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Supplementary material

Are humans exposed to increasing amounts of unidentified organofluorine?

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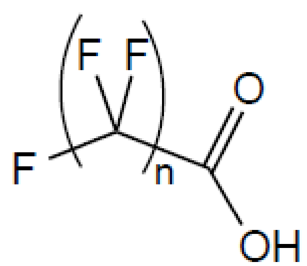
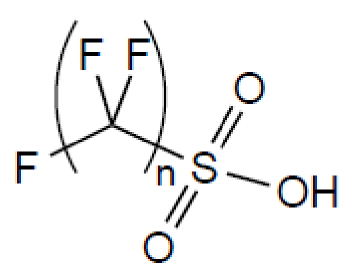
Structures of different classes of targeted PFASs

Perfluoroalkyl acids (PFAAs)

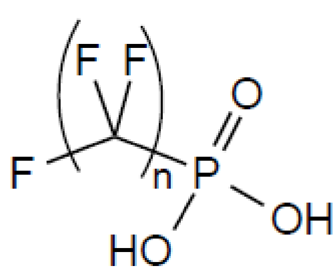
Perfluorinated carboxylic acids (PFCAs), *n* = 4–13.



Perfluoroalkyl sulfonic acids (PFSAs), *n* = 4–8, 10.



Perfluorinated phosphonic acids (PFPAs), *n* = 6, 8, 10.



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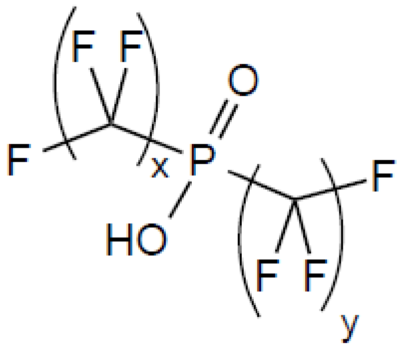
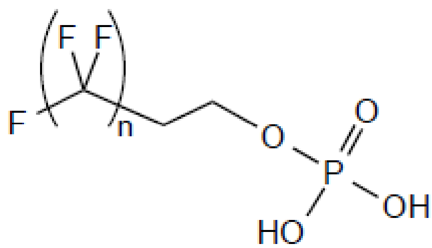
Perfluorinated phosphinic acids (PFPiAs), *x* = 6, 8, 10, 12; *y* = 6, 8, 10, 12.

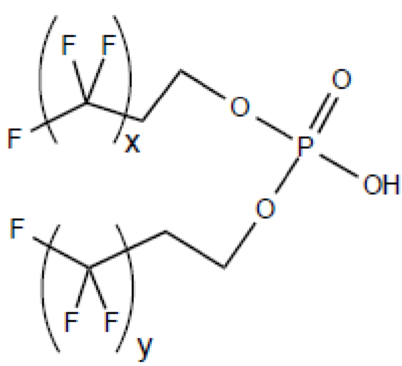


PFCA precursors/intermediates

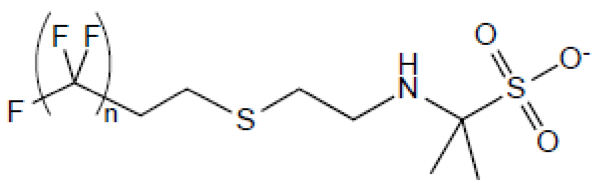
Polyfluoroalkyl phosphoric acid monoesters (monoPAPs), *n* = 6, 8.



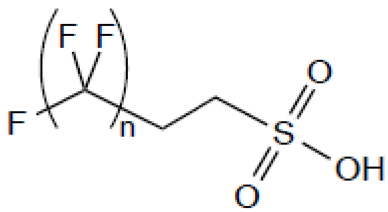
Polyfluoroalkyl phosphoric acid diesters (diPAPs), *x* =, 4, 6, 8, 10; *y* = 4, 6, 8, 10.



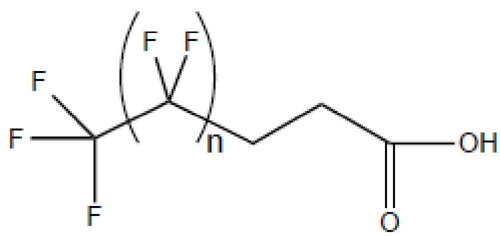
Fluorotelomermercaptoalkylamido sulfonate (FTSAS), *n* = 6, 8.



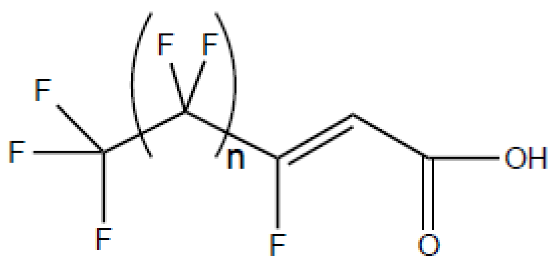
Fluorotelomer sulfonic acids (FTSAs), *n* = 4, 6, 8.



Fluorotelomer carboxylic acids (FTCAs), *n* = 2, 4, 6.

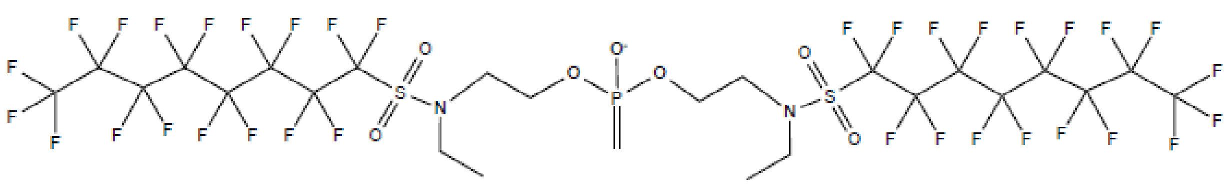


Fluorotelomer unsaturated carboxylic acids (FTUCAs), *n* = 4, 6, 8.

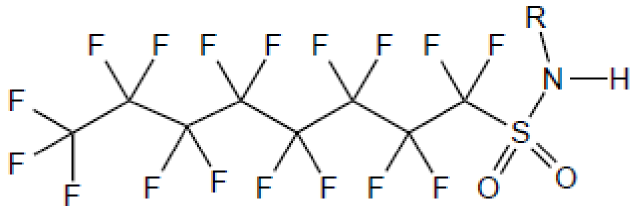


PFSA precursors

Perfluorooctanesulfonamidoethanol (EtFOSE)-based polyfluoroalkyl phosphate ester (di-SAmPAP).



Perfluoroalkanesulfonamides (FASAs), R = H, Methyl, Ethyl.



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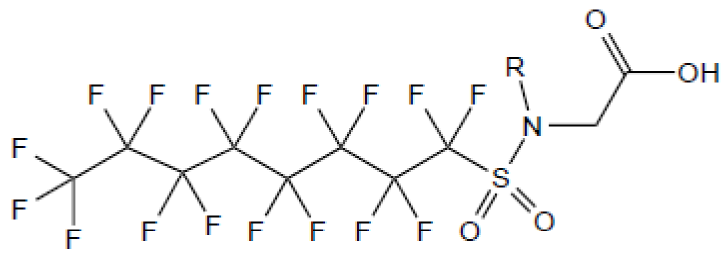
Perfluoroalkanesulfonamidoacetic acids (FOSAAs), R = H; *N*-alkyl FOSAAs, R = Methyl, Ethyl.



Analytical standards and reagents

Potassium salts of perfluorobutane sulfonate (PFBS), perfluorooctane sulfonate (PFOS) and $^{13}C_4$ PFOS; sodium salts of perfluorodecane sulfonate (PFDS), perfluoroheptane sulfonate (PFHpS), perfluorohexane sulfonate (PFHxS) and $^{18}O_2$PFHxS, MeFOSAA, EtFOSAA, perfluorooctanesulfonamido acetate (FOSAA), d_3MeFOSAA, d_5EtFOSAA, 6:2-, 8:2-, $^{13}C_2$ 6:2- and $^{13}C_2$ 8:2-monoPAPs, 6:2-, 8:2-, $^{13}C_4$ 6:2-, and $^{13}C_4$ 8:2- diPAPs, 4:2-, 6:2-, 13C_2 6:2-, and 8:2-FTSAs, and 6:6-, 6:8-, 8:8- perfluoroalkyl phosphinates (PFPiAs); perfluorooctanesulfonamide (FOSA), $^{13}C_8$ FOSA, *N*-methyl FOSA (MeFOSA), d_3MeFOSA, *N*-ethyl FOSA (EtFOSA), d_5EtFOSA, perfluorohexanoate (PFHxA), $^{13}C_2$PFHxA, perfluoroheptanoate (PFHpA), PFOA, $^{13}C_4$PFOA, perfluorononanoate (PFNA), $^{13}C_5$PFNA, perfluorodecanoate (PFDA), $^{13}C_2$PFDA, perfluoroundecanoate (PFUnDA), $^{13}C_2$PFUnDA, perfluorododecanoate (PFDoDA), $^{13}C_2$PFDoDA, perfluorotridecanoate (PFTriDA), perfluorotetradecanoate (PFTeDA), 3:3, 5:3, 7:3 fluorotelomer saturated carboxylates (FTCAs), 6:2, $^{13}C_2$ 6:2, 8:2, $^{13}C_2$ 8:2, 10:2, $^{13}C_2$ 10:2 fluorotelomer unsaturated carboxylates (FTUCAs), C6-, C8-, C10- perfluoroalkyl phosphonates (PFPAs) were obtained from the Wellington Laboratories (Guelph, ON, Canada). 4:2- and 10:2- diPAPs were synthesised as described elsewhere.[3] The purity of all standards was over 98%. The diethyl perfluorooctanesulfonamidoethanol (EtFOSE)-based polyfluoroalkyl phosphate ester (di-SAmPAP) was obtained from Wuhan Defu Chemical Company (Wuhan, China). Detailed purity analysis of di-SAmPAP was not available. The standards for the congeners of PFSA, FOSA, FOSAA, and PFOA were the linear isomer, whereas the samples were composed of both branched and linear isomers; the concentrations reported for the present study included both linear and branched isomers based on the linear isomer of the standard.

Tetrabutylammonium hydrogen sulphate (TBAS, 99%), horse whole blood, newborn calf serum, ammonium acetate (>99%), formic acid (88%), and ammonia (NH_3, 30%) were obtained from Sigma–Aldrich. Methanol (MeOH, LCMS grade) and methyl-*tert*-butyl ether (MTBE, Omnisolv, >99%) were acquired from EMD Chemicals Inc. (Mississauga, ON, Canada). Standard reference material (SRM1957: Organic Contaminants in Non-Fortified Human Serum) was purchased from the National Institute of

Standards and Technology (NIST) (Gaithersburg, MD, USA); SRM1957 is certified for C7–C12 PFCAs, C6 and C8 PFSAs (Tables S1–S2). All whole blood and plasma samples were stored at –20 °C.

Extraction

In a 15-mL falcon tube, 1 mL of 0.5 M TBAS solution (either adjusted to pH 10 with 30 % aqueous NH_3 or without pH adjustment (pH ~ 3–4)) was added to 0.5–1.0 mL of sample. After adding 4 mL of MTBE, the sample was shaken at 250 rpm for 20 min, then the organic and aqueous layers were separated by centrifugation at 4180*g* at room temperature (23 °C) for 10 min. The organic layers were decanted to a new falcon tube. The sample was then extracted with 4-mL aliquots of MTBE and the entire extraction procedure repeated. The MTBE aliquots were combined, evaporated to dryness under a gentle stream of nitrogen, and reconstituted in 0.2 mL of MeOH.

For samples extracted at pH 4, 0.5 ng of mass-labelled standards were spiked into the sample before extraction, whereas mass-labelled standards were spiked into the samples extracted at pH 10 after extraction and before LC-MS/MS analysis. The samples extracted at pH 10 were used for mass balance analysis for all quantifiable PFASs (except PFPAs and monoPAPs) and EOF, while PFPAs and monoPAPs were extracted at pH 4.

Locally weighted regression smoother (LOESS) and statistical tests of time series

Linear and non-linear smoothers and statistical tests of trends were performed using the following equations:

year	value	constant	linear regression		LOESS smoother	
x_t	y_t	$y_t - \bar{y}$	$a + b \times x_t$	$y_t - (a + bx_t)$	$z(y_t)$	$y_t - z(y_t)$
		RSS_1		RSS_2		RSS_3
		$df_1(= T-1)$		$df_2(= T-2)$	$df_3 = T - tr(2S - SS')$	

where a is the intercept and b is the slope

Effect	d.f.	Residual Sum of Squares (RSSQ)	*F*–ratio	% probability
Time	$d.f._1 - d.f._3$	$RSS_1 - RSS_3$	$[RSS_1 - RSS_3] d.f._3 / RSS_3 [d.f._1 - d.f._3]$	$100[1 - P(F, d.f._1 - d.f._3, d.f._3)]$
non–linear	$d.f._2 - d.f._3$	$RSS_2 - RSS_3$	$[RSS_2 - RSS_3] d.f._3 / RSS_3 [d.f._2 - d.f._3]$	$100[1 - P(F, d.f._2 - d.f._3, d.f._3)]$
Error	$d.f._3$	RSS_3	$s^2 = RSS_3 / d.f._3$	

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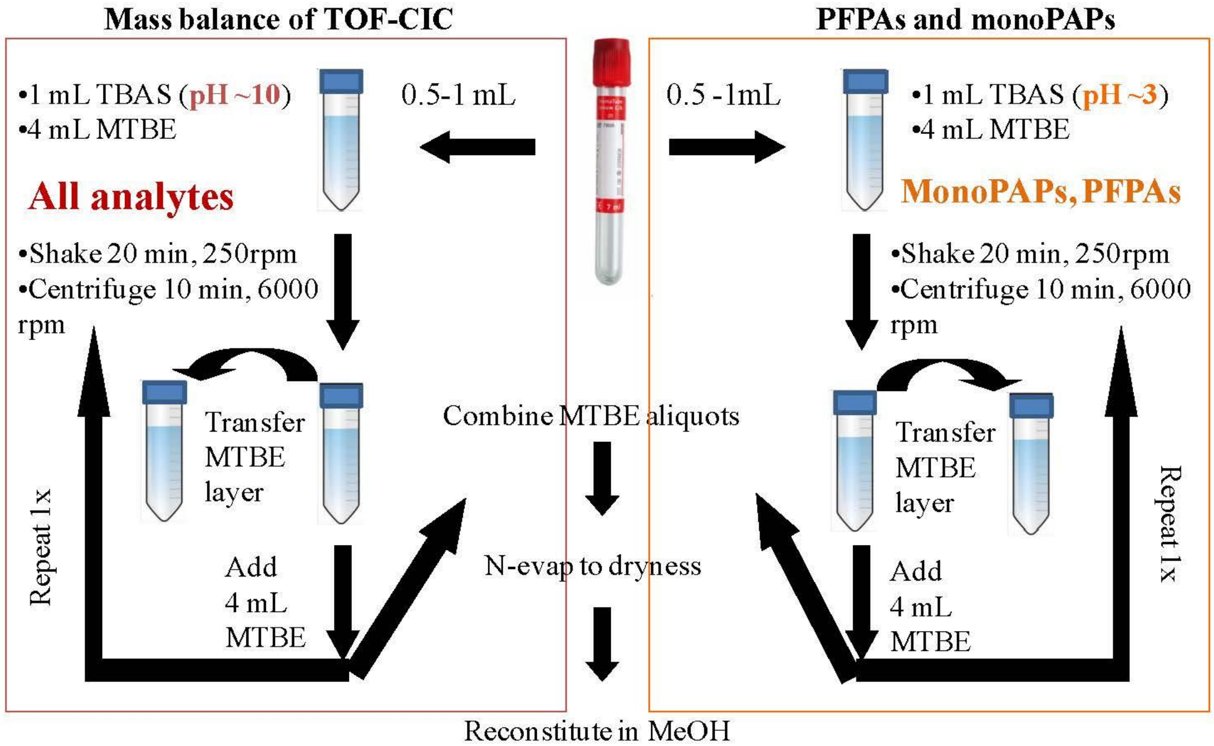

Fig. S1. A schematic diagram for a modified ion-pair extraction for PFPAs and monoPAPs and all other quantifiable PFASs.

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(a)

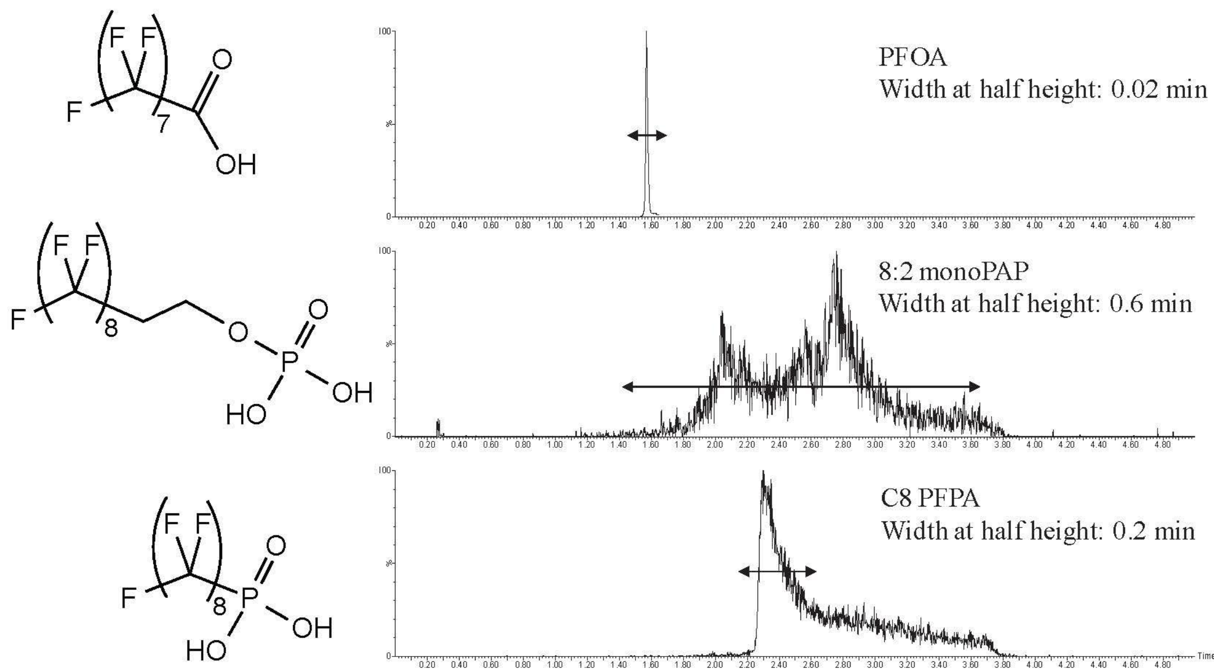

Fig. S2. (a) Chromatograms showing PFOA, 8:2 monoPAP, and C8 PFPA using a previous HPLC method for PFAS analysis. (b) Chromatograms of 8:2 monoPAP using different columns and differing pH. (c) Chromatograms of two closely related compounds (PFOS and PFNA) before (left) and after (right) optimisation of LC methods (e.g. LC gradient, column, and column temperature).

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(b)

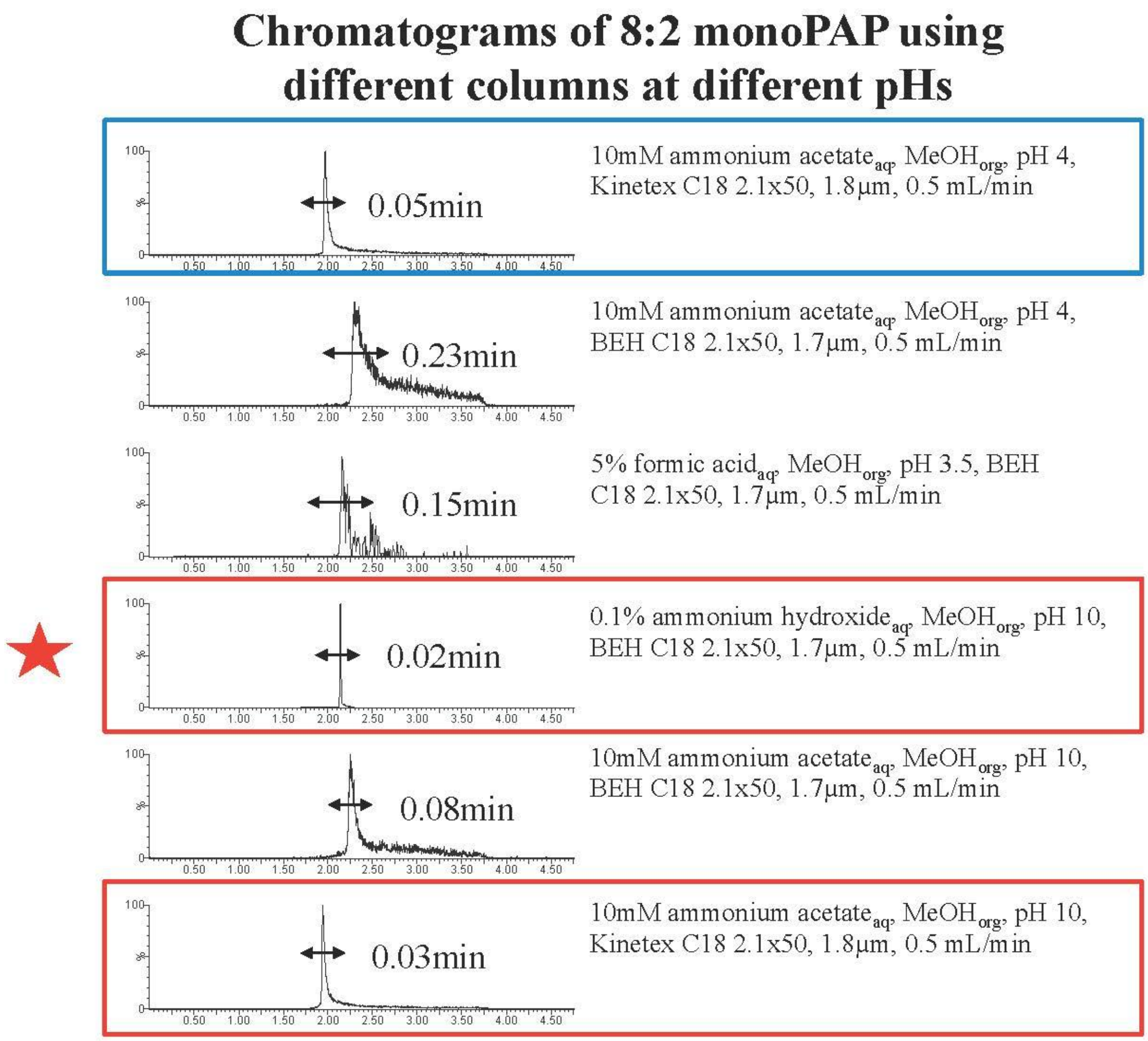

Fig. S2. (*Cont.*)

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(c)

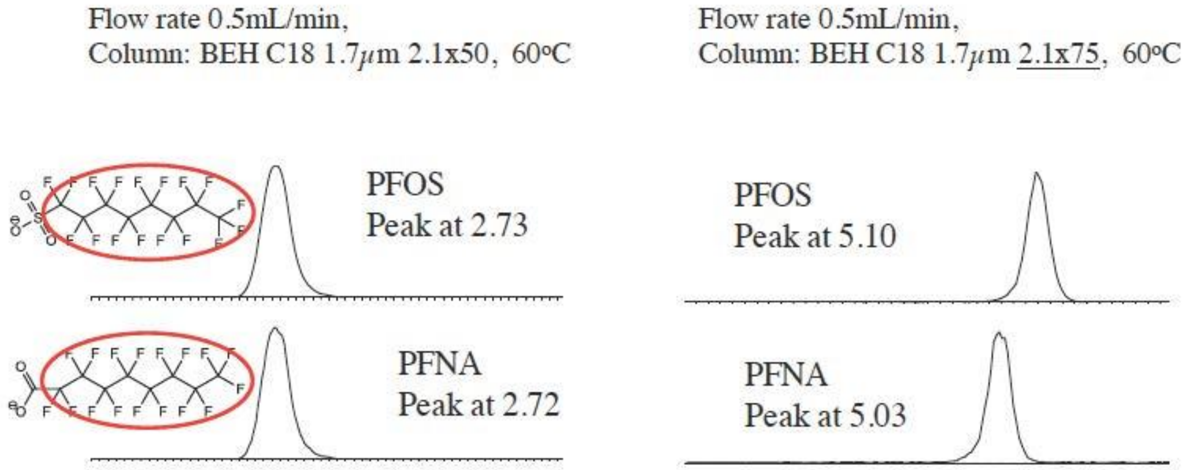

Fig. S2. (*Cont.*)

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Table S1. Information for Chinese data (Table S2) on province, geographical location, population, economy and references

Chinese sample locations	Province	Geographical location in China	Population (million)	Economy	Reference
Xiamen	Fujian	South-east	6.66	Fishery, ship building, food processing, tanning, textile, chemicals	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Fuzhou	Fujian	South-east	6.05	Industrial chemicals, food-processing, paper making, textile	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Zhoushan	Zhejiang	Eastern	0.97	Fishery, ship building and repairing	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Nanjing	Jiangsu	Southern	5.82	Electrical, mechanical, and steel factories, tourism	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Jintan	Jiangsu	Southern	0.54	Farming and agriculture	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Wuhan	Hubei	Central	7.88	optic-electronic, automobile manufacturing, iron and steel manufacturing, new pharmaceutical sector, biology engineering,	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)
Guiyang	Guizhou	South-west	3.48	Steel and Iron refinery plants, pharmaceuticals	People's Republic of China Administrative divisions Blooklet 2006 (in Chinese)

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Table S2. Sample information for samples from (a) China, (b) Halle, Germany, and (c) Münster, Germany

M: male, F: female. *p* values are pooled samples. Information on province, geographical location, population, economy and references for China are available in Table S1

	Sex	Age (mean (range))
(a) Chinese samples (*n* = 47)		
Xiamen *n* = 10	5M, 5F	31 (19–46)
Fuzhou *n* = 15	7M, 8F	38.6 (22–58)
Zhoushan *n* = 8	8F	26.8 (21–35)
Nanjing *n* = 5	3M, 2F	28.2 (18–40)
Jintan *n* = 3	2M, 1F	56 (43–66)
Wuhan *n* = 3	2M, 1F	32.6 (22–40)
Guiyang *n* = 3	2M, 1F	33.6 (21–45)
(b) Halle, Germany (*n* = 42)		
1995 *n* = 3	1M, 2F	22.3 (21–25)
1996 *n* = 4	2M, 2F	22 (20–25)
1997 *n* = 6	2M, 4F	23.3 (20–27)
1998 *n* = 3	1M, 2F	22 (20–25)
1999 *p* = 2	1M, 2M (pooled)	22 (20–25)
2000 *p* = 1	3F (pooled)	23 (20–27)
2001 *n* = 4	1M, 3F	23 (20–25)
2002 *p* = 1	3M (pooled)	23.3 (20–27)
2003 *n* = 3	2M, 1F	24 (23–25)
2004 *p* = 3	2M (pooled), 2F (pooled), 2F (pooled)	21.5 (20–23)
2005 *p* = 1	3M (pooled)	21.6 (20–23)
2006 *p* = 2	3M (pooled), 2F (pooled)	24.4 (22–27)
2007 *n* = 3	2M, 1F	21.3 (20–23)

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	Sex	Age (mean (range))
2008 *n* = 4	2M, 2F	22 (21–23)
2009 *n* = 2	1M, 1F	20.5 (20–21)
(c) Münster, Germany (*n* = 80)		
1982 *p* = 1	3M (pooled)	22 (20–25)
1983 *n* = 5	3M, 2F	21.7 (20–25)
1984 *n* = 2	2M	22.5 (21–24)
1985 *n* = 8	4M, 4F	22.8 (20–27)
1986 *n* = 2	1M, 1F	24 (23–25)
1987 *n* = 2	1M, 1F	23 (22–24)
1988 *n* = 2	1M, 1F	20.5 (20–21)
1989 *n* = 5	2M, 3F	22.2 (20–26)
1990 *n* = 6	2M, 4F	21.5 (20–23)
1991 *n* = 4	3M, 1F	22 (21–23)
1992 *n* = 3	1M, 2F	22.3 (22–23)
1993 *n* = 2	1M, 1F	23.5 (22–25)
1995 *n* = 2	2F	22
1996 *n* = 2	2F	22.5 (22–23)
1997 *n* = 5	2M, 3F	22.2 (21–24)
1998 *n* = 2	1M, 1F	22.5 (21–24)
1999 *n* = 3	1M, 2F	21.7 (21–22)
2000 *n* = 2	2M	22 (21–23)
2001 *p* = 2	2M (pooled), 2F (pooled)	23.3 (20–26)
2002 *n* = 2	1M, 1F	22 (21–23)
2003 *p* = 1	2M	21.5 (21–22)
2004 *n* = 2	1M, 1F	22 (21–23)
2005 *n* = 2	2M (pooled), 1F	23.3 (21–26)

	Sex	Age (mean (range))
2006 *n* = 2	2M (pooled), 1F	22.7 (21–24)
2007 *n* = 2	1M, 1F	22 (21–23)
2008 *n* = 7	2M, 1F	21.7 (21–23)
2009 *n* = 2	1M, 1F	21.5 (21–22)

Table S3. Optimised LC method

This method was used on an Acquity UPLC equipped with a BEH C18 column (2.1 × 75 mm, 1.7 um, 100 Å) and the column temperature was kept at 60 °C

Time	Flow (mL min^{-1})	0.1% NH_4OH in Milli Q water	MeOH	Curve
0.00	0.5	99	1	6
1.00	0.5	99	1	6
2.00	0.5	60	40	6
7.50	0.5	5	95	6
8.00	0.5	5	95	6
8.10	0.5	99	1	6
9.50	0.5	99	1	6

Table S4. Limit of quantifications (LOQs) in MeOH and in the presence of matrix

On column, MeOH:	On column, whole blood:	
20 fg (10 pg mL^{-1})	20 fg (10 pg mL^{-1})	
– diPAPs (6:2, 8:2)		– diPAPs (6:2, 8:2)
– FTSAs (4:2, 6:2, 8:2)		– FTSAs (4:2, 6:2, 8:2)
– PFCAs (C8–C11)		– PFCAs (C8–C11)
– PFSAs (C4–C8)		– PFSAs (C4–C8)
– PFPiA (C6/C6, C6/C8)		– PFPiA (C6/C6)
50 fg (25 pg mL^{-1})	50 fg (25 pg mL^{-1})	
– diPAPs (4:2, 10:2)		– diPAPs (4:2, 10:2)
– SAmPAP		– SAmPAP
– PFCAs (C5–7, 12–14)		– PFCAs (12–14)
– PFSAs(C10)		– PFSAs(C10)
– PFPAs (C6, C8, C10)		– PFPAs (C6, C8, C10)
– PFPiA (C8/C8)		– PFPiA (C6/C8, C8/C8)
– monoPAPs (6:2, 8:2)		– monoPAPs (6:2, 8:2)
– FTUCAs (6:2, 8:2)		– FTUCAs (6:2, 8:2)
– FTCAs (3:3, 5:3, 7:3)		– FTCAs (3:3, 5:3, 7:3)
100 fg (50 pg mL^{-1})	100 fg (50 pg mL^{-1})	
– PFCA (C4)		– PFCAs (C5–7)
– PFPA (C10)		– PFPA (C10)

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Table S5. Matrix recoveries (0.5 ng) in (a) horse whole blood, and (b) calf serum at pH 3 and 10

pH 10	pH 3
a) horse whole blood	
– C5–C12 PFCAs: 78 – 115%	– C6 C8, C10 PFPAs: 78 – 89%
– C4–C10 PFSAs: 91–95%	– 6:2, 8:2 monoPAPs: 61–71%
– FOSAA:78%, MeFOSAA: 102%, EtFOSAA: 105%	
– 4:2, 6:2, 8:2, 10:2 diPAPs: 95–102%	
–SAmPAP 83%	
– 4:2, 6:2, 8:2 FTSAs: 85–92%	
– C6/C6, C6/C8, C8/C8 PFPiAs: 87–91%	
b) calf serum	
– C5–C12 PFCAs: 75 – 116%	– C6 C8, C10 PFPAs: 75 – 85%
– C4–C10 PFSAs: 89–94%	– 6:2, 8:2 monoPAPs: 64–73%
– FOSAA:74%, MeFOSAA: 104%, EtFOSAA: 98%	
– 4:2, 6:2, 8:2, 10:2 diPAPs: 95–108%	
–SAmPAP 80%	
– 4:2, 6:2, 8:2 FTSAs: 88–96%	
– C6/C6, C6/C8, C8/C8 PFPiAs: 87–92%	

Table S6. Measured PFAS concentrations in the present and other studies

NIST Certificate of Analysis data obtained from certificate of analysis available on the NIST website (www.nist.gov/srm). Interlaboratory Study data obtained from Keller et al.[5] Chiron standards were used for quantification of Lee and Mabury data.[4] NA, not analysed; ND, not detected (i.e. analytes were either not detected or concentrations were below corresponding LOQs)

	Measured concentrations (ng mL^{-1})				
Analyte	NIST Certificate of Analysis	Interlaboratory Study[5]	Lee and Mabury[4]	Yeung et al.[6,7]	Present study
PFHpA	0.305 ± 0.036	0.28–0.33	0.27 ± 0.10	0.198 ± 0.057	0.231 ± 0.050
PFOA	5.00 ± 0.40	4.08–5.86	5.06 ± 0.86	4.10 ± 0.349	4.23 ± 0.441
PFNA	0.880 ± 0.068	0.76–0.97	0.880 ± 0.10	0.764 ± 0.077	0.754 ± 0.069
PFDA	0.39 ± 0.10	0.29–0.53	0.33 ± 0.06	0.293 ± 0.030	0.342 ± 0.032
PFUnDA	0.174 ± 0.031	0.11–0.22	0.15 ± 0.02	0.118 ± 0.12	0.153 ± 0.010
PFHxS	4.00 ± 0.75	3.01–6.49	3.49 ± 0.94	4.14 ± 0.458	4.08 ± 0.328
PFOS	21.1 ± 1.2	19.5–38.0	13.66 ± 1.13	12.3 ± 1.18	16.4 ± 3.00
FOSAA	NA	NA	0.16 ± 0.02	0.165 ± 0.022	0.156 ± 0.020
MeFOSAA	NA	NA	0.74 ± 0.06	0.681 ± 0.047	0.621 ± 0.058
EtFOSAA	NA	NA	0.15 ± 0.01	0.147 ± 0.011	0.122 ± 0.011
6:2 diPAP	NA	NA	0.044 ± 0.09^{A}	0.052 ± 0.006^{B}	0.062 ± 0.008^{B}
8:2 diPAP	NA	NA	0.013 ± 0.05^{A}	0.013 ± 0.008^{B}	0.015 ± 0.008^{B}

^{A}Concentration corrected with Wellington standard.

^{B}Wellington standards were used for quantification.

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Table S7. PFAS concentrations (ng mL^{-1}) for (a) samples of whole blood from seven Chinese cities, and plasma samples from two German cities, (b) Halle and (c) Münster

Half LOQ was used to calculate the mean concentrations when sample concentrations were below LOQ. A blank cell indicates the sample concentration was below LOQ (Table S4). *p* values are pooled samples

		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
(a) China											
Xiamen	Mean	2.45	0.906	20.3	0.041	2.37			0.683	0.761	0.026
n = 10	s.d.	2.39	0.78	22.1	0.012	3.09			0.789	0.639	
	Range	0.0315–7.30	<0.010–2.27	0.345–65.5	<0.010–0.056	0.270–10.4			0.069–2.43	<0.025–1.90	
	n > LOQ	10	8	10	4	10			10	9	1
Fuzhou	Mean	1.29	0.292	8.94		1.51			0.348	0.41	0.043
n = 15	s.d.	0.929	0.23	6.83		1.8			0.25	0.282	
	Range	0.221–3.78	0.078–1.01	1.82–25.0	0.047–0.075	0.351–7.51			0.049–1.00	0.059–0.903	
	n > LOQ	15	15	15	2	15			15	15	1
Zhoushan	Mean	1.3	0.184	6.24	0.15	0.561			0.137	0.309	
n = 8	s.d.	0.428	0.082	2.37	0.192	0.246			0.048	0.26	
	Range	0.872–2.15	0.085–0.286	3.60–10.7	<0.010–0.371	0.328–1.13			<0.025–0.199	<0.025–0.693	0.039–0.394
	n > LOQ	8	8	8	3	8			7	6	2
Nanjing	Mean	0.296		0.354		0.184			0.133	0.141	
n = 5	s.d.	0.15		0.151		0.121			0.071	0.099	
	Range	0.093–0.485		0.213–0.538		<0.050–0.344			<0.025–0.186	<0.025–0.272	
	n > LOQ	5		5		4			4	4	
Jintan	Mean	0.424	0.07	1.49		0.143			0.074	0.076	
n = 3	s.d.	0.115	0.004	0.542		0.007			0.012	0.034	
	Range	<0.010–0.505	<0.010–0.073	0.864–1.83		<0.050–0.148			<0.025–0.083	<0.025–0.100	
	n > LOQ	2	2	3		2			2	2	
Wuhan	Mean	0.636	0.354	3.2		0.462			0.307	0.581	
n = 3	s.d.	0.281	0.232	3.11		0.444			0.36	0.713	
	Range	0.429–0.956	0.211–0.622	1.12–6.78		0.203–0.974			0.060–0.720	0.096–1.40	
	n > LOQ	3	3	3		3			3	3	
Guiyang	Mean	0.658	0.13	3.27		0.454			0.168	0.37	
n = 3	s.d.	0.239	0.08	1.62		0.169			0.038	0.344	
	Range	0.516–0.934	0.078–0.222	2.22–5.13		0.262–0.577			0.130–0.206	0.152–0.767	
	n > LOQ	3	3	3		3			3	3	

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		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
(b) Halle, Germany											
1995	Mean	2.53	0.195	16.9				0.517	0.437	0.315	0.4
n = 3	s.d.	1.32	0.051	0.733					0.061	0.27	0.107
	Range	1.18–3.81	0.146–0.249	16.2–17.6		0.024–0.025			0.370–0.489	0.150–0.626	0.288–0.501
	n > LOQ	3	3	3		2		1	3	3	3
1996	Mean	2.58	0.299	23.4		0.028		0.695	0.581	0.486	0.626
n = 4	s.d.	0.904	0.053	3.06				0.329	0.258	0.438	0.287
	Range	1.86–3.89	0.247–0.370	20.0–27.4				<0.050–1.07	0.397–0.959	0.191–1.14	0.400–1.02
	n > LOQ	4	4	4		1		3	4	4	4
1997	Mean	3.41	0.202	15.8	0.031	0.025	0.14		0.385	0.449	0.567
n = 6	s.d.	0.979	0.054	4.24		0.011			0.156	0.295	0.192
	Range	2.36–4.94	0.124–0.257	9.91–19.5		0.009–0.039		0.223–1.00	0.224–0.636	0.164–0.996	0.387–0.919
	n > LOQ	6	6	6	1	6	1	2	6	6	6
1998	Mean	2.47	0.194	12.3		0.035		0.294	0.255	0.432	0.333
n = 3	s.d.	1.83	0.101	10.4				0.109	0.134	0.391	0.179
	Range	0.559–4.20	0.122–0.265	2.30–23.1				0.191–0.408	0.111–0.377	0.159–0.880	0.165–0.521
	n > LOQ	3	3	3		1		3	3	3	3
1999	Mean	2.97	0.251	17.5		0.031	0.022		0.245	0.215	0.333
p = 2	s.d.	2.54	0.078	9.75					0.088	0.155	0.086
	Range	1.18–4.77	0.196–0.306	10.6–24.4					0.183–0.307	0.106–0.324	0.272–0.393
	n > LOQ	2	2	2		1	1		2	2	2
2000	Mean	3.12	0.234	14.5		0.011			0.227	0.667	0.173
p = 1	s.d.										
	Range										
	n > LOQ	1	1	1		1			1	1	1
2001	Mean	5.28	0.22	17.4		0.03	0.043	0.136	0.275	0.487	0.243
n = 4	s.d.	4.31	0.13	12.1		0.013			0.09	0.524	0.086
	Range	2.21–11.5	0.054–0.338	2.82–28.5		0.016–0.043			0.146–0.355	0.155–1.26	0.150–0.352
	n > LOQ	4	4	4		3	1	1	4	4	4
2002	Mean	3.72	0.364	25		0.018		0.062	0.134	0.081	0.266
p = 1	s.d.										
	Range										
	n > LOQ	1	1	1		1		1	1	1	1
2003	Mean	8.37	0.367	20.2		0.006	0.1	0.185	0.089	0.435	0.084
n = 3	s.d.	6.44	0.19	7.91		0.005			0.062	0.257	0.041
	Range	1.01–13.0	0.198–0.573	14.5–29.3		0.003–0.010			0.053–0.160	0.196–0.708	0.053–0.131
	n > LOQ	3	3	3		2	1	1	3	3	3
	Mean	2.15	0.149	8.54					0.058	0.111	0.081

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		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
2004											
p = 3	s.d.	0.515	0.036	2.91					0.041	0.015	0.061
	Range	1.77–2.73	0.117–0.189	6.57–11.9					0.031–0.105	0.101–0.129	0.037–0.151
	n > LOQ	3	3	3					3	3	3
2005	Mean	2.725	0.236	5.594						0.163	
p = 1	s.d.										
	Range										
	n > LOQ	1	1	1						1	
2006	Mean	4.76	0.26	13.6					0.019	0.141	0.012
p = 2	s.d.	1.69	0.114	6.43					0.007	0.008	0.004
	Range	3.57–5.95	0.180–0.341	9.06–18.2					0.014–0.024	0.136–0.147	0.009–0.015
	n > LOQ	2	2	2					2	2	2
2007	Mean	3.64	0.114	5.26		0.003			0.02	0.098	0.007
n = 3	s.d.	2.39	0.029	1.92					0.017	0.108	0.002
	Range	2.15–6.40	0.089–0.146	3.64–7.38					0.009–0.040	0.027–0.223	0.004–0.009
	n > LOQ	3	3	3		1			3	3	3
2008	Mean	2.04	0.135	4.85		0.004	0.062		0.026	0.099	0.009
n = 4	s.d.	0.945	0.063	2.51		0.003			0.009	0.116	0.007
	Range	1.03–2.93	0.053–0.205	2.17–8.10		0.002–0.006			0.019–0.032	0.020–0.272	0.003–0.017
	n > LOQ	4	4	4		2	1		2	4	4
2009	Mean	4.67	0.195	6.28		0.002	0.091		0.004	0.024	0.004
n = 2	s.d.	0.886	0.054	2.54			0.019		0.006	0.005	0.002
	Range	4.04–5.29	0.157–0.233	4.49–8.07			0.078–0.104		0.003–0.009	0.020–0.027	0.002–0.005
	n > LOQ	2	2	2		1	2		2	2	2
(c) Münster, Germany											
1982	Mean	2.7	0.257	18.7		0.219		0.603	0.664	0.019	0.577
p = 1	s.d.										
	Range										
	n > LOQ	1	1	1		1		1	1	1	1
1983	Mean	2.42	0.304	19.9		0.148	4.6	1.92	1.81	0.106	1.6
n = 5	s.d.	1.2	0.109	6.081		0.072		0.628	1.11	0.023	0.875
	Range	0.875–4.22	0.176–0.464	13.2–26.0		0.069–0.213		<0.050–2.53	0.350–3.05	0.068–0.123	0.634–2.76
	n > LOQ	5	5	5		5	1	4	5	5	5
1984	Mean	4.48	0.264	20.4		0.134		0.22	1.2	0.101	1.15
n = 2	s.d.	0.973	0.154	14.6		0.151			1.26	0.102	1.4
	Range	3.80–5.17	0.155–0.372	10.0–30.8		0.028–0.241			0.308–2.09	0.029–0.173	0.161–2.14
	n > LOQ	2	2	2		2		1	2	2	2
	Mean	1.29	0.276	23		0.104		1.28	1.08	0.142	1.24

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		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
1985											
n = 8	s.d.	0.718	0.097	6.04		0.108		1.37	1.21	0.128	1.18
	Range	0.404–2.33	0.134–0.381	15.6–33.0		0.012–0.361	1.67–4.93	0.321–4.34	0.279–3.97	0.046–0.448	0.255–3.83
	n > LOQ	8	8	8		8	2	8	8	8	8
1986	Mean	2.83	0.552	47.9		0.261			1.72	0.126	1.42
n = 2	s.d.	0.625	0.233	19.8		0.237			1.27	0.052	0.363
	Range	2.39–3.28	0.387–0.716	33.9–61.9		0.093–0.428			0.820–2.62	0.089–0.162	1.16–1.68
	n > LOQ	2	2	2		2			2	2	2
1987	Mean	2.82	0.247	21.7		0.136			0.811	0.098	0.758
n = 2	s.d.	2.64	0.121	9.16		0.14			0.778	0.01	0.604
	Range	0.950–4.69	0.161–0.332	15.2–28.2		0.037–0.236			0.261–1.36	0.091–0.105	0.331–1.18
	n > LOQ	2	2	2		2			2	2	2
1988	Mean	6.26	0.377	27.7		0.079			0.462	0.233	0.294
n = 2	s.d.	0.26	0.015	2.05		0.019			0.086	0.206	0.03
	Range	6.074–6.44	0.367–0.387	26.3–29.1		0.066–0.092			0.402–0.523	0.087–0.378	0.273–0.315
	n > LOQ	2	2	2		2			2	2	2
1989	Mean	3.79	0.643	53.2		0.105		0.912	0.488	0.126	0.792
n = 5	s.d.	2.14	0.765	58.4		0.162		0.851	0.323	0.047	1.063
	Range	1.40–6.93	0.202–2.01	18.0–157		0.007–0.348		0.301–2.16	0.205–1.01	0.044–0.161	0.108–2.68
	n > LOQ	5	5	5		4		4	5	5	5
1990	Mean	2.39	0.471	36.9		0.026	2.54	0.531	0.425	0.091	0.475
n = 6	s.d.	1.101	0.185	11.4		0.019		0.137	0.3	0.032	0.188
	Range	1.28–4.18	0.257–0.773	23.1–54.9		0.006–0.057		0.420–0.718	0.078–0.909	0.051–0.133	0.158–0.708
	n > LOQ	6	6	6		5	1	5	6	6	6
1991	Mean	3.75	0.53	40.3		0.268			1.372	0.191	0.725
n = 4	s.d.	1.04	0.115	17.2		0.499			2.292	0.204	0.956
	Range	2.20–4.32	0.450–0.701	30.6–65.9		0.016–1.02			0.145–4.81	0.076–0.497	0.134–2.15
	n > LOQ	4	4	4		4			4	4	4
1992	Mean	2.02	0.356	27.7		0.023			0.433	0.184	0.551
n = 3	s.d.	0.585	0.134	12		0.005			0.116	0.13	0.04
	Range	1.38–2.53	0.207–0.468	17.1–40.8		0.018–0.026			0.335–0.561	0.067–0.324	0.505–0.581
	n > LOQ	3	3	3		3			3	3	3
1993	Mean	4.25	0.527	32.9		0.032			0.427	0.136	0.836
n = 2	s.d.	1.02	0.041	0.989		0.001			0.006	0.007	0.051
	Range	3.53–4.97	0.498–0.556	32.2–33.6		0.032–0.033			0.423–0.432	0.130–0.141	0.800–0.872
	n > LOQ	2	2	2		2			2	2	2
1995	Mean	1	0.192	20.6		0.726			0.329	0.218	0.651
n = 2	s.d.	0.501	0.106	12.2		0.986			0.276	0.111	0.147
	Range	0.650–1.36	0.117–0.267	12.0–29.1		0.029–1.42			0.134–0.524	0.140–0.297	0.547–0.755
	n > LOQ	2	2	2		2			2	2	2

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		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
1996	Mean	2.47	0.412	26.6		0.019			0.663	0.422	1.772
n = 2	s.d.	0.304	0.102	5.35		0.002			0.059	0.232	0.006
	Range	2.26–2.69	0.340–0.484	22.9–30.4		0.017–0.020			0.621–0.705	0.258–0.586	1.77–1.78
	n > LOQ	2	2	2		2			2	2	2
1997	Mean	3.65	0.522	35.6		0.043	3.19	1.02	0.728	0.906	0.913
n = 5	s.d.	2.38	0.236	19.3		0.039	1.63	1.03	0.525	0.89	1.064
	Range	1.21–7.05	0.252–0.853	17.0–64.9		<0.010–0.101	<0.050–4.93	0.456–2.86	0.342–1.63	0.112–2.42	0.298–2.81
	n > LOQ	5	5	5		4	3	5	5	5	5
1998	Mean	5.24	0.356	21.9		0.033		0.348	0.324	0.302	0.337
n = 2	s.d.	3.17	0.022	1.49				0.196	0.219	0.184	0.247
	Range	3.00–7.48	0.340–0.371	20.8–22.9				0.209–0.487	0.170–0.479	0.171–0.432	0.163–0.512
	n > LOQ	2	2	2		1		2	2	2	2
1999	Mean	3.79	0.365	24.3	0.099	0.041	23.9	0.356	0.445	0.515	0.416
n = 3	s.d.	1.36	0.063	5.17		0.02		0.298	0.286	0.407	0.275
	Range	2.31–4.99	0.308–0.432	21.1–32.3		<0.010–0.055		0.048–0.643	0.269–0.775	0.277–0.985	0.196–0.724
	n > LOQ	3	3	3	1	2	1	3	3	3	3
2000	Mean	3.94	0.555	33.1		0.02			0.272	0.484	0.247
n = 2	s.d.	0.371	0.137	11.1		0.008			0.144	0.053	0.022
	Range	3.68–4.20	0.458–0.652	25.3–41.0		0.015–0.026			0.171–0.374	0.446–0.521	0.231–0.262
	n > LOQ	2	2	2		2			2	2	2
2001	Mean	3.24	0.291	21.5		0.015			0.454	0.964	0.215
n = 2	s.d.	0.77	0.006	2.1		0.003			0.042	0.284	0.026
	Range	2.70–3.79	0.287–0.295	20.1–23.0		0.013–0.017			0.424–0.484	0.763–1.17	0.96–0.233
	n > LOQ	2	2	2		2			2	2	2
2002	Mean	2.35	0.231	17.9		0.014			0.326	0.696	0.438
n = 2	s.d.	0.492	0.103	7.44		0.002			0.065	0.022	0.06
	Range	2.00–2.69	0.159–0.304	12.6–23.1		0.012–0.015			0.280–0.372	0.681–0.712	0.395–0.480
	n > LOQ	2	2	2		2			2	2	2
2003	Mean	1.98	0.167	9.47		0.018		0.422	0.134	0.081	0.666
p = 1	s.d.										
	Range										
	n > LOQ	1	1	1		1		1	1	1	1
2004	Mean	8.49	0.367	18.6		0.006	0.129		0.057	0.175	0.045
n = 2	s.d.	5.28	0.266	14.2		0.001	0.072		0.055	0.129	0.028
	Range	4.76–12.2	0.180–0.555	8.49–28.6		0.005–0.006	0.0780–0.180		0.018–0.096	0.084–0.267	0.026–0.065
	n > LOQ	2	2	2		2	2		2	2	2
2005	Mean	2.48	0.237	12.1		0.003			0.027	0.109	0.04
n = 2	s.d.	1.47	0.127	5.23					0.017	0.011	0.029
	Range	1.44–5.52	0.148–0.327	8.38–15.8					0.015–0.039	0.101–0.117	0.019–0.060
	n > LOQ	2	2	2		1			2	2	2

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		PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA
2006	Mean	2.74	0.192	10.2		0.004	15.3		0.033	0.254	0.013
n = 2	s.d.	1.48	0.018	1.52					0.025	0.271	0.004
	Range	1.69–3.78	0.179–0.205	9.13–11.3					0.015–0.051	0.063–0.446	0.011–0.016
	n > LOQ	2	2	2		1	1		2	2	2
2007	Mean	3.12	0.226	9.86		0.003			0.036	0.136	0.051
n = 2	s.d.	3.37	0.132	4.4					0.034	0.119	0.062
	Range	0.742–5.50	0.132–0.319	6.75–13.0					0.012–0.059	0.052–0.220	0.008–0.095
	n > LOQ	2	2	2		1			2	2	2
2008	Mean	3.57	0.239	9.97		0.001	3.07		0.061	0.285	0.047
n = 7	s.d.	1.87	0.083	2.74			4.26		0.046	0.283	0.036
	Range	1.39–6.75	0.108–0.320	5.20–13.2			0.063–6.08		0.008–0.120	0.049–0.839	0.006–0.098
	n > LOQ	7	7	7		3	2		6	7	6
2009	Mean	1.24	0.184	6.31					0.008	0.056	0.008
n = 2	s.d.	0.548	0.069	2.85						0.046	0.002
	Range	0.851–1.63	0.136–0.233	4.29–8.33						0.024–0.088	0.007–0.010
	n > LOQ	2	2	2					1	2	2

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Table S8. Concentrations (ng F mL^{-1}) of PFOS precursor, PFSA, PFCA precursor, PFCA, PFPiA, and EOF in (a) Chinese blood, and (b,c) and German plasma samples

p values are pooled samples

		PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	EOF
(a) Chinese blood							
Xiamen	Mean	2.83	21	0.027	4.26		38.8
n = 8	s.d.	2.54	15.9		4.04		26.7
	Range	0.247–7.94	5.81–50.9		1.45–13.8		14.1–94.4
Fuzhou	Mean	1.69	9.44		2.67		18.7
n = 11	s.d.	1.43	4.52		1.83		6.15
	Range	0.518–5.68	4.95–18.9		0.558–6.05		9.36–28.8
Zhoushan	Mean	0.648	5.79		3.76		15.2
n = 7	s.d.	0.249	2.14		1.54		4.64
	Range	0.308–0.963	3.79–9.06		2.40–7.05		10.4–22.7
Jintan	Mean	0.119	2.03		4.25		20.1
n = 3	s.d.	0.106	0.588		1.17		3.77
	Range	0.000–0.201	1.37–2.50		2.92–5.11		17.0–24.3
Wuhan	Mean	1.1	5.76		1.6		9.81
n = 2	s.d.	1.05	4.63		0.878		2.25
	Range	0.358–1.84	2.49–9.03		0.983–2.22		8.22–11.4
Guiyang	Mean	0.602	4.49		0.691		11.9
n = 3	s.d.	0.302	2.1		0.301		4.51
	Range	0.331–0.928	3.18–6.91		0.481–1.04		8.28–17.0
Nanjing	Mean	0.228	0.424		0.365		
n = 5	s.d.	0.171	0.167		0.135		
	Range	0.035–0.423	0.206–0.666		0.191–0.522		
(b) Halle, Germany							
1995	Mean	0.77	12.618	0.006	1.91		24.8
n = 3	s.d.	0.155	1.323	0.001	1.049		16.8
	Range	0.594–0.882	11.3–13.9	0.005–0.007	1.00–3.056		12.6–43.9
1996	Mean	1.28	16.921	0.069	2.59	0.003	23.8
n = 4	s.d.	0.764	1.547	0.125	0.491	0.002	3.8
	Range	0.814–2.42	15.4–19.1	0.003–0.257	1.87–2.98	0.001–0.005	20.6–28.6

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		PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	EOF
1997	Mean	0.949	12.4	0.066	1.45	0.001	15.9
n = 6	s.d.	0.572	3	0.147	0.347	0.001	3.9
	Range	0.623–2.08	8.51–15.8	0.003–0.367	0.825–1.70	0.001–0.002	10.0–19.5
1998	Mean	0.765	9.59	0.015	1.31	0.005	12.3
n = 3	s.d.	0.334	6.51	0.01	1.06	0.007	7.97
	Range	0.419–1.09	4.09–16.8	0.004–0.023	0.191–2.30	0.001–0.013	5.29–21.0
1999	Mean	0.317	7.705		2.725		8.2
p = 2	s.d.						
	Range						
2000	Mean	0.613	11.479	0.046	2.057	0.008	17.3
p = 1	s.d.						
	Range						
2001	Mean	0.612	14.7	0.028	1.57		18.3
n = 4	s.d.	0.329	6.86	0.01	1.19		6.26
	Range	0.339–1.09	4.86–20.0	0.016–0.040	0.242–2.67		10.5–24.4
2002	Mean	0.318	18.799	0.038	2.512		23.5
p = 1	s.d.						
	Range						
2003	Mean	0.406	18.5	0.017	1.88	0.001	20.9
n = 3	s.d.	0.147	8.03	0.001	0.421		7.71
	Range	0.294–0.573	11.7–27.4	0.015–0.017	1.56–2.36		13.9–29.1
2004	Mean	0.142	6.95	0.072	1.76	0.012	10.6
p = 3	s.d.	0.054	1.75	0.115	0.99	0.009	4.53
	Range	0.110–0.204	5.53–8.90	0.006–0.205	0.626–2.44	0.006–0.023	6.26–15.3
2005	Mean	0.094	5.454	0.005	1.881	0.005	13
p = 1	s.d.						
	Range						
2006	Mean	0.098	11.9	0.012	2.45	0.006	16.7
p = 2	s.d.	0.007	5.28	0.007	0.25		7.31
	Range	0.093–0.103	8.18–15.6	0.007–0.017	2.28–2.63		11.6–21.9
2007	Mean	0.072	5.73	0.138	1.47	0.008	9.42
n = 3	s.d.	0.071	1.08	0.233	1.3	0.009	3.91
	Range	0.028–0.154	4.49–6.37	0.001–0.406	0.620–2.97	0.000–0.018	6.83–13.9
2008	Mean	0.08	4.49	0.02	2.1	0.003	10.9
n = 4	s.d.	0.078	2.09	0.016	1.79	0.004	3.61
	Range	0.013–0.184	2.08–7.18	0.005–0.042	0.656–4.65	0.000–0.007	6.60–14.2

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		PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	EOF
2009	Mean	0.103	8.91	0.017	1.73		12.4
n = 2	s.d.	0.047	1.46	0.009	0.242		3.03
	Range	0.069–0.136	7.88–9.94	0.010–0.023	1.56–1.90		10.2–14.5
(c) Münster, Germany							
1982	Mean	1.23	13.9	0.011	1.88		18
p = 1	s.d.						
	Range						
1983	Mean	3.62	14.6	0.002	1.6	0.026	24
n = 5	s.d.	2.77	4.51	0.001	0.628		12.1
	Range	0.637–6.76	9.24–19.7	0.001–0.004	1.07–2.34		11.2–40.7
1984	Mean	1.54	16.1	0.003	1.74	0.001	19
n = 2	s.d.	1.56	10.2		1.97		13.8
	Range	0.437–2.65	8.95–23.3		0.348–3.13		9.20–28.8
1985	Mean	2.76	15.9	0.004	1.9	0.002	21
n = 8	s.d.	2.67	4.06	0.008	0.757	0.004	5.52
	Range	0.589–8.63	10.6–22.2	0.000–0.021	0.952–3.27	0.000–0.010	14.5–29.4
1986	Mean	2.03	33.1	0.007	4.11	0.004	39.3
n = 2	s.d.	1.12	13.3	0.001	2.61	0.001	18.4
	Range	1.23–2.82	23.7–42.6	0.007–0.008	2.27–5.95	0.003–0.005	26.3–52.3
1987	Mean	1.03	16	0.002	2.13	0.047	14.9
n = 2	s.d.	0.882	7.64		1.53	0.063	3.36
	Range	0.410–1.66	10.6–21.4		1.05–3.21	0.002–0.092	12.5–17.3
1988	Mean	0.614	22	0.027	3.76	0.022	25.9
n = 2	s.d.	0.096	1.48	0.037	1.11	0.017	3.36
	Range	0.547–0.682	21.0–23.1	0.001–0.054	2.97–4.54	0.009–0.034	23.6–28.3
1989	Mean	1.29	37.2	0.005	3.79	0.002	42.5
n = 5	s.d.	1.38	38	0.007	3.39		40.9
	Range	0.223–3.70	13.7–104	0.000–0.016	1.64–9.56		16.6–115
1990	Mean	1.11	25.7	0.006	2.86	0.007	32.5
n = 6	s.d.	0.777	7.89		1.46	0.012	11.4
	Range	0.180–2.48	15.9–37.8		1.41–5.28	0.000–0.031	18.3–50.5
1991	Mean	1.48	28.7	0.007	3.63	0.008	33.6
n = 4	s.d.	2.15	11.5	0.005	1.64	0.002	16.4
	Range	0.227–4.69	21.5–45.8	0.002–0.013	1.69–5.24	0.006–0.010	23.4–58.0

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		PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	EOF
1992	Mean	0.676	19.4	0.004	3.57	0.013	23.3
n = 3	s.d.	0.114	8.06	0.002	0.95	0.002	7.93
	Range	0.598–0.806	12.1–28.1	0.002–0.005	2.70–4.58	0.011–0.014	14.6–30.1
1993	Mean	0.809	24.3	0.005	3.45	0.025	29.3
n = 2	s.d.	0.029	1.3	0	0.462	0.017	2.76
	Range	0.788–0.829	23.4–25.2	0.005–0.006	3.12–3.77	0.013–0.037	27.3–31.2
1995	Mean	1.15	14	0.006	2.54	0.006	23.4
n = 2	s.d.	0.335	8.25		0.421		4.09
	Range	0.909–1.38	8.21–19.9		2.225–2.84		20.5–26.3
1996	Mean	1.62	19	0.01	3.83	0.008	24.1
n = 6	s.d.	0.17	3.72	0.003	1.42	0.011	5.37
	Range	1.50–1.74	16.4–21.7	0.008–0.012	2.83–4.83	0.000–0.015	20.3–27.9
1997	Mean	3.3	25.6	0.076	3.2	0.006	30.8
n = 5	s.d.	2.22	12.2	0.137	1.18	0.009	14.2
	Range	1.23–6.66	11.9–43.6	0.000–0.320	1.72–4.35	0.000–0.021	13.6–51.3
1998	Mean	0.77	17.6	0.032	2.53	0.006	21.1
n = 2	s.d.	0.504	1.01	0.007	0.368	0.002	1.45
	Range	0.414–1.13	16.9–18.4	0.027–0.037	2.27–2.79	0.005–0.008	20.1–22.2
1999	Mean	6.03	18.3	0.171	3.47	0.002	28.1
n = 3	s.d.	8.24	3.63	0.256	0.943	0.004	5.43
	Range	0.730–15.5	15.6–22.4	0.018–0.466	2.61–4.48	0.000–0.006	22.7–33.6
2000	Mean	0.582	24.2	0.029	3.47	0.005	27
n = 2	s.d.	0.131	7.04	0.008	1.29	0.006	9.96
	Range	0.489–0.674	19.3–29.2	0.024–0.035	2.56–4.38	0.001–0.009	20.0–34.1
2001	Mean	0.939	16.1	0.038	2.56	0.005	21.5
n = 2	s.d.	0.169	0.885	0.006	0.582	0.003	0.212
	Range	0.819–1.06	15.5–16.8	0.034–0.042	2.15–2.98	0.003–0.008	21.3–21.6
2002	Mean	0.835	13.2	0.017	2.17	0.006	15.1
n = 2	s.d.	0.016	4.57	0.003	1.32	0.002	7.78
	Range	0.824–0.846	9.95–16.4	0.015–0.020	1.23–3.10	0.004–0.008	9.61–20.6
2003	Mean	0.761	7.459	0.019	1.059	0.004	14.4
p = 1	s.d.						
	Range						
2004	Mean	1.96	5.86	0.105	2.11	0.004	18.7
n = 2	s.d.	2.72	1.34	0.137	0.299		9.48
	Range	0.040–3.89	4.91–6.81	0.008–0.202	1.90–2.32		12.0–25.4

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		PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	EOF
2005	Mean	0.1	9.51	0.025	3.01	0.008	14.5
n = 2	s.d.	0.031	4.38	0.021	1.89		6.88
	Range	0.078–0.122	6.41–12.6	0.010–0.040	1.68–4.35		9.60–19.3
2006	Mean	5.01	8.42	0.019	4.05	0.036	19.1
n = 2	s.d.	7.01	0.077	0.007	2.35	0.031	2.23
	Range	0.056–9.97	8.36–8.37	0.015–0.024	2.39–5.72	0.014–0.058	17.5–20.6
2007	Mean	0.127	8.46	0.107	2.75	0.004	15.8
n = 2	s.d.	0.123	5.01	0.134	1.2		5.32
	Range	0.040–0.214	4.91–12.0	0.012–0.202	1.90–3.60		12.0–19.5
2008	Mean	0.768	8.82	0.014	3.11	0.005	22.6
n = 7	s.d.	1.39	2.4	0.009	2.87	0.007	9.36
	Range	0.090–3.89	4.96–11.7	0.004–0.027	1.20–9.18	0.000–0.018	10.2–34.0
2009	Mean	0.039	4.97	0.011	5.28		19.7
n = 2	s.d.	0.028	1.55	0.015	3.27		9.05
	Range	0.019–0.058	3.87–6.07	0.000–0.021	2.97		13.3–26.1

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Table S9. Spearman rank correlations of PFASs in Chinese blood

Numbers in red indicates significant correlation. P<0.05

	PFHxS	PFHpS	PFOS	FOSA	FOSAA	MeFOSAA	PFOA	PFNA	PFDA	PFUnDA
PFHxS		0.6541	0.8894	0.7593	0.5060	0.4956	0.3664	0.4180	0.3168	0.3986
PFHpS	0.6541		0.7500	0.5057	0.3979	0.3863	0.0135	0.1653	0.1492	0.1230
PFOS	0.8894	0.7500		0.8087	0.6307	0.6449	0.3077	0.3465	0.3201	0.3513
FOSA	0.7593	0.5057	0.8087		0.7370	0.6900	0.0930	0.0790	0.0775	0.1894
FOSAA	0.5060	0.3979	0.6307	0.7370		0.7412	–0.0025	–0.0419	0.0334	–0.0639
MeFOSAA	0.4956	0.3863	0.6449	0.6900	0.7412		0.2054	0.2335	0.2053	0.0839
PFOA	0.3664	0.0135	0.3077	0.0930	–0.0025	0.2054		0.7760	0.6260	0.3507
PFNA	0.4180	0.1653	0.3465	0.0790	–0.0419	0.2335	0.7760		0.7232	0.4182
PFDA	0.3168	0.1492	0.3201	0.0775	0.0334	0.2053	0.6260	0.7232		0.7669
PFUnDA	0.3986	0.1230	0.3513	0.1894	–0.0639	0.0839	0.3507	0.4182	0.7669	

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Table S10. Test statistics for linear regression analyses (a) 8:2 FTSA, (b) unidentified organofluorine, and (c) quantifiable PFAS

(a) 8:2 FTSA					
i. Halle					
1995–2000					
Linear Regression					
Regression Statistics					
r	0.96571				
R^2	0.93261				
Adjusted R^2	0.91576				
S	0.00694				
Total number of observations	6				
y =– 24.6368 + 0.0123x					
ANOVA					
	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	0.00267	0.00267	55.35194	0.00174
Residual	4	0.00019	0.00005		
Total	5	0.00286			
2000–2009					
Linear Regression					
Regression Statistics					
r	0.74962				
R^2	0.56194				
Adjusted R^2	0.50718				
S	0.01258				
Total number of observations	10				
y = 8.9159 – 0.0044x					
ANOVA					
	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	0.00162	0.00162	10.26214	0.01255
Residual	8	0.00127	0.00016		
Total	9	0.00289			
ii. Münster					
1995–2000					
Linear Regression					
Regression Statistics					
r	0.8279				
R^2	0.68542				
Adjusted R^2	0.60677				
S	0.01041				
Total number of observations	6				
y =– 14.6460 + 0.0073x					
ANOVA					

	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	0.00094	0.00094	8.71522	0.04188
Residual	4	0.00043	0.00011		
Total	5	0.00138			
2000–2009					
Linear Regression					
Regression Statistics					
r	0.71166				
R^2	0.50646				
Adjusted R^2	0.44477				
S	0.0108				
Total number of observations	10				
y = 6.8552 – 0.0034x					
ANOVA					
	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	0.00096	0.00096	8.20939	0.02098
Residual	8	0.00093	0.00012		
Total	9	0.00189			
(b) Unidentified organofluorine					
i. Halle					
2000–2009					
Linear Regression					
Regression Statistics					
r	0.19269				
R^2	0.03713				
Adjusted R^2	–0.08323				
S	1.55282				
Total number of observations	10				
y =– 187.8995 + 0.0950x					
ANOVA					
	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	0.74385	0.74385	0.30849	0.5938
Residual	8	19.29	2.41125		
Total	9	20.03385			
ii. Münster					
2000–2009					
Linear Regression					
Regression Statistics					
r	0.78199				
R^2	0.61151				
Adjusted R^2	0.56295				
S	2.3377				
Total number of observations	10				
y =– 1827.0194 + 0.9133x					
ANOVA					
	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	68.81695	68.81695	12.59267	0.00752
Residual	8	43.71873	5.46484		
Total	9	112.53568			

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(c) Quantifiable PFAS

i. Halle

2000–2009

Linear Regression

Regression Statistics

R	0.64088
R^2	0.41073
Adjusted R^2	0.33707
S	4.5305
Total number of observations	10

y = 2373.8826 – 1.1778x

ANOVA

	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	114.44989	114.44989	5.57601	0.04586
Residual	8	164.20331	20.52541		
Total	9	278.6532			

ii. Münster

2000–2009

Linear Regression

Regression Statistics

r	0.68674
R^2	0.47161
Adjusted R^2	0.40556
S	4.48059
Total number of observations	10

y = 2658.0463 – 1.3181x

ANOVA

	d.f.	*SS*	*MS*	*F*	*P*
Regression	1	143.34503	143.34503	7.14023	0.02827
Residual	8	160.60561	20.0757		
Total	9	303.95064			

Table S11. Test statistics for non-linear smoothers

Effect	d.f.	RSSQ	*F*-ratio	*P*
Halle				
Year	3.57	272.268	5.4	*0.0181*
Non-linear	2.57	162.333	4.473	*0.041*
Error	10.43	147.301	s^2 = 14.123	
Münster				
Year	6.63	754.166	3.349	*0.0201*
Non-linear	5.63	555.18	2.903	*0.0412*
Error	19.37	657.923	s^2 = 33.966	

References

[1] W. S. Cleveland, Robust locally weighted regression and smoothing scatterplots. *J. Am. Stat. Assoc.* **1979**, *74*, 829. doi:10.1080/01621459.1979.10481038

[2] R. J. Fryer, M. D. Nicholson, Using smoothers for comprehensive assessment of contaminant time series in marine biota. *ICES J. Mar. Sci.* **1999**, *56*, 779. doi:10.1006/jmsc.1999.0499

[3] Z. Wang, I. T. Cousins, M. Scheringer, K. Hungerbühler, Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environ. Int.* **2013**, *60*, 242. doi:10.1016/j.envint.2013.08.021

[4] H. Lee, S. A. Mabury, A pilot survey of legacy and current commercial fluorinated chemicals in human sera from United States donors in 2009. *Environ. Sci. Technol.* **2011**, *45*, 8067. doi:10.1021/es200167q

[5] J. M. Keller, A. M. Calafat, K. Kato, M. E. Ellefson, W. K. Reagen, M. Strynar, S. O'Connell, C. M. Butt, S. A. Mabury, J. Small, D. C. G. Muir, S. D. Leigh, M. M. Schantz, Determination of perfluorinated alkyl acid concentrations in human serum and milk standard reference materials. *Anal. Bioanal. Chem.* **2010**, *397*, 439. doi:10.1007/s00216-009-3222-x

[6] L. W. Y. Yeung, S. J. Robinson, J. Koschorreck, S. A. Mabury, Part I. A temporal study of PFCAs and their precursors in human plasma from two German cities 1982. *Environ. Sci. Technol*. **2013**, *47*, 3865. doi:10.1021/es303716k

[7] L. W. Y. Yeung, S. J. Robinson, J. Koschorreck, S. A. Mabury, Part II. A temporal study of PFOS and its precursors in human plasma from two German cities in 1982–2009. *Environ. Sci. Technol*. **2013**, *47*, 3875. doi:10.1021/es4004153