Supporting information

A pilot study on extractable organofluorine and per- and polyfluoroalkyl substances (PFAS) in water from drinking water treatment plants around Taihu Lake, China: what is missed by target PFAS analysis?

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Table S1 Chemicals and MRM transition

Class	Abbreviation	Name	Quantification ion (m/z)	Qualification ion (m/z)	Internal standard
PFCAs	TFA	Trifluoroacetic acid	112.9/68.96		$^{13}C_4$-PFBA
	PFPrA	Perfluoropropanoic acid	162.97/118.9		$^{13}C_4$-PFBA
	PFBA	Perfluorobutanoic acid	212.97/169		$^{13}C_4$-PFBA
	PFPeA	Perfluoropentanoic acid	262.97/219		$^{13}C_3$-PFPeA
	PFHxA	Perfluorohexanoic acid	312.97/269	312.97/118.95	$^{13}C_2$-PFHxA
	PFHpA	Perfluoroheptanoic acid	362.97/319	362.97/168.97	$^{13}C_4$-PFHpA
	PFOA	Perfluorooctanoic acid	412.97/369	412.97/168.97	$^{13}C_4$-PFOA
	PFNA	Perfluorononanoic acid	462.99/419	462.99/219	$^{13}C_5$-PFNA
	PFDA	Perfluorodecanoic acid	512.97/469	512.97/219	$^{13}C_2$-PFDA
	PFUnDA	Perfluoroundecanoic acid	562.97/519	562.97/268.99	$^{13}C_2$-PFUnDA
	PFDoDA	Perfluorododecanoic acid	612.97/569	612.97/168.96	$^{13}C_2$-PFDoDA
	PFTrDA	Perfluorotridecanoic acid	662.9/619	662.9/168.96	$^{13}C_2$-PFDoDA
	PFTDA	Perfluorotetradecanoic acid	712.9/669	712.9/168.97	$^{13}C_2$-PFTDA
	PFHxDA	Perfluorohexadecanoic acid	812.9/769	812.9/168.96	$^{13}C_2$-PFHxDA
	PFOcDA	Perfluorooctadecanoic acid	912.9/869	912.9/168.96	$^{13}C_2$-PFHxDA
PFSAs	TFMS	Trifluoromethane sulfonic acid	149.12/79.91	149.12/98.95	$^{13}C_3$-PFBS
	PFEtS	Perfluoroethane sulfonic acid	198.8/79.8	198.8/98.9	$^{13}C_3$-PFBS
	PFPrS	Perfluoropropane sulfonic acid	248.9/79.9	248.9/98.9	$^{13}C_3$-PFBS
	PFBS	Perfluorobutane sulfonic acid	298.9/98.9	298.9/79.96	$^{13}C_3$-PFBS
	PFPeS	Perfluoropentane sulfonic acid	348.9/98.96	348.9/79.96	$^{18}O_2$-PFHxS
	PFHxS	Perfluorohexane sulfonic acid	398.9/98.9	398.9/79.96	$^{18}O_2$-PFHxS
	PFHpS	Perfluoroheptanesulfonic acid	448.97/98.9	448.97/79.96	$^{13}C_4$-PFOS

	PFOS	Perfluorooctane sulfonic acid	498.97/98.9	498.97/79.96 498.97/169.03	$^{13}C_4$-PFOS
	PFNS	Perfluorononane sulfonic acid	548.9/98.96	548.9/79.96	$^{13}C_4$-PFOS
	PFDS	Perfluorodecane sulfonic acid	598.97/98.9	598.97/79.96	$^{13}C_4$-PFOS
	PFDoDS	Perfluorododecane sulfonic acid	698.9/98.9	698.9/79.96	$^{13}C_4$-PFOS
FTSAs	4:2 FTSA	4:2 fluorotelomer sulfonic acid	327/307	327/81	$^{13}C_2$-6:2 FTSA
	6:2 FTSA	6:2 fluorotelomer sulfonic acid	427/407	427/81	$^{13}C_2$-6:2 FTSA
	8:2 FTSA	8:2 fluorotelomer sulfonic acid	527/507	527/81	$^{13}C_2$-8:2 FTSA
FTCAs	5:3 FTCA	5:3 fluorotelomer carboxylic acid	340.9/236.97	340.9/216.93	$^{13}C_2$-6:2 FTUCA
	7:3 FTCA	7:3 fluorotelomer carboxylic acid	440.9/316.93	440.9/336.89	$^{13}C_2$-8:2 FTUCA
	ADONA	3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid]	376.97/250.8	376.97/84.69	$^{18}O_2$-PFHxS
	HFPO-DA	hexafluoropropylene oxide dimer acid	284.92/168.72	328.95/284.86	$^{13}C_3$-HFPO-DA
Novel PFAS	8:2 Cl-PFESA	8:2 chlorinated polyfluorinated ether sulfonate	630.904/450.98	630.904/83.027	$^{13}C_4$-PFOS
	6:2 Cl-PFESA	6:2 chlorinated polyfluorinated ether sulfonate	530.904/350.98	530.904/83.027	$^{13}C_4$-PFOS
	PFECHS	Perfluoro-4-ethylcyclohexane sulfonate	460.84/380.9	460.84/98.88	$^{13}C_4$-PFOA

Table S2 Parameters for QTOF analysis

The following parameters were set for initial filtering: (1) S/N > 3; (2) LC peak width less than 30 s; and (3) intensity >5 times the intensity in the procedural blank. Suspect screening was conducted with the PFAS suspect list followed previous studies[1, 2], and the screening processes were performed by R scripts (R v3.6.2, R Foundation for Statistical Computing, Vienna, Austria).

UPLC conditions			ESI- parameters
Analytical column: Acquity UPLC-BEH C18 (100 mm x 2.1 mm x 1.7 μm)			Ionization: ESI-
Mobile phase: (A) 2 mM NH_4Ac + H2O / MeOH (70/30); (B) 2 mM NH_4Ac + MeOH			Acquisition time: 0.5 to 15 min
Column temperature: 50 °C			Acquisition function: MS^E
Injection volume: 10 μL			Mass range: m/z 50-1200
Rinse solvent: H_2O:MeOH:ACN:IPA 1:1:1:1			Analyzer mode: Sensitivity
Sample temperature: 10 °C			Capillary voltage: 0.5 kV
Flow rate: 0.3 mL/min			Sample cone: 10 V
Source temperature: 100 °C			Cone gas flow: 100 L/h
Mobile phase gradient:			Desolvation gas flow: 1000 L/h
Time	Composition A	Composition B	Desolvation temperature: 350°C
0 min	99%	1%	Scan rate: 5 Hz
0.5 min	99%	1%	Low energy: 4 eV
13 min	0%	100%	High energy ramp: 20-70
14 min	0%	100%	Lockspray: Leucine Enkephalin m/z 554.2620 Scan time 0.25 s
14.2 min	99%	1%	
16 min	99%	1%	Interval: 10s

Table S3 Spike recovery test results using Milli-Q water (n=3, 2 ng)

Compounds	Mean recovery (%)	RSD	Compounds	Mean recovery (%)	RSD
PFBA	101	9%	PFTrDA	74	5%
PFPeA	96	5%	PFBS	86	4%
PFHxA	96	5%	PFHxS	96	4%
PFHpA	96	3%	PFOS	89	8%
PFOA	96	5%	6:2 FTSA	102	6%
PFNA	90	14%	HFPO-DA	76	17%
PFDA	96	6%	ADONA	83	18%
PFUnDA	96	6%	F-53B	80	3%
PFDoDA	95	6%			

Table S4 Internal standard recovery in raw and treated water samples (n=16, 2 ng)

Compounds	Mean recovery (%)	RSD	Compounds	Mean recovery (%)	RSD
$^{13}C_4$-PFBA	56	24%	$^{13}C_2$-PFTDA	48	34%
$^{13}C_3$-PFPeA	82	6%	$^{13}C_2$-PFHxDA	32	50%
$^{13}C_2$-PFHxA	82	6%	$^{13}C_3$-PFBS	90	12%
$^{13}C_4$-PFHpA	90	10%	$^{18}O_2$-PFHxS	92	6%
$^{13}C_4$-PFOA	84	5%	$^{13}C_4$-PFOS	89	7%
$^{13}C_5$-PFNA	74	28%	$^{13}C_2$-6:2 FTSA	181	35%
$^{13}C_2$-PFDA	81	9%	$^{13}C_3$-HFPO-DA	59	33%
$^{13}C_2$-PFUnDA	75	10%	$^{13}C_2$-8:2 FTSA	63	16%
$^{13}C_2$-PFDoDA	67	16%			

Table S5 MDL and MQL of the target PFAS (ng/L)

Individual compounds	**Batch1**		**Batch2**		**Batch3**		**Batch4**	
	MDL	**MQL**	**MDL**	**MQL**	**MDL**	**MQL**	**MDL**	**MQL**
PFBA	0.0660	0.0720	0.0770	0.142	0.102	0.148	0.167	0.389
PFPeA	/	0.0200	/	0.0200	/	0.0200	/	0.0200
PFHxA	0.0190	0.0250	0.0300	0.063	0.0350	0.0590	0.0350	0.0460
PFHpA	/	0.0200	/	0.0200	0.0160	0.0250	0.111	0.293
PFOA	0.0470	0.0810	0.0540	0.103	0.0380	0.0380	0.0450	0.0560
PFNA	/	0.0200	/	0.0200	0.0360	0.0810	0.0260	0.0350
PFDA	0.0270	0.0560	0.0280	0.0400	0.0230	0.0400	0.0210	0.0220
PFUnDA	0.0120	0.0130	0.0160	0.0220	0.0340	0.0750	0.0170	0.0170
PFDoDA	/	0.0200	/	0.0200	0.00900	0.0160	/	0.0200
PFTrDA	/	0.0200	/	0.0200	0.00900	0.0180	/	0.0200
PFBS	0.0200	0.0230	0.0310	0.0530	0.0420	0.0860	0.0320	0.0430
PFPeS	/	0.0200	/	0.0200	/	0.0200	/	0.0200
PFHxS	0.0260	0.0570	0.0180	0.0330	0.0200	0.0280	0.0210	0.0270
PFOS	0.0410	0.100	0.0690	0.181	0.0280	0.0540	0.0340	0.0560
6:2 FTSA	/	0.0200	/	0.0200	0.0670	0.119	0.0460	0.0480
HFPO-DA	/	0.0500	/	0.0500	/	0.0500	/	0.0500
ADONA	/	0.0500	/	0.0500	/	0.0500	/	0.0500
F-53B	/	0.0500	/	0.0500	/	0.0500	/	0.0500
TFA	/	0.0200	0.0270	0.0280	0.224	0.448	0.449	1.05
PFPrA	/	0.0200	7.35	12.6	1.48	2.85	1.76	4.08
TFMS	/	0.0200	0.0170	0.0370	0.100	0.266	0.0810	0.208
PFEtS	/	0.0200	/	0.0200	0.00700	0.0190	/	0.0200
PFPrS	/	0.0200	/	0.0200	/	0.020	/	0.0200

Table S6 Changes of EOF and different classes of PFAS after treatment processes

	D3	D4	D5	D8
	(Treated-Raw)/Raw	(Treated-Raw)/Raw	(Treated-Raw)/Raw	(Treated-Raw)/Raw
EOF	2.1%	-9.9%	-33.3%	59.4%
Short-chain PFCAs	-7.1%	2.0%	-15.2%	10.1%
Short-chain PFSAs	-2.8%	9.2%	25.8%	91.9%
Long-chain PFCAs	-1.1%	12.8%	-10.3%	-47.6%
Long-chain PFSAs	-2.3%	7.4%	17.6%	-31.6%
Novel PFAS	25.8%	8.4%	-0.7%	8.8%
Ultra-short PFAS	-53.7%	35.2%	36.8%	99.4%

Table S7 Concentrations of PFAS in raw and treated water from 8 DWTPs in China (ng/L)

Individual PFAS	Concentrations of PFAS in raw and treated water from 8 DWTPs in China (ng/L)															
	D1		D2		D3		D4		D5		D6		D7		D8	
	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water
PFBA	8.34	8.35	10.4	10.4	10.8	9.83	12.7	11.0	10.1	8.39	1.90	1.82	0.457	0.678	4.44	4.80

PFPeA	3.04	3.10	3.98	3.73	3.97	3.55	4.41	4.56	3.81	3.31	0.640	0.632	0.138	0.153	0.444	0.561
PFHxA	8.42	9.37	8.83	9.11	9.44	8.86	11.6	13.2	5.96	5.12	1.63	1.69	0.188	0.212	0.606	0.770
PFHpA	3.61	4.24	4.45	4.50	4.56	4.47	5.08	5.67	4.49	3.88	0.768	0.941	<MQL	<MQL	0.650	0.636
PFOA	24.6	29.4	30.1	29.5	32.9	32.6	42.5	49.0	34.5	31.5	5.41	6.47	1.37	1.36	7.85	4.12
PFNA	3.87	4.22	4.12	3.00	3.49	3.56	3.57	3.52	3.52	3.11	0.672	0.748	0.225	0.197	0.348	0.173
PFDA	1.66	1.58	1.59	1.85	2.07	1.92	1.92	1.57	2.54	1.86	0.474	0.277	0.121	0.0680	0.0970	0.0520
PFUnDA	0.472	0.205	0.416	0.602	0.757	0.475	0.523	0.396	1.85	0.509	0.293	0.0460	0.105	0.0250	<MQL	<MQL
PFDoDA	0.0650	<MQL	0.0690	0.103	0.112	0.0340	0.0840	0.0220	0.395	0.0290	0.0620	<MQL	0.0210	<MQL	<MQL	<MQL
PFTrDA	0.0410	<MQL	0.0440	0.0780	0.0930	<MQL	0.0590	<MQL	0.113	<MQL	0.0560	<MQL	<MQL	<MQL	<MQL	<MQL
PFBS	3.01	3.37	4.92	4.96	5.19	5.11	6.90	7.51	1.61	1.99	0.631	0.737	0.100	0.141	1.35	2.66
PFPeS	0.381	0.391	0.401	0.380	0.479	0.401	0.515	0.592	0.0240	0.0610	0.0570	0.110	<MQL	<MQL	0.0660	0.0570
PFHxS	44.0	48.7	50.1	45.9	57.4	57.2	54.2	61.4	2.57	3.47	7.43	13.4	0.0340	0.187	1.55	1.23
PFOS	5.13	6.234	11.0	12.3	15.4	13.9	13.2	11.0	2.97	3.05	1.50	1.34	0.194	0.193	0.674	0.292
6:2 FTSA	0.0290	<MQL	<MQL	0.249	0.0360	0.0830	0.108	0.195	<MQL	<MQL	0.240	0.280	0.0490	0.0530	0.0480	0.0970
HFPO-DA	0.345	0.393	0.615	0.490	0.785	0.799	1.06	1.12	1.32	1.54	0.165	0.182	<MQL	<MQL	<MQL	0.101
F-53B	1.58	2.46	4.14	4.76	5.03	6.48	4.27	4.57	3.19	2.95	0.453	0.541	0.0890	0.0770	0.133	<MQL
TFA	3.61	1.61	2.31	2.44	3.03	<MQL	<MQL	<MQL	<MQL	0.567	4.14	8.96	7.94	<MQL	<MQL	<MQL
PFPrA	13.5	3.20	19.7	12.45	11.8	<MQL	4.87	8.33	7.19	8.62	14.2	36.1	17.9	14.3	<MQL	4.18
TFMS	61.3	5.07	9.01	11.1	4.31	8.72	4.59	4.544	8.49	12.3	1.08	0.580	<MQL	<MQL	7.48	10.7
PFEtS	0.0830	0.0480	0.0580	0.0650	0.0540	0.0490	0.0440	0.0400	0.0390	0.0320	0.0320	<MQL	<MQL	0.0220	0.0330	0.0590
PFPrS	0.162	0.0610	0.0600	0.0580	0.0650	0.147	0.126	0.108	<MQL	<MQL	0.0680	0.0690	0.0280	11.7	0.0200	0.0770

Table S8 PFASs identified in samples by suspect screening with a confidence level of 2 or 3 (target PFAS not included)

Class	Name	Theoretical m/z	Observed m/z	Mass error (ppm)	Molecular formula	RT (min)	Product ions formula	Confidence level	Semi-quantification reference PFAS	Concentrations (ng/L)
H-PFCAs	H-PFPeA	244.9854	244.9851	-1.34	C5H2F8O2	3.38	C4F7-	2	PFPeA	0.161-0.975
	H-PFOA	394.9759	394.9752	-1.65	C8H2F14O2	7.32	C3F7-	3	PFOA	0.0120-0.0180
	H-PFNA	444.9727	444.9712	-3.26	C9H2F16O2	8.28	C7F13- C8F15-	3	PFNA	0.0190
H-PFSAs	H-PFBS	280.9524	280.9523	-0.43	C4H2F8O3S	3.57	SO3- FSO3- C3F5-	3	PFBS	0.00500-0.0150
	H-PFOS	480.9396	480.9396	-0.08	C8H2F16O3S	8.21	SO3- FSO3- FSO2-	3	PFOS	0.00100-0.00200
Cl-PFESAs	5:2 Cl-PFESA	480.8988	480.8985	-0.58	C7HF14O4SCl	9.5	C5OF10Cl-	2	PFOS	0.00100-0.00300
H-PFESAs	2:2 H-PFESA	296.9473	296.9473	-0.10	C4H2F8O4S	4.39	FSO2- C2OF3- C2HOF4-	2	PFBS	0.00700-0.0320
	4:2 H-PFESA	396.9409	396.9404	-1.36	C6H2F12O4S	7.43	C3F5- C4OF7- C4HOF8-	2	PFHxS	0.00200-0.0130
	6:2 H-PFESA	496.9346	496.9346	0.08	C8H2F16O4S	8.83	FSO3- FSO2- C5F9- C6OF11- C6HOF12-	2	PFOS	0.00800-0.439

							COF3-			
OBS	OBS	602.9564	602.9560	-0.71	C15H5F17O4S	10.75	C6H4O2- C6H4O4S- C11H4O3F7S- C13H4O4F11S-	2	PFOS	0.00100-0.0372

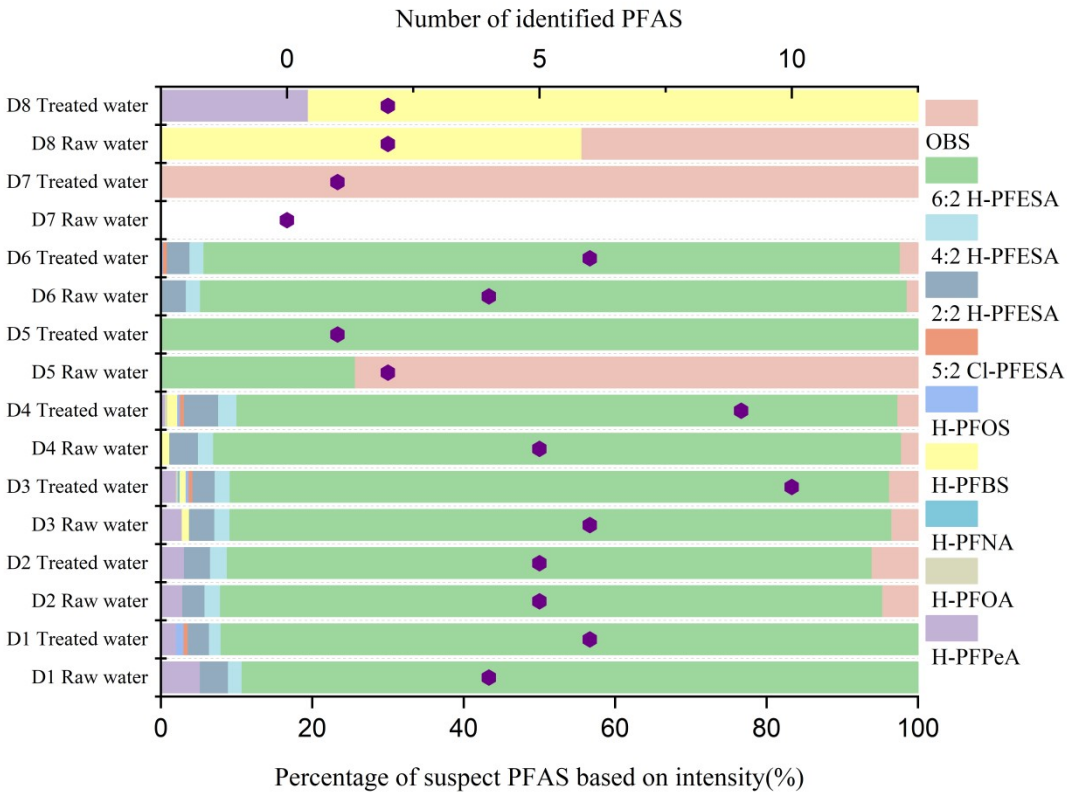

Figure S1 Composition of identified PFAS suspects based on intensity

References:

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