Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.
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Temporal trends of suspect- and target-per/polyfluoroalkyl substances (PFAS), extractable organic fluorine (EOF) and total fluorine (TF) in pooled serum from first-time mothers in Uppsala, Sweden, 1996-2017

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Targeted method validation, intercomparison, and ongoing QC

Method B

Extraction and clean up

0.5 g serum was pre-weighed into a 13 mL PP-centrifuge tube. The serum sample was then spiked with a mixture of isotopically labeled standards (50 µL at 10 pg/µL) in MeOH. A volume of 4 mL of ACN was added and the sample was subsequently vortex mixed for 30 seconds. The sample was ultrasonicated for 15 minutes at room temperature and then centrifuged for 10 min at 3000 rpm. The supernatant was transferred into a new 13 mL PP-tube. The extraction procedure was repeated with 4 mL acetonitrile and the combined extracts were concentrated to 1 mL using a TurboVap evaporator (Biotage).

Cleanup of the extract was carried out using 25 mg ENVI-Carb and 50 µl glacial acetic acid in an eppendorf tube. The concentrated extracts were transferred to the eppendorf tubes and vortex-mixed thoroughly for 30 seconds and then centrifuged at 10000 rpm for 10 min. 500 µL was transferred to a clean eppendorf tube. 50 µl recovery standard ($^{13}C_8$-PFOS and $^{13}C_8$-PFOA at 10 pg/µl) was added together with 200 µl 4 mM NH_4OAc in water. 200 µL was transferred to a 300 µl autosampler vial (PP) for instrumental analysis.

Instrumental analysis

All extracts were analyzed by ultra-performance liquid chromatography coupled to tandem mass spectrometer (UPLC/MS/MS). The UPLC was an Acquity UPLC system (Waters) equipped with a BEH C18 (1.7 µm particles, 50 × 2.1 mm) analytical separation column (Waters). A volume of 5 µL extract was injected in the partial loop injection mode. Mobile phase A consisted of 90% water and 10% acetonitrile with 2 mM ammonium acetate while Mobile phase B consisted of 99% acetonitrile and 1% water with 2 mM ammonium acetate. A gradient elution with a flow rate of 0.4 mL/min was applied. The initial conditions were 90% of solvent (A) and 10% of solvent (B). The percentage of B was linearly increased to 100% from injection to 5 min and held at 100% B until 7.5 min. Initial conditions at 90% A 10% B were regained at 8 min and held until 10 min for column equilibration. The detection system was a Xevo-TQS triple quadrupole mass spectrometer (Waters), operated in negative electrospray ionization (ESI^-) mode. The following instrumental parameters were used: Capillary voltage 1.0 kV, source temperature 150°C, desolvation temperature 350°C, desolvation gas flow 650 L/h and cone gas flow 150 L/h. The mass spectrometer was operated in multiple reaction monitoring mode (MRM). MRM transitions and further method details can be found in Gyllenhammar et al. 2018.[16]

Method C

Extraction and clean up

0.5 g serum was pre-weighed into a 13 mL PP-centrifuge tube. The serum sample was then spiked with a mixture of isotopically labeled standards (50 µL at 10 pg/µL) in MeOH. A volume of 3 mL of AcN was added and the sample was subsequently vortex mixed for 30 seconds. The sample was ultrasonicated for 15 minutes at room temperature and then centrifuged for 10 min at 3000 rpm. The supernatant was transferred into a new 13 mL PP-tube. The extraction procedure was repeated with 3 mL acetonitrile and the combined extracts were concentrated to 1 mL using a TurboVap evaporator (Biotage). 9 mL of HPLC grade water was added. The extract was vortex mixed thoroughly.

For extract cleanup, an OASIS WAX SPE column (6 cc, 150 mg sorbent, 30 µm particles) (Waters, Milford, USA) was washed and conditioned with 6 ml 1% ammonium hydroxide solution in methanol, 6 ml methanol, and 6 ml water. The sample extract was ultrasonicated for 5 min before loading onto the SPE column. The column was then washed with 1 mL 2% formic acid in HPLC grade water and then with 2 mL of HPLC grade water (discarded). The column was allowed to run dry. The target compounds were eluted stepwise, first with 1 mL MeOH (Fraction 1, containing the neutral targets) and then washed with 2 mL MeOH (discarded). Then with 4 mL 1% NH_4OH in MeOH (Fraction 2, containing the ionic targets). 150 µl of Fraction 1 was transferred 300 µl autosampler vial (PP) and 50

µl recovery standards ($^{13}C_8$-PFOS and $^{13}C_8$-PFOA at 10 pg/µl) was added. Fraction 2 was evaporated to near dryness and resolved in 150 µL MeOH and 50 µl recovery standard ($^{13}C_8$-PFOS and $^{13}C_8$-PFOA 10 pg/µl) was added. The final extract was vortex mixed and ultrasonicated for 5 minutes and then transferred to a 300 µl autosampler vial (PP) for instrumental analysis.

Instrumental analysis

All extracts were analyzed by ultra-performance liquid chromatography coupled to tandem mass spectrometer (UPLC/MS/MS). The UPLC instrumentation was an Acquity UPLC system (Waters) with a BEH C18 (1.7 µm particles, 50 × 2.1 mm) analytical separation column (Waters). A volume of 5 µL extract was injected in the partial loop injection mode. The mobile phases used had the composition; Mobile phase A 95% water and 5% acetonitrile with 2 mM ammonium acetate and 5 mM methyl piperidine (1-MP) and Mobile phase B 75% methanol, 20% acetonitrile and 5% water with 2 mM ammonium acetate and 5 mM 1-MP. A gradient elution with a flow rate of 0.3 mL/min was applied. The initial conditions were 90% of solvent (A) and 10% of solvent (B). The percentage of B was linearly increased to 100% from injection to 5 min and held at 100% B until 7 min. Initial conditions at 90% A were regained at 7.5 min and held until 11 min for column equilibration. The detection system was a Xevo-TQS triple quadrupole mass spectrometer (Waters), operated in negative electrospray ionization (ESI^-) mode. The following instrumental parameters were used: Capillary voltage 3.0 kV, source temperature 150°C, desolvation temperature 350°C, desolvation gas flow 650 L/h and cone gas flow 150 L/h. The mass spectrometer was operated in multiple reaction monitoring mode (MRM). MRM transitions and further method details can be found in Gebbink et al. 2015.[17]

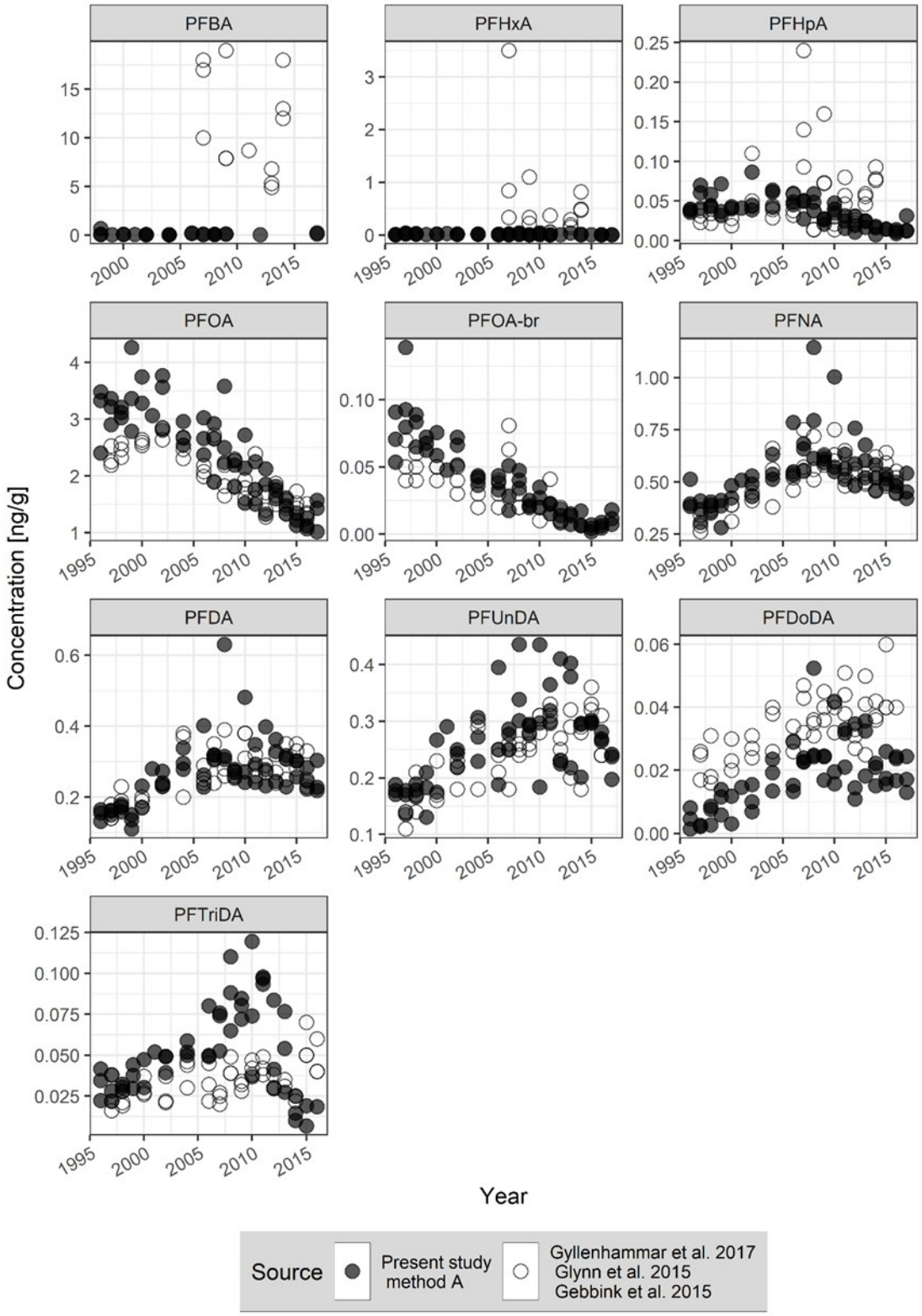

Figure S1: Comparison of concentration time trends with previous studies on the same cohort for the time period 1996–2017.

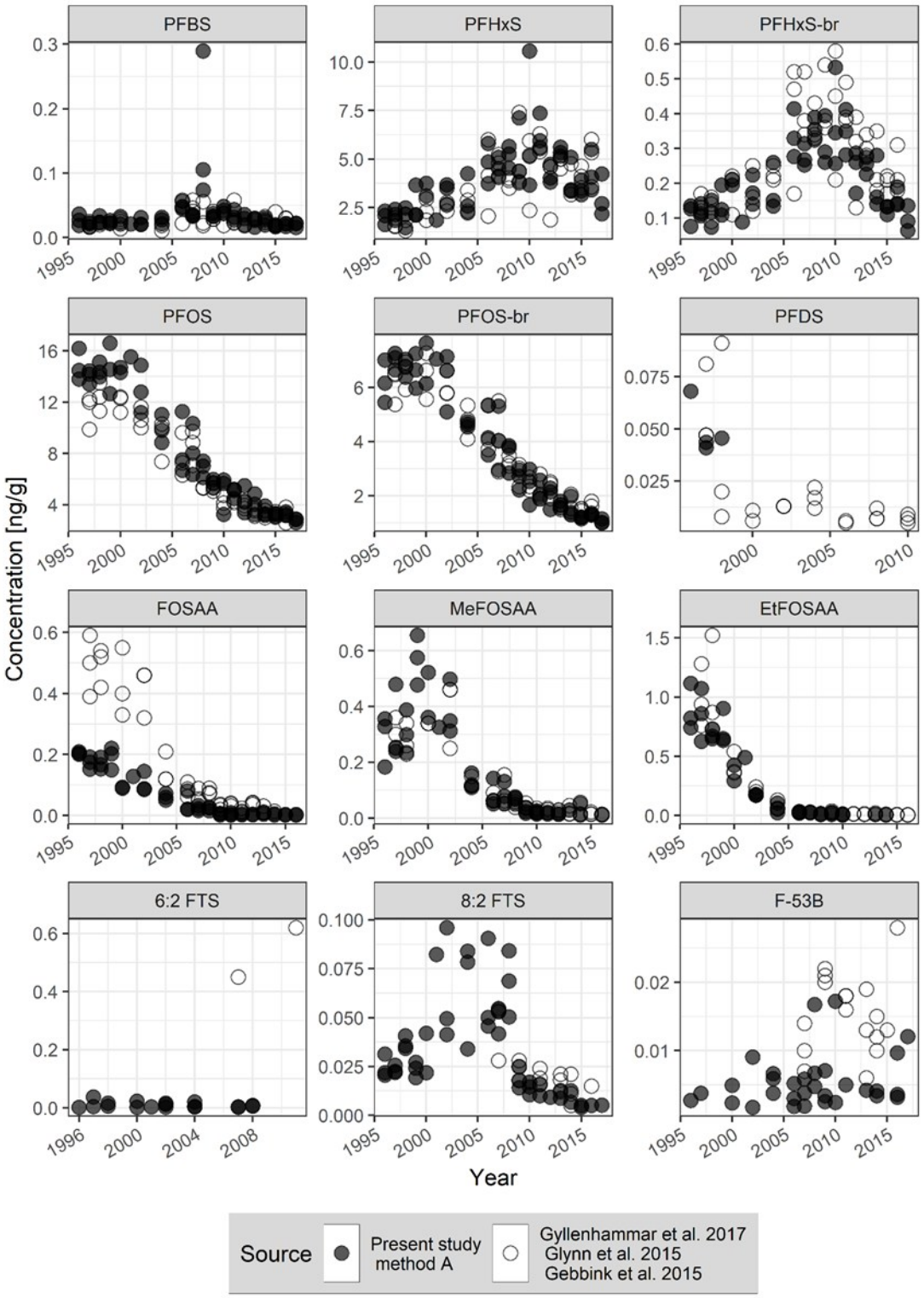

Figure S2: Comparison of concentration time trends with previous studies[12,17,29] for 1996–2017.

Table S1: List of target ions with formula and internal standard (IS). Marked in white if an exactly-matched authentic standard was used for quantification, otherwise marked in blue (i.e. semi-quantitative).

		Compound	Abbreviation	Formula	mass [Da]	IS
1	C4	Perfluorobutanoate	PFBA	C4F7O2	212.9786	M4PFBA
2	C5	Perfluoropentanoate	PFPeA	C5F9O2	262.9754	M2PFDoDA
3	C6	Perfluorohexanoate	PFHxA	C6F11O2	312.9722	M4PFHpA
4	C7	Perfluoroheptanoate	PFHpA	C7F13O2	362.969	M4PFHpA
5	C8	Perfluorooctanoate linear isomer	lin-PFOA	C8F15O2	412.9658	M4PFOA
6		Perlfuorooctanoate branched isomers	br-PFOA	C8F15O2	412.9658	M4PFOA
7	C9	Perfluorononanoate	PFNA	C9F17O2	462.9626	M5PFNA
8	C10	Perfluorodecanoate	PFDA	C10F19O2	512.9594	M2PFDA
9	C11	Perfluoroundecanoate	PFUnDA	C11F21O2	562.9562	M2PFUnDA
10	C12	Perfluorododecanoate	PFDoDA	C12F23O2	612.953	M2PFDoDA
11	C13	Perfluorotridecanoate	PFTriDA	C13F25O2	662.9498	M2PFDoDA
12	C14	Perfluorotetradecanoate	PFTeDA	C14F27O2	712.9466	M2PFDoDA
13	C15	Perfluoropentadecanoate	PFPeDA	C15F29O2	762.9434	M2PFDoDA
14	C16	Perfluorohexadecanoate	PFHxDA	C16F31O2	812.9402	M2PFDoDA
15	C18	Perfluorooctadecanoate	PFOcDA	C18F35O2	912.9338	M2PFDoDA
16	C4	Perfluorobutanesulfonate	PFBS	C4F9O3S	298.9424	18O2-PFHxS
17	C5	Perfluoropentanesulfonate	PFPeS	C5F11O3S	348.9392	18O2-PFHxS
18	C6	Perfluorohexanesufonate lin.	lin-PFHxS	C6F13O3S	398.936	18O2-PFHxS
19		Perfluorohexanesulfonate br.	br-PFHxS	C6F13O3S	398.936	18O2-PFHxS
20	C7	Perfluoroheptanesulfonate lin.	lin-PFHpS	C7F15O3S	448.9328	M4PFOS
21		Perfluoroheptanesulfonate br.	br-PFHpS	C7F15O3S	448.9328	M4PFOS
22	C8	Perfluorooctanesulfonate lin.	lin-PFOS	C8F17O3S	498.9296	M4PFOS
23		Perfluorooctanesulfonate br.	br-PFOS	C8F17O3S	498.9296	M4PFOS
24	C9	Perfluorononanesulfonate lin.	lin-PFNS	C9F19O3S	548.9264	M4PFOS
25		Perfluorononanesulfonate br.	br-PFNS	C9F19O3S	548.9264	M4PFOS
26	C10	Perfluorodecanesulfonate lin.	lin-PFDS	C10F21O3S	598.9232	M4PFOS
27		Perfluorodecanesulfonate br.	br-PFDS	C9F19O3S	548.9264	M4PFOS
28	C11	Perfluoroundecanesulfonate	PFUnDS	C11F23O3S	648.92	M4PFOS
29		Sodium Dodecafluoro-3H-4,8,-dioxanonanoate	NaDONA	C7F12HO4	376.9683	M4PFOA
30		Potassium 9-chlorohexadecafluoro-3-oxanonanoe-1-sulfonate	9Cl-PF3ONS	C8ClF16O4S	530.895	M2PFDA
31		Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	C10ClF20O4S	630.8886	M2PFDA
32		3:3 Fluorotelomer carbonate	3:3 FTA (FPrPA)	C6F7H4O2	241.0099	M2PFHxA
33		5:3 Fluorotelomer carbonate	5:3 FTA (FPePA)	C8F11H4O2	341.0035	M4PFOA
34		7:3 Fluorotelomer carbonate	7:3 FTA (FHpPA)	C10F15H4O2	440.9971	M2PFDA
35		4:2 Fluorotelomer sulfonate	4:2 FTS	C6F9H4O3S	326.9737	M2 6:2 FTS
36		6:2 Fluorotelomer sulfonate	6:2 FTS	C8F13H4O3S	426.9673	M2 6:2 FTS
37		8:2 Fluorotelomer sulfonate	8:2 FTS	C10F17H4O3S	526.9609	M2 6:2 FTS
38		Perfluorooctane sulfonamide lin,	lin-FOSA	C8F17HNO2S	497.9456	M8FOSA
39		Perfluorooctane sulfonamide br.	br-FOSA	C8F17HNO2S	497.9456	M8FOSA
40		Methyl perfluorooctane sulphonamide	MeFOSA	C9F17H3NO2S	511.9613	d3-MeFOSA
41		Ethyl perfluorooctane sulfonamide	EtFOSA	C10F17H5NO2S	525.9769	d5-EtFOSA
42		Perfluorooctane sulfonamidoacetate lin.	lin-FOSAA	C10F17H3NO4S	555.9511	d3-MeFOSAA
43		Perfluorooctane sulfonamidoacetate br.	br-FOSAA	C10F17H3NO4S	555.9511	d3-MeFOSAA
44		Methyl perfluorooctane sulfonamidoacetate	MeFOSAA	C11F17H5NO4S	569.9667	d3-MeFOSAA
45		Ethyl perfluorooctane sulfonamidoacetate	EtFOSAA	C12F17H7NO4S	583.9824	d5-EtFOSAA
46		Methyl perfluorooctane sulfonamidoethanol	MeFOSE	C9F17H5NOS	497.982	d3-MeFOSA
47		Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	C10F17H7NOS	511.9977	d5-EtFOSA
48		4:2 Fluorotelomer phosphate diester	4:2 diPAP	C12F18H8O4P	588.9872	M4 6:2/6:2 diPAP
49		6:2 Fluorotelomer phosphate diester	6:2 diPAP	C16F26H8O4P	788.9744	M4 6:2/6:2 diPAP
50		6:2/8:8 Fluorotelomer phosphate diester	6:2/8:2 diPAP	C18F30H8O4P	888.968	M4 8:2/8:2 diPAP
51		6:2/10:2 Fluorotelomer phosphate diester	6:2/10:2 diPAP	C20F34H8O4P	988.9616	M4 8:2/8:2 diPAP
52		8:2 Fluorotelomer phosphate diester	8:2 diPAP	C20F34H8O4P	988.9616	M4 8:2/8:2 diPAP
53		6:2/12:2 Fluorotelomer phosphate diester	6:2/12:2 diPAP	C22F38H8O4P	1088.955	M4 8:2/8:2 diPAP
54		8:2/10:2 Fluorotelomer phosphate diester	8:2/10:2 diPAP	C22F38H8O4P	1088.955	M4 8:2/8:2 diPAP
55		10:2 Fluorotelomer phosphate diester	10:2 diPAP	C24F42H8O4P	1188.949	M4 8:2/8:2 diPAP
56		6:2/14:2 Fluorotelomer phosphate diester	6:2/14:2 diPAP	C24F42H8O4P	1188.949	M4 8:2/8:2 diPAP
57		8:2/12:2 Fluorotelomer phosphate diester	8:2/12:2 diPAP	C24F42H8O4P	1188.949	M4 8:2/8:2 diPAP
58		4:2 Fluorotelomer phosphate monoester	4:2 monoPAP	C6F9H5O4P	342.9782	M2 6:2 mono PAP
59		6:2 Fluorotelomer phosphate monoester	6:2 monoPAP	C8F13H5O4P	442.9718	M2 6:2 mono PAP
60		8:2 Fluorotelomer phosphate monoester	8:2 monoPAP	C10F17H5O4P	542.9654	M2 8:2 mono PAP
61		10:2 Fluorotelomer phosphate monoester	10:2 monoPAP	C12F21H5O4P	642.959	M2 8:2 mono PAP

Table S2: Scan parameter, HESI source and acquisition set-up used for the Orbitrap Q Exactive HF.

SCAN PARAMETERS	
Scan type	Full MS / ddMS2
Scan range	200 to 1200.0 m/z
Fragmentation	None or NCE(35) (z=1)
Resolution	120000 / 15000
Polarity	Negative
AGC target	3e6 / 2e5
Maximum inject time	250 / 30
HESI SOURCE	
Sheath gas flow rate	30
Aux gas flow rate	10
Sweep gas flow rate	0
Spray voltage (|kV|)	3.70
Spray current (µA)	
Capillary temp. (°C)	350
S-lens RF level	55.0
Aux gas heater temp (°C)	350

Table S3: *Compound Discoverer* settings for suspect screening on negative mode

SELECT SPECTRA	
Lower RT Limit	0.5
Uppper RT Limit	15
Min Precursor Mass	200 Da
Max Precursor Mass	1200 Da
Total Intensity Threshold	6000
Align Retention Times	
Alignment Model	Adaptive Curve
Mass Tolerance	5 ppm
Maximum Shift [min]	0.5
DETECT UNKNOWN COMPOUNDS	
General Settings	
Mass Tolerance	5 ppm
Intensity Tolerance [%]	30
S/N Tolerance	20
Min Peak Intensity	1500000
Ions	[M-H]-1
Min Element Counts	C
Max Element Counts	C90 [13]C15 H190 Br10 Cl10 D15 F50 K2 N10 Na O15 P S5
Peak Detection	
Filter Peaks	True
Max Peak Width [min]	1
Remove Singlets	False
Min # Scans per Peak	5
Min # Isotopes	1
GROUP UNKNOWN COMPOUNDS	
Compound Consolidation	
Mass Tolerance	5 ppm
RT Tolerance [min]	0.2
Fragment Data Selection	
Preferred Ion	[M-H]-1
Fill Gaps	
Mass Tolerance	5 ppm
S/N Threshold	5
Use Real Peak Detection	True
Mark Background Compounds	
Max Sample/Blank	5
PREDICT COMPOSITIONS	
Prediction Settings	
Mass Tolerance	5 ppm
Min Element Counts	C
Max Element Counts	C90 H190 Br10 Cl10 F30 N10 O15 P2 S5
Min RDBE	-1
Max RDBE	40
Min H/C	0.1
Max H/C	3
Max # Candidates	15
Pattern Matching	
Intensity Tolerance [%]	30
Intensity Threshold [%]	0.1
S/N Threshold	3
Min Spectral Fit [%]	10
Min Pattern Cov. [%]	90
Use Dynamic Recalibration	True

Search Mass Lists	
Consider Retention Time	False
Mass Tolerance	5 ppm
mzCloud search	
Compound Classes	All
Match Ion Activation Type	False
Match Iona Activation Energy	Match with Tolerance
Ion Activation Energy Tolerance	40
Apply Intensity Threshold	True
Precursor Mass Tolerance	5 ppm
FT Fragment Mass Tolerance	10 ppm
Identity Search	HighChem HighRes
Similarity Search	None
Match Factor Threshold	50

Table S4: Summary of spike/recovery experiments (2.5ng of individual PFAS spiked into 0.5g serum; n=4) showing the mean percent recovery (± standard deviation) and coefficient of variation (CV). Internal Standard (IS) recoveries are also provided for spiked samples, determined for PFCAs relative to M8PFOA and for PFSAs relative to M8PFOS.

Compound	Mean ±SD [%]	CV
PFBA	147±20	13.5
PFPeA	68.5±7.9	11.5
PFHxA	94.4±3.5	3.69
PFHpA	91.8±3.0	3.28
lin-PFOA	91.5±3.2	3.50
PFNA	92.9±3.0	3.25
PFDA	103±3	2.42
PFUnDA	105±2	1.65
PFDoDA	110±3	2.33
PFTrDA	154±15	9.57
PFTeDA	148±6	4.21
PFHxDA	133±16	12.0
PFOcDA	117±10	8.15
PFBS	76.8±1.4	1.82
lin-PFHxS	93.5±2.4	2.60
lin-PFOS	85.2±11.3	13.2
lin-PFDS	87.7±5.0	5.68
NaDONA	80.4±5.1	6.40
9Cl-PF3ONS	88.3±3.0	3.43
11Cl-PF3OUdS	56.9±3.5	6.18
3:3 FTA (FPrPA)	46.7±2.0	4.38
5:3 FTA (FPePA)	50.1±4.3	8.68
7:3 FTA (FHpPA)	83.4±4.4	5.24
4:2 FTS	91.0±3.8	4.15
6:2 FTS	111±3	3.06
8:2 FTS	94.3±1.6	1.68
lin-FOSA	94.8±2.7	2.88
MeFOSA	94.5±2.4	2.53
EtFOSA	62.4±15.8	25.4
lin-FOSAA	91.5±4.0	4.42
MeFOSAA	90.9±8.6	9.46
EtFOSAA	---	---
MeFOSE	84.8±6.2	7.31
EtFOSE		
4:2 diPAP	94.6±5.2	5.51
6:2 diPAP	97.5±2.5	2.53
8:2 diPAP	55.8±10.5	18.7
6:2/8:2 diPAP	21.5±6.6	30.9
10:2 diPAP	---	---
4:2 monoPAP	---	---
6:2 monoPAP	---	---
8:2 monoPAP	---	---
10:2 monoPAP	147±20	13.5

IS	Mean ±SD [%]	CV
M4PFBA	5.85±1.77	30.3
M3PFPeA	19.4±4.2	21.6
M2PFHxA	34.6±6.8	19.7
M4PFHpA	91.9±16.7	18.2
M4PFOA	67.1±10.6	15.8
M5PFNA	62.5±11.0	17.7
M2PFDA	76.7±14.7	19.2
M2PFUnDA	62.8±13.6	21.6
M2PFDoDA	58.7±13.1	22.3
18O2-PFHxS	65.2±10.0	15.3
M4PFOS	83.1±13.4	16.1

Table S5: Comparison of PFAS concentrations (in ng/g or ng/mL) reported in NIST certified reference material 1957.

COMPOUND	GEBBINK[1*] (N=9)	THIS STUDY* (N=2)	NIST[2**]	YEUNG[3,4***] (N=42)
PFHpA	0.200±0.02	0.223±0.0176	0.305±0.051	0.198±0.057
PFOA	3.86±0.13	4.33±0.106	5.00±0.44	4.10±0.349
PFNA	0.720±0.04	0.774±0.0413	0.878±0.077	0.764±0.077
PFDA	0.240±0.01	0.238±0.0185	0.390±0.12	0.293±0.030
PFUnDA	0.110±0.01	0.117±0.000336	0.172±0.036	0.118±0.12
PFDoDA	0.017±0.003	0.0967±0.00162		
PFTriDA	0.009±0.004	0.00562±0.0120		
PFHxS	3.25±0.06	3.40±0.139	4.00±0.83	4.14±0.458
lin-PFOS	10.7±0.3	11.3±0.328		
br-PFOS	7.89±041	7.31±0.743		
tot-PFOS	18.5±0.7	18.6±1.07	21.1±1.3	19.3±1.18
tot-FOSA	0.029±0.007	0.00325±0.00213		
FOSAA	0.21±0.03	0.152±0.0224		0.165±0.022
MeFOSAA	0.60±0.03	0.594±0.0201		0.681±0.047
EtFOSAA	0.16±0.02	0.123±0.00961		0.147±0.011

* Reported value in ng/g ± standard deviation

** Reported value in ng/g ± uncertainty value calculated by combining a pooled within method variance with a between method variance following the ISO/JCGM guidelines.

*** Reported value in ng/mL ± standard deviation

Table S6: Comparison of percent recoveries (2.5ng of each PFAS fortified into 0.5g serum; n=2 per method denoted as Rep. 1 and Rep. 2) for Methods A, B, and C and correlation coefficients from the pairwise comparison of methods A, B, and C. NA-spike/recovery experiment was not carried out either due to an absence of standard or because the target was not measured as part of the method.

	Percent recoveries in spiked samples						Correlation coefficients, unspiked samples (n=20)		
	Method A		Method B		Method C				
Target	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	A vs B	A vs C	B vs C
PFBA	102	102	139	137	118	127			
PFPeA	103	106	104	96	115	106			
PFHxA	105	106	109	103	112	97			
PFHpA	106	103	107	94	108	100			
lin-PFOA	102	106	124	129	126	103	0.93	0.97	0.90
br-PFOA	NA	NA	NA	NA	NA	NA			
PFNA	109	108	107	104	113	101	0.80	0.95	0.71
PFDA	106	108	103	126	107	110	0.81	0.97	0.84
PFUnDA	109	106	118	123	113	103	0.75	0.99	0.58
PFDoDA	107	104	112	134	109	115			
PFTriDA	114	112	138	150	56	57			
PFTeDA	120	116	130	143	22	25			
PFPeDA	NA	NA	NA	NA	NA	NA			
PFHxDA	132	119	NA	NA	NA	NA			
PFOcDA	96	88	NA	NA	NA	NA			
PFBS	85	84	99	96	96	91	0.92		
PFPeS	NA	NA	NA	NA	NA	NA	0.89		
lin-PFHxS	103	103	141	136	112	109	0.99	1.00	0.98
br-PFHxS							0.98	0.98	0.91
lin-PFHpS	NA	NA	NA	NA	NA	NA			
lin-PFOS	95	106	92	100	143	137	0.94	0.99	0.93
br-PFOS	NA	NA	NA	NA	NA	NA	0.94	0.99	0.91
lin-PFNS	NA	NA	NA	NA	NA	NA			
lin-PFDS	102	102	125	143	74	76			
br-PFDS	NA	NA	NA	NA	NA	NA			
lin-PFUnDS	NA	NA	NA	NA	NA	NA			
NaDONA	79	86	112	126	NA	NA			
9Cl-PF3ONS	90	96	133	138	102	113			
11Cl-PF3OUdS	91	93	139	149	NA	NA			
3:3 FTA (FPrPA)	84	85	59	75	NA	NA			
5:3 FTA (FPePA)	84	86	84	72	NA	NA			
7:3 FTA (FHpPA)	79	75	93	67	NA	NA			
4:2 FTS	68	68	93	109	11	80			
6:2 FTS	117	115	110	112	449	144			
8:2 FTS	132	138	191	157	7	72			
lin-FOSA	113	112	122	139	120	123			
br-FOSA	NA	NA	NA	NA	NA	NA			
MeFOSA	104	107	NA	NA	107	108			
EtFOSA	114	109	NA	NA	114	119			

Continued on next page

Table S6 continued

TARGET	QC-1	QC-2	QC-1	QC-2	QC-1	QC-2	A vs B	A vs C	B vs C
lin-FOSAA	69	33	58	24	126	120			
MeFOSAA	122	114	127	126	118	113			
EtFOSAA			100	122	124	116			
MeFOSE	87	89	NA	NA	NA	NA			
EtFOSE	106	96	NA	NA	NA	NA			
4:2 diPAP	NA	NA	NA	NA	197	196			
6:2 diPAP	116	112	166	147	114	116			
6:2/8:2 diPAP	162	188	143	169	34	36			
8:2 diPAP	113	124	116	104	112	96			
10:2 diPAP	NA	NA	NA	NA	85	191			
4:2 monoPAP	NA	NA	NA	NA	48	56			
6:2 monoPAP	NA	NA	NA	NA	133	137			
8:2 monoPAP	NA	NA	NA	NA	212	184			
10:2 monoPAP	NA	NA	NA	NA	146	126			

Table S7: 95% confidence intervals of the slopes and intercepts for individual PFASs compared using linear regressions of method A vs B, A vs C, and B vs C. Slopes and intercepts highlighted in red were significantly different from ideal values (1, 0, respectively) at the 95% confidence level.

	A vs B		A vs C		B vs C	
compound	Intercept (mean; confint)	Slope (mean; confint)	Intercept (mean; confint)	Slope (mean; confint)	Intercept (mean; confint)	Slope (mean; confint)
PFHpA	0.02; -0.649-0.689	0.857; -14.4-16.1				
lin-PFOA	0.273; -0.135-0.681	0.948; 0.765-1.13	-0.176; -0.443-0.0904	1.02; 0.901-1.14	-0.116; -0.66-0.427	0.923; 0.695-1.15
br-PFOA						
PFNA	0.0512; -0.208-0.311	1.11; 0.691-1.53	-0.346; -0.454- -0.238	1.03; 0.857-1.2	-0.124; -0.328-0.0798	0.555; 0.283-0.828
PFDA	0.00425; -0.111-0.119	1.13; 0.718-1.54	-0.218; -0.292--0.145	0.916; 0.704-1.13	-0.116; -0.253-0.0212	0.548; 0.199-0.896
PFUnDA	0.12; 0.0049-0.236	0.881; 0.472-1.29	-0.239; -0.301--0.176	0.999; 0.824-1.17	-0.121; -0.443-0.2	0.506; -0.205-1.22
PFDoDA	0.0638; 0.0269-0.101	-0.33; -1.59-0.928				
PFTriDA	0.0856; 0.034-0.137	0.0347; -0.627-0.697				
PFTeDA						
PFBS	0.00886; -0.0215-0.0392	1.02; 0.595-1.44				
PFPeS	0.0226; -0.0881-0.133	0.858; 0.565-1.15				
lin-PFHxS	-0.48; -1.05-0.0882	1.32; 1.23-1.42	-0.143; -0.405-0.118	0.979; 0.935-1.02	0.314; -0.203-0.831	0.723; 0.654-0.791
br-PFHxS	-0.0271; -0.123-0.0691	1.65; 1.43-1.86	-0.119; -0.247-0.0096	1.08; 0.859-1.29	-0.0449; -0.274-0.184	0.584; 0.347-0.821
lin-PFHpS	0.0507; -0.0403-0.142	0.515; 0.109-0.92				
lin-PFOS	-1.26; -3.52-1.01	1.46; 1.19-1.74	-0.513; -1.18-0.152	1.12; 1.04-1.2	1.36; -0.0765-2.79	0.677; 0.547-0.806
br-PFOS	-0.559; -1.63-0.516	1.43; 1.17-1.69	-0.402; -0.736--0.0678	1.18; 1.1-1.26	0.605; -0.276-1.49	0.711; 0.551-0.871
MeFOSAA	0.0961; -0.167-0.36	-0.456; -6.45-5.54				
9Cl-PF3ONS						

Table S8: Limits of quantification (ng/g) for each method calculated from the methods intercomparison experiment. Note that these values differ slightly than those in Tables S8 and S9 because they were derived from different batches. The high LOQ shown here was due to blank levels of PFOA observed in the method intercomparison experiment.

	Method A LOQ	Method B LOQ	Method C LOQ
PFBA	0.008	0.09	1
PFPeA	0.008	0.09	0.3
PFHxA	0.008	0.09	0.1
PFHpA	0.008	0.09	0.1
lin-PFOA	0.14	0.09	0.1
br-PFOA	0.008	0.09	0.1
PFNA	0.008	0.09	0.1
PFDA	0.008	0.09	0.1
PFUnDA	0.008	0.09	0.1
PFDoDA	0.008	0.09	0.1
PFTriDA	0.008	0.09	0.1
PFTeDA	0.008	0.09	0.1
PFPeDA	0.008	0.09	0.1
PFHxDA	0.008		
PFOcDA	0.008		
PFBS	0.007	0.07	0.1
PFPeS	0.008	0.08	
lin-PFHxS	0.008	0.08	0.1
br-PFHxS	0.008	0.08	0.1
lin-PFHpS	0.008	0.08	
lin-PFOS	0.008	0.08	0.1
br-PFOS	0.008	0.08	0.1
PFNS	0.008	0.08	
lin-PFDS	0.008	0.08	0.1
br-PFDS	0.008	0.08	0.1
PFUnDS	0.008	0.08	
9Cl-PF3ONS	0.008	0.09	0.1
11Cl-PF3OUdS	0.008	0.3	
NaDONA	0.008	0.09	
3:3 FTA (FPrPA)	0.008	1.04	
5:3 FTA (FPePA)	0.008	0.3	
7:3 FTA(FHpPA)	0.008	0.09	
4:2 FTS	0.008	0.3	0.1
6:2 FTS	0.181	0.3	43
8:2 FTS	0.008	0.3	0.1
lin-FOSA	0.008	0.09	0.1
br-FOSA	0.008	0.09	0.1
MeFOSA	0.008		0.1
EtFOSA	0.008		0.1
FOSAA	0.009	0.3	0.1
MeFOSAA	0.009	0.09	0.1
EtFOSAA	0.008	0.3	0.1
MeFOSE	0.008		
EtFOSE	0.008		
4:2 diPAP			0.4
6:2 diPAP	0.009	0.31	0.1
6:2/8:2 diPAP	0.008	0.3	0.1
8:2 diPAP	0.008	0.3	0.1
10:2 diPAP	0.341		3.5
4:2 monoPAP			1.1
6:2 monoPAP			0.3
8:2 monoPAP			0.3
10:2 monoPAP			1

Table S9: Concentration [ng/g] in serum samples for PFCAs.

	Code	Pool x-Year	PFBA	PFPeA	PFHxA	PFHpA	lin-PFOA	br-PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA
1	H0900192	Pool 25-1996	<LOQ	<LOQ	<LOQ	0.038	2.405	0.054	0.394	0.132	0.188	<LOQ	0.041	<LOQ	<LOQ	<LOQ
2	H0900193	Pool 26-1996	<LOQ	<LOQ	<LOQ	0.036	3.483	0.091	0.383	0.156	0.178	<LOQ	0.034	<LOQ	<LOQ	<LOQ
3	H0900194	Pool 27-1996	<LOQ	<LOQ	<LOQ	0.040	3.329	0.071	0.512	0.165	0.171	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4	H0900168	Pool 1-1997	<LOQ	<LOQ	0.016	0.070	3.365	0.139	0.367	0.161	0.178	<LOQ	0.038	<LOQ	<LOQ	<LOQ
5	H0900169	Pool 2-1997	<LOQ	<LOQ	0.038	0.060	2.904	0.093	0.304	0.150	0.136	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
6	H0900170	Pool 3-1997	<LOQ	<LOQ	0.030	0.041	3.216	0.080	0.408	0.163	0.170	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
7	H0900171	Pool 4-1998	0.666	<LOQ	0.029	0.058	3.116	0.089	0.403	0.177	0.166	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
8	H0900172	Pool 5-1998	0.085	<LOQ	0.021	0.043	3.210	0.084	0.383	0.172	0.190	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
9	H0900173	Pool 6-1998	0.050	<LOQ	<LOQ	0.044	3.023	0.065	0.350	0.159	0.178	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
10	H0900195	Pool 28-1999	<LOQ	<LOQ	<LOQ	0.032	2.787	0.062	0.280	0.111	0.131	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
11	H0900196	Pool 29-1999	<LOQ	<LOQ	<LOQ	0.037	4.263	0.072	0.384	0.151	0.183	<LOQ	0.038	<LOQ	<LOQ	<LOQ
12	H0900197	Pool 30-1999	0.012	<LOQ	<LOQ	0.072	3.362	0.068	0.411	0.136	0.209	<LOQ	0.044	<LOQ	<LOQ	<LOQ
13	H0900174	Pool 7-2000	0.071	<LOQ	0.016	0.040	3.747	0.076	0.482	0.232	0.267	<LOQ	0.047	<LOQ	<LOQ	<LOQ
14	H0900175	Pool 8-2000	0.040	<LOQ	0.016	0.042	3.280	0.059	0.423	0.172	0.175	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
15	H0900176	Pool 9-2001	0.038	<LOQ	0.028	0.041	3.065	0.048	0.508	0.280	0.291	<LOQ	0.052	<LOQ	<LOQ	<LOQ
16	H0900177	Pool 10-2002	0.046	<LOQ	0.015	0.039	2.806	0.052	0.433	0.231	0.218	<LOQ	0.039	<LOQ	<LOQ	<LOQ
17	H0900178	Pool 11-2002	0.036	<LOQ	0.014	0.086	3.564	0.066	0.528	0.273	0.243	<LOQ	0.049	<LOQ	<LOQ	<LOQ
18	H0900179	Pool 12-2002	0.046	<LOQ	0.016	0.044	3.769	0.072	0.489	0.236	0.250	<LOQ	0.049	<LOQ	<LOQ	<LOQ
19	H0900180	Pool 13-2004	0.027	<LOQ	0.016	0.061	2.681	0.043	0.632	0.338	0.307	<LOQ	0.052	<LOQ	<LOQ	<LOQ
20	H0900181	Pool 14-2004	0.019	<LOQ	0.016	0.042	2.541	0.042	0.512	0.279	0.272	<LOQ	0.059	<LOQ	<LOQ	<LOQ
21	H0900182	Pool 15 -2004	0.016	<LOQ	<LOQ	0.064	2.962	0.036	0.536	0.295	0.229	<LOQ	0.050	<LOQ	<LOQ	<LOQ
22	H0900183	Pool 16-2006	0.194	<LOQ	<LOQ	0.049	3.027	0.033	0.785	0.402	0.395	<LOQ	0.080	<LOQ	<LOQ	<LOQ
23	H0900184	Pool 17-2006	0.139	<LOQ	0.014	0.060	2.661	0.044	0.531	0.229	0.188	<LOQ	0.050	<LOQ	<LOQ	<LOQ
24	H0900185	Pool 18-2006	<LOQ	<LOQ	<LOQ	0.045	2.373	0.038	0.548	0.263	0.250	<LOQ	0.049	<LOQ	<LOQ	<LOQ
25	H0900186	Pool 19-2007	0.012	<LOQ	<LOQ	0.050	2.653	0.028	0.683	0.319	0.249	<LOQ	0.074	<LOQ	<LOQ	<LOQ
26	H0900187	Pool 20-2007	0.090	<LOQ	0.025	0.051	2.921	0.051	0.658	0.318	0.277	<LOQ	0.053	<LOQ	<LOQ	<LOQ
27	H0900188	Pool 21-2007	<LOQ	<LOQ	<LOQ	0.027	1.895	0.018	0.555	0.305	0.286	<LOQ	0.076	<LOQ	<LOQ	<LOQ
28	H0900189	Pool 22-2008	0.055	<LOQ	0.039	0.049	2.501	0.034	0.794	0.315	0.338	<LOQ	0.088	<LOQ	<LOQ	<LOQ

Continued on next page

Table S9 continued

	Code	Pool x-Year	PFBA	PFPeA	PFHxA	PFHpA	lin-PFOA	br-PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA
29	H0900190	Pool 23-2008	0.039	<LOQ	<LOQ	0.038	2.235	0.040	0.612	0.306	0.301	<LOQ	0.065	<LOQ	<LOQ	<LOQ
30	H0900191	Pool 24-2008	0.068	<LOQ	0.018	0.059	3.582	0.047	1.144	0.630	0.435	<LOQ	0.110	<LOQ	<LOQ	<LOQ
31	H1000035	Pool 1-2009	<LOQ	<LOQ	<LOQ	<LOQ	1.806	0.020	0.595	0.253	0.277	<LOQ	0.080	<LOQ	<LOQ	<LOQ
32	H1000036	Pool 2-2009	0.092	<LOQ	<LOQ	0.027	2.189	0.021	0.610	0.278	0.295	<LOQ	0.072	<LOQ	<LOQ	<LOQ
33	H1000037	Pool 3-2009	0.099	<LOQ	<LOQ	0.027	2.272	0.025	0.622	0.273	0.292	<LOQ	0.085	<LOQ	<LOQ	<LOQ
34	H1000038	Pool 1-2010	<LOQ	<LOQ	0.016	0.048	2.722	0.027	1.004	0.482	0.435	<LOQ	0.120	<LOQ	<LOQ	<LOQ
35	H1000039	Pool 2-2010	<LOQ	<LOQ	0.039	0.040	1.523	0.020	0.549	0.242	0.184	<LOQ	0.037	<LOQ	<LOQ	<LOQ
36	H1000040	Pool 3-2010	<LOQ	<LOQ	<LOQ	0.035	2.138	0.035	0.570	0.272	0.297	<LOQ	0.074	<LOQ	<LOQ	<LOQ
37	H1200009	Pool 1 -2011	<LOQ	<LOQ	<LOQ	0.031	2.250	0.023	0.632	0.348	0.296	<LOQ	0.093	<LOQ	<LOQ	<LOQ
38	H1200010	Pool 2 -2011	<LOQ	<LOQ	<LOQ	<LOQ	1.504	0.022	0.511	0.242	0.319	<LOQ	0.098	<LOQ	<LOQ	<LOQ
39	H1200011	Pool 3 -2011	<LOQ	<LOQ	<LOQ	<LOQ	1.761	0.015	0.563	0.293	0.365	<LOQ	0.097	<LOQ	<LOQ	<LOQ
40	H1400025	Pool 1-2012	<LOQ	<LOQ	<LOQ	0.031	1.854	0.019	0.585	0.277	0.231	<LOQ	0.041	<LOQ	<LOQ	<LOQ
41	H1400026	Pool 2-2012	<LOQ	<LOQ	<LOQ	<LOQ	2.124	0.014	0.757	0.398	0.410	<LOQ	0.084	<LOQ	<LOQ	<LOQ
42	H1400027	Pool 3-2012	0.028	<LOQ	<LOQ	<LOQ	1.327	0.008	0.485	0.232	0.224	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
43	H1400028	Pool 1-2013	<LOQ	<LOQ	<LOQ	<LOQ	1.600	0.007	0.602	0.363	0.378	<LOQ	0.077	<LOQ	<LOQ	<LOQ
44	H1400029	Pool 2-2013	<LOQ	<LOQ	<LOQ	<LOQ	1.754	0.014	0.519	0.245	0.218	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
45	H1400030	Pool 3-2013	<LOQ	<LOQ	0.039	0.025	1.819	0.015	0.676	0.329	0.402	<LOQ	0.054	<LOQ	<LOQ	<LOQ
46	H1400031	Pool 1-2014	<LOQ	<LOQ	<LOQ	<LOQ	1.475	0.007	0.582	0.318	0.296	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
47	H1400032	Pool 2-2014	<LOQ	<LOQ	<LOQ	<LOQ	1.613	0.017	0.455	0.229	0.201	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
48	H1500001	Pool 3-2014	<LOQ	<LOQ	0.014	<LOQ	1.337	0.006	0.519	0.307	0.295	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
49	H1600041	Pool 1-2015	<LOQ	<LOQ	<LOQ	<LOQ	1.349	0.007	0.536	0.302	0.302	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
50	H1600042	Pool 2-2015	<LOQ	<LOQ	<LOQ	<LOQ	1.127	0.004	0.490	0.257	0.298	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
51	H1600043	Pool 3-2015	<LOQ	<LOQ	<LOQ	<LOQ	1.221	<LOQ	0.515	0.303	0.296	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
52	H1700015	Pool 1-2016	<LOQ	<LOQ	<LOQ	<LOQ	1.122	0.006	0.479	0.245	0.269	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
53	H1700016	Pool 2-2016	<LOQ	<LOQ	<LOQ	<LOQ	1.258	0.009	0.498	0.283	0.281	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
54	H1700017	Pool 3-2016	<LOQ	<LOQ	<LOQ	<LOQ	1.068	0.005	0.444	0.223	0.265	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
55	H1800017	Pool 1-2017	0.103	<LOQ	<LOQ	<LOQ	1.016	0.007	0.420	0.219	0.197	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
56	H1800018	Pool 2-2017	0.217	<LOQ	<LOQ	<LOQ	1.430	0.018	0.452	0.228	0.237	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
57	H1800019	Pool 3-2017	<LOQ	<LOQ	<LOQ	0.031	1.568	0.011	0.541	0.304	0.242	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	LOQ final		0.004	0.004	0.014	0.025	0.026	0.004	0.010	0.026	0.004	0.058	0.034	0.117	0.187	0.026

Table S10: Concentration [ng/g] in serum samples for PFSAs and sulfonamides

	Code	Pool x-Year	PFBS	lin-PFHxS	br-PFHxS	lin-PFOS	br-PFOS	PFDS	FOSA	MeFOSA	lin-FOSAA	br-FOSAA	EtFOSA	MeFOSAA	EtFOSAA	EtFOSE
1	H0900192	Pool 25-1996	0.019	1.624	0.076	13.797	5.446	<LOQ	<LOQ	<LOQ	0.204	0.146	<LOQ	0.356	1.115	<LOQ
2	H0900193	Pool 26-1996	0.027	2.322	0.127	16.185	7.010	<LOQ	<LOQ	<LOQ	0.209	0.144	<LOQ	0.328	0.822	<LOQ
3	H0900194	Pool 27-1996	0.037	2.085	0.135	14.471	6.157	0.068	<LOQ	<LOQ	0.201	0.129	<LOQ	0.184	0.741	<LOQ
4	H0900168	Pool 1-1997	0.022	2.406	0.141	14.173	7.258	<LOQ	0.028	<LOQ	0.192	0.153	<LOQ	0.479	0.859	<LOQ
5	H0900169	Pool 2-1997	0.023	1.848	0.107	13.393	6.644	0.041	<LOQ	<LOQ	0.175	0.154	<LOQ	0.240	1.071	<LOQ
6	H0900170	Pool 3-1997	<LOQ	2.133	0.113	14.434	7.096	0.044	<LOQ	<LOQ	0.152	0.123	<LOQ	0.254	0.626	<LOQ
7	H0900171	Pool 4-1998	0.024	1.460	0.074	15.115	7.040	<LOQ	<LOQ	<LOQ	0.167	0.127	<LOQ	0.299	0.727	<LOQ
8	H0900172	Pool 5-1998	0.023	2.145	0.116	14.323	6.744	0.046	<LOQ	<LOQ	0.153	0.112	<LOQ	0.235	0.670	<LOQ
9	H0900173	Pool 6-1998	0.034	2.483	0.151	13.963	6.376	<LOQ	<LOQ	<LOQ	0.191	0.145	<LOQ	0.388	0.649	<LOQ
10	H0900195	Pool 28-1999	0.023	2.108	0.124	12.639	5.969	<LOQ	<LOQ	<LOQ	0.150	0.118	<LOQ	0.654	0.634	<LOQ
11	H0900196	Pool 29-1999	0.026	3.661	0.195	14.551	6.648	<LOQ	<LOQ	<LOQ	0.220	0.137	<LOQ	0.575	0.648	<LOQ
12	H0900197	Pool 30-1999	0.022	2.123	0.108	16.588	7.249	<LOQ	<LOQ	<LOQ	0.202	0.138	<LOQ	0.477	0.903	<LOQ
13	H0900174	Pool 7-2000	0.033	3.090	0.211	14.313	6.146	<LOQ	<LOQ	<LOQ	0.089	0.063	<LOQ	0.361	0.294	<LOQ
14	H0900175	Pool 8-2000	0.021	3.743	0.195	14.697	7.632	<LOQ	<LOQ	<LOQ	0.093	0.118	0.205	0.521	0.423	0.031
15	H0900176	Pool 9-2001	0.021	1.857	0.089	15.529	7.052	<LOQ	<LOQ	<LOQ	0.129	0.115	0.091	0.325	0.490	<LOQ
16	H0900177	Pool 10-2002	0.020	2.679	0.140	11.185	5.099	<LOQ	<LOQ	<LOQ	0.086	0.063	<LOQ	0.349	0.174	<LOQ
17	H0900178	Pool 11-2002	0.031	3.674	0.224	12.790	6.617	<LOQ	<LOQ	<LOQ	0.088	0.075	0.195	0.498	0.178	0.066
18	H0900179	Pool 12-2002	0.021	3.506	0.172	14.873	7.137	<LOQ	<LOQ	<LOQ	0.145	0.108	0.132	0.312	0.174	0.024
19	H0900180	Pool 13-2004	0.028	2.587	0.150	11.019	4.731	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.182	0.161	0.061	<LOQ
20	H0900181	Pool 14-2004	0.032	4.248	0.259	9.817	4.543	<LOQ	0.063	<LOQ	<LOQ	<LOQ	0.691	0.114	0.103	<LOQ
21	H0900182	Pool 15 -2004	0.022	2.225	0.134	8.839	4.639	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.115	0.023	<LOQ
22	H0900183	Pool 16-2006	0.057	4.849	0.329	11.251	5.328	<LOQ	<LOQ	<LOQ	0.081	0.060	<LOQ	0.143	0.029	<LOQ
23	H0900184	Pool 17-2006	0.047	5.805	0.414	7.495	4.138	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.051	0.027	<LOQ
24	H0900185	Pool 18-2006	0.045	3.732	0.277	6.670	3.513	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.061	0.023	<LOQ
25	H0900186	Pool 19-2007	0.033	4.503	0.267	8.018	4.034	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.079	0.024	<LOQ
26	H0900187	Pool 20-2007	0.035	5.083	0.314	10.330	5.313	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.053	<LOQ	<LOQ
27	H0900188	Pool 21-2007	0.035	4.112	0.253	6.356	2.956	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.131	0.025	<LOQ
28	H0900189	Pool 22-2008	0.106	5.253	0.324	7.003	3.779	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.068	<LOQ	<LOQ

Continued on next page

Table S10 continued

	Code	Pool x-Year	PFBS	lin-PFHxS	br-PFHxS	lin-PFOS	br-PFOS	PFDS	FOSA	MeFOSA	lin-FOSAA	br-FOSAA	EtFOSA	MeFOSAA	EtFOSAA	EtFOSE
29	H0900190	Pool 23-2008	0.290	4.527	0.354	6.126	2.846	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.076	0.017	<LOQ
30	H0900191	Pool 24-2008	0.074	5.654	0.389	7.392	3.849	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.051	0.009	<LOQ
31	H1000035	Pool 1-2009	0.033	3.831	0.260	5.318	2.217	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.038	0.007	<LOQ
32	H1000036	Pool 2-2009	0.033	7.120	0.394	5.652	2.722	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
33	H1000037	Pool 3-2009	0.037	4.376	0.290	5.966	2.951	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.025	<LOQ
34	H1000038	Pool 1-2010	0.042	5.145	0.345	5.656	2.530	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ
35	H1000039	Pool 2-2010	0.038	3.657	0.257	3.237	1.663	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ
36	H1000040	Pool 3-2010	0.049	10.572	0.533	5.918	2.977	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
37	H1200009	Pool 1 -2011	0.027	5.540	0.282	5.164	2.573	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
38	H1200010	Pool 2 -2011	0.044	5.941	0.349	4.482	1.906	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
39	H1200011	Pool 3 -2011	0.032	7.364	0.412	5.194	2.054	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
40	H1400025	Pool 1-2012	0.036	4.024	0.260	4.211	2.145	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
41	H1400026	Pool 2-2012	0.030	4.734	0.286	5.488	2.289	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
42	H1400027	Pool 3-2012	0.019	3.808	0.171	3.368	1.495	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
43	H1400028	Pool 1-2013	<LOQ	5.327	0.226	4.028	1.573	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.029	<LOQ	<LOQ
44	H1400029	Pool 2-2013	0.029	5.157	0.255	3.218	1.662	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.008	<LOQ
45	H1400030	Pool 3-2013	0.027	5.610	0.275	4.837	1.798	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
46	H1400031	Pool 1-2014	0.030	3.392	0.161	3.225	1.312	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
47	H1400032	Pool 2-2014	0.027	5.090	0.280	3.899	1.984	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.052	0.004	<LOQ
48	H1500001	Pool 3-2014	0.020	3.339	0.140	3.285	1.389	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
49	H1600041	Pool 1-2015	0.019	3.366	0.133	3.273	1.201	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
50	H1600042	Pool 2-2015	<LOQ	3.907	0.133	3.318	1.217	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
51	H1600043	Pool 3-2015	<LOQ	3.164	0.110	3.027	1.148	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
52	H1700015	Pool 1-2016	<LOQ	5.493	0.189	3.171	1.303	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
53	H1700016	Pool 2-2016	0.022	3.412	0.142	3.425	1.294	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
54	H1700017	Pool 3-2016	0.021	4.062	0.138	3.156	1.329	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
55	H1800017	Pool 1-2017	<LOQ	2.173	0.064	2.859	1.004	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
56	H1800018	Pool 2-2017	0.022	2.695	0.091	2.867	1.018	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
57	H1800019	Pool 3-2017	0.023	4.233	0.136	2.601	1.149	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		LOQ final	0.018	0.027	0.001	0.044	0.001	0.033	0.027	0.040	0.075	0.001	0.029	0.027	0.004	0.015

Table S11: Concentration [ng/g] in serum samples for FTAs, FTSs, F53B, monoPAPs, diPAPs and NaDONA.

	Code	Pool x-Year	9Cl-PF3ONS	11Cl-PF3OUdS	NaDONA	3:3 FTA (FPrPA)	5:3 FTA (FPePA)	7:3 FTA (FHpPA)	4:2 FTS	6:2 FTS	8:2 FTS	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	10:2 diPAP
1	H0900192	Pool 25-1996	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.020	<LOQ	<LOQ	<LOQ	<LOQ
2	H0900193	Pool 26-1996	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.031	<LOQ	<LOQ	<LOQ	<LOQ
3	H0900194	Pool 27-1996	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.022	<LOQ	<LOQ	<LOQ	<LOQ
4	H0900168	Pool 1-1997	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.026	<LOQ	<LOQ	<LOQ	<LOQ
5	H0900169	Pool 2-1997	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.004	0.022	<LOQ	<LOQ	<LOQ	<LOQ
6	H0900170	Pool 3-1997	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.037	0.022	<LOQ	<LOQ	<LOQ	<LOQ
7	H0900171	Pool 4-1998	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.015	0.035	<LOQ	<LOQ	<LOQ	<LOQ
8	H0900172	Pool 5-1998	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.006	0.041	<LOQ	<LOQ	<LOQ	<LOQ
9	H0900173	Pool 6-1998	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.034	<LOQ	<LOQ	<LOQ	<LOQ
10	H0900195	Pool 28-1999	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.027	<LOQ	<LOQ	<LOQ	<LOQ
11	H0900196	Pool 29-1999	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.024	<LOQ	<LOQ	<LOQ	<LOQ
12	H0900197	Pool 30-1999	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.019	<LOQ	<LOQ	<LOQ	<LOQ
13	H0900174	Pool 7-2000	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.022	0.022	<LOQ	<LOQ	<LOQ	<LOQ
14	H0900175	Pool 8-2000	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.042	<LOQ	<LOQ	<LOQ	<LOQ
15	H0900176	Pool 9-2001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.082	<LOQ	<LOQ	<LOQ	<LOQ
16	H0900177	Pool 10-2002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.049	<LOQ	<LOQ	<LOQ	<LOQ
17	H0900178	Pool 11-2002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.012	0.096	0.100	<LOQ	<LOQ	<LOQ
18	H0900179	Pool 12-2002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.016	0.041	<LOQ	<LOQ	<LOQ	<LOQ
19	H0900180	Pool 13-2004	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.078	<LOQ	<LOQ	<LOQ	<LOQ
20	H0900181	Pool 14-2004	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.004	0.034	<LOQ	<LOQ	<LOQ	<LOQ
21	H0900182	Pool 15-2004	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.020	0.084	<LOQ	<LOQ	<LOQ	<LOQ
22	H0900183	Pool 16-2006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.091	<LOQ	<LOQ	<LOQ	<LOQ
23	H0900184	Pool 17-2006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.050	<LOQ	<LOQ	<LOQ	<LOQ
24	H0900185	Pool 18-2006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.046	<LOQ	<LOQ	<LOQ	<LOQ
25	H0900186	Pool 19-2007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.053	<LOQ	<LOQ	<LOQ	<LOQ
26	H0900187	Pool 20-2007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.055	0.155	<LOQ	<LOQ	<LOQ
27	H0900188	Pool 21-2007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.042	<LOQ	<LOQ	<LOQ	<LOQ
28	H0900189	Pool 22-2008	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.006	0.069	<LOQ	<LOQ	<LOQ	<LOQ

Continued on next page

Table S11 continued

	Code	Pool x-Year	9Cl-PF3ONS	11Cl-PF3OUdS	NaDONA	3:3 FTA (FPrPA)	5:3 FTA (FPePA)	7:3 FTA (FHpPA)	4:2 FTS	6:2 FTS	8:2 FTS	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	10:2 diPAP
29	H0900190	Pool 23-2008	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.009	0.050	<LOQ	<LOQ	<LOQ	<LOQ
30	H0900191	Pool 24-2008	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.084	<LOQ	<LOQ	<LOQ	<LOQ
31	H1000035	Pool 1-2009	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.018	<LOQ	<LOQ	<LOQ	<LOQ
32	H1000036	Pool 2-2009	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.025	<LOQ	<LOQ	<LOQ	<LOQ
33	H1000037	Pool 3-2009	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.014	<LOQ	<LOQ	<LOQ	<LOQ
34	H1000038	Pool 1-2010	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
35	H1000039	Pool 2-2010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ
36	H1000040	Pool 3-2010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ
37	H1200009	Pool 1 -2011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
38	H1200010	Pool 2 -2011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.010	<LOQ	<LOQ	<LOQ	<LOQ
39	H1200011	Pool 3 -2011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.016	<LOQ	<LOQ	<LOQ	<LOQ
40	H1400025	Pool 1-2012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
41	H1400026	Pool 2-2012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	<LOQ
42	H1400027	Pool 3-2012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
43	H1400028	Pool 1-2013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	<LOQ
44	H1400029	Pool 2-2013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.013	<LOQ	<LOQ	<LOQ	<LOQ
45	H1400030	Pool 3-2013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
46	H1400031	Pool 1-2014	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
47	H1400032	Pool 2-2014	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.013	<LOQ	<LOQ	<LOQ	<LOQ
48	H1500001	Pool 3-2014	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
49	H1600041	Pool 1-2015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
50	H1600042	Pool 2-2015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
51	H1600043	Pool 3-2015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
52	H1700015	Pool 1-2016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
53	H1700016	Pool 2-2016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
54	H1700017	Pool 3-2016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
55	H1800017	Pool 1-2017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
56	H1800018	Pool 2-2017	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
57	H1800019	Pool 3-2017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		LOQ final	0.010	0.093	0.004	0.344	0.446	0.508	0.001	0.001	0.007	0.074	0.074	0.074	4.590

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