07	5.0E-06	9.79	12.0
10:2 diPAP		C24H9F42O4P	1190.2	1.3E-10	321	3.6E-09	5.2E-06	10.6	15.1

30

Table S6. LC-MS/MS method accuracy as % recovery (spike recovery), method precision as % RSD (n = 3). The fortification amount was 10 ng per analyte.

Target polar analytes	PFAS-free cosmetic		Sweat incubated with PFAS-free cosmetic	
	Average recovery [%]	RSD [%]	Average recovery [%]	RSD [%]
PFBA	72	25	105	1
PFPeA	68	6	98	0.5
PFHxA	85	14	112	0.6
PFHpA	73	6	102	2
PFOA	78	20	113	4
PFNA	79	16	106	1
PFDA	80	14	108	2
PFUnDA	68	9	96	4
PFDoDA	80	14	110	4
PFTriDA	99	15	106	11
PFTeDA	43*	7	89	14
PFBS	44	33	90	0.7
L-PFHxS	68	15	97	1
PFOS-80	74	10	98	0.8
PFDS	64	35	79	2
4:2 monoPAP	39	17	59	10
6:2 monoPAP	74	13	85	5
8:2 monoPAP	46	12	54	3
10:2 monoPAP	13	54	21	11
4:2/4:2 diPAP	39	34	138	20
6:2/6:2 diPAP	92	14	119	2
6:2/8:2 diPAP	22	6	34	5
8:2/8:2 diPAP	85	7	108	6

*n=2 replicates

Table S7. GC-ECD method accuracy as % recovery (spike recovery), method precision as % RSD (n = 3). The fortification amount was 12.5 µg per analyte.

Target non-polar analytes	PFAS-free cosmetic		Sweat incubated with PFAS-free cosmetic	
	Average recovery [%]	RSD [%]	Average recovery [%]	RSD [%]
Perfluorohexane	N/A	N/A	N/A	N/A
Methyl perfluoro(iso)butyl ether	49	7	73	20
Perfluorodimethyl cyclohexane	52	16	77	3
Perfluorodecalin	82	4	56	2
Perfluoroperhydrophenanthrene	82	6	84	5
Perfluorooctyl triethoxysilane	44	6	57	7

Table S8. The average concentration of PFCAs (ng/g) in cosmetics and sweat and LODs.

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA
Cosmetic products	LOD	2.63	1.17	1.26	1.18	0.86	1.28	1.40	1.08	0.30	1.14	1.92
	Mask 2	29300	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mask 3	22500	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Concealer	23.73	52.00	23.63	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Foundation/BB cream	265	387	1290	332	17.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Loose Powder	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sweat	LOD	0.71	0.32	0.34	0.32	0.23	0.34	0.38	0.29	0.08	0.31	0.52
	Mask 2	169	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mask 3	149	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Concealer	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Foundation/BB cream	1.45	2.69	9.79	1.38	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Loose Powder	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

41 **Table S9.** The average concentration of mono- and diPAPs (ng/g) in cosmetics and sweat and LODs.

		4:2 monoPAP	6:2 monoPAP	8:2 monoPAP	10:2 monoPAP	4:2/4:2 diPAP	4:2/6:2 diPAP	6:2/6:2 diPAP	6:2/8:2 diPAP	8:2/8:2 diPAP
Cosmetic products	LOD	1.59	2.02	4.87	30.83	2.95	2.45	2.45	5.95	4.28
	Mask 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mask 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Concealer	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Foundation/BB cream	<LOD	151000	<LOD	<LOD	<LOD	17900	2427000	<LOD	<LOD
	Loose Powder	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sweat	LOD	0.43	0.54	1.31	8.30	0.80	0.66	0.66	1.60	1.15
	Mask 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mask 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Concealer	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Foundation/BB cream	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Loose Powder	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

42

43

Table S10. The average concentration of non-polar/volatile PFAS (ng/g) in cosmetics and sweat and LODs.

		Perfluorohexane	Methyl perfluoro(iso)butyl ether	Perfluoro-1,3-dimethyl cyclohexane	Perfluorodecalin	Perfluoroperhydrophenanthrene	Perfluorooctyltriethoxysilane
Cosmetic products	LOD	N/A	17900	190	130	370	30900
	Mask 2	N/A	N/A	504700	840800	132500	N/A
	Mask 3	N/A	875800	<LOD	<LOD	<LOD	<LOD
	Concealer	N/A	<LOD	<LOD	<LOD	<LOD	164000
	Foundation/BB cream	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Loose Powder	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
Sweat	LOD	N/A	1250	7	6.2	13	1090
	Mask 2	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Mask 3	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Concealer	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Foundation/BB cream	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Loose Powder	N/A	<LOD	<LOD	<LOD	<LOD	<LOD
	Treatment	N/A	<LOD	<LOD	<LOD	<LOD	<LOD

Table S11. The concentration of TF (µg F/g) and polar/non-polar EOF (µg F/g) in cosmetics and LODs.

Cosmetic products	**TF (µg F/g)**	**EOF($_{polar}$) (µg F/g)**	**EOF($_{non-polar}$) (µg F/g)**
Mask 2	10581.04 ± 904	36.6 ± 12	935.65 ± 306
Mask 3	595.56	32.99	377.86 ± 51
Concealer	797.02	3.91	730.57 ± 282
Foundation/BB cream	3307.21	3106.3	<7.06
Loose powder	6006.30	<0.33	37.75 ± 6
Treatment (PFAS-free)	<33.2	<0.33	<7.06

References

1. Stefaniak AB, Harvey CJ. Artificial Skin Surface Film Liquids. US20080311613A1. https://patents.google.com/patent/US20080311613A1/en. 2008.

2. Schultes L, Vestergren R, Volkova K, Westberg E, Jacobson T, Benskin JP. Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: implications for environmental emissions and human exposure. Environ Sci: Processes Impacts. 2018;20(12):1680–90.