Supplementary Information

Human exposure to per- and polyfluoroalkyl substances and other emerging contaminants in drinking water

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Supplementary Table 1. Frequency (%) and median concentrations (ng/L) based on individual chemical concentrations reported in the last 10 years assessing PFAS concentrations in Spain and the Barcelona metropolitan area [1,2]

	Llorca *et al*. (2012) (N= 17)				Schwanz *et al*. (2016) (N= 29)				This study (N=42)			
	Spain 2011		Barcelona 2011		Spain 2014		Barcelona 2014		Barcelona 2020		Barcelona 2021	
	%	Median	%	Median	%	Median	%	Mean	%	Median	%	Median
PFBA	56	10	56	9.8	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
PFPeA	41	1.7	33	2.4	n.a.	n.a.	n.a.	n.a.	64	3.3	62	4.0
PFHxA	19	3.0	11	3.0	6.9	36	18	36	31	13	n.d.	n.d.
PFHpA	14	11	11	1.6	35	15	55	3.5	52	3.0	24	1.6
PFOA	39	2.9	78	4.6	21	13	36	13.5	12	11	n.d.	n.d.
PFNA	34	0.8	44	0.4	17	14	9.1	8.7	n.d.	n.d.	n.d.	n.d.
PFDA	8.9	2.3	n.d.	n.d.	6.9	18	9.1	11.6	2.4	6.0	2.4	4.4
PFUdA	6.3	1.1	n.d.	n.d.	3.5	7.7	9.1	7.7	2.4	7.2	n.d.	n.d.
PFDoA	1.3	2.1	n.d.	n.d.	3.5	12	n.d.	n.d.	4.8	25 *	n.d.	n.d.
PFTrDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	37	2.4	44	8.3	31	11	55	10.5	64	9.2	45	6.8
PFHxS	38	0.4	22	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.4	22 *
PFOS	54	7.0	67	13	38	41	55	43	52	12.5	4.8	11.5
PFDS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	10	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	5.1	4.1	n.d.	n.d.	3.5	18	9.1	18.4	n.a.	n.a.	n.a.	n.a.
PFHxDA	n.d.	n.d.	n.d.	n.d.	3.5	2.6	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.
PFODA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.
PFHxPA	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PFOPA	6.3	4.5	33	4.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PFDPA	6.3	11	22	8.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

* It should be noted that this analyte was only detected in two samples.
n.d.: not detected; n.a.: not analysed

Supplementary Table 2. List of organic compounds included in the non-target screening of drinking water of the first sampling (August-October 2020)

	Name	Class of compound	Formula
1	Acetaminophen	Pharmaceutical	$C_8H_9NO_2$
2	Acridone	Pharmaceutical	$C_{13}H_9NO$
3	Albendazol	Pharmaceutical	$C_{12}H_{15}N_3O_2S$
4	Alprazolam	Pharmaceutical	$C_{17}H_{13}ClN_4$
5	Amlodipine	Pharmaceutical	$C_{20}H_{25}ClN_2O_5$
6	Atenolol	Pharmaceutical	$C_{14}H_{22}N_2O_3$
7	Atorvastatin	Pharmaceutical	$C_{33}H_{35}FN_2O_5$
8	Azaperol	Pharmaceutical	$C_{19}H_{24}FN_3O$
9	Azaperone	Pharmaceutical	$C_{19}H_{22}FN_3O$
10	Azithromycin	Pharmaceutical	$C_{38}H_{72}N_2O_{12}$
11	Bezafibrate	Pharmaceutical	$C_{19}H_{20}ClNO_4$
12	Carazolol	Pharmaceutical	$C_{18}H_{22}N_2O_2$
13	Carbamazepine	Pharmaceutical	$C_{15}H_{12}N_2O$
14	10,11-epoxide carbamazepine	Pharmaceutical (metabolite)	$C_{15}H_{12}N_2O_2$
15	Cefalexin	Pharmaceutical	$C_{16}H_{17}N_3O_4S$
16	Cimetidine	Pharmaceutical	$C_{10}H_{16}N_6S$
17	Ciprofloxacin	Pharmaceutical	$C_{17}H_{18}FN_3O_3$
18	Citalopram	Pharmaceutical	$C_{20}H_{21}N_2FO$
19	Desmethylcitalopram	Pharmaceutical (metabolite)	$C_{19}H_{19}FN_2O$
20	Clarithromycin	Pharmaceutical	$C_{38}H_{69}NO_{13}$
21	Clopidogrel	Pharmaceutical	$C_{16}H_{16}ClNO_2S$
22	Codeine	Pharmaceutical	$C_{18}H_{21}NO_3$
23	Dihydrocodeine	Pharmaceutical (metabolite)	$C_{18}H_{23}NO_3$
24	6-acetylcodeine	Pharmaceutical (metabolite)	$C_{20}H_{23}NO_4$
25	Desloratidine	Pharmaceutical	$C_{19}H_{19}ClN_2$
26	Dexamethasone	Pharmaceutical	$C_{22}H_{29}FO_5$
27	17-OXO-dexamethasone	Pharmaceutical (metabolite)	$C_{20}H_{25}FO_3$
28	Dexamethasone acefurate	Pharmaceutical (metabolite)	$C_{29}H_{33}FO_8$
29	Dexamethasone 21-(4-pyridinecarboxylate)	Pharmaceutical (metabolite)	$C_{28}H_{32}FNO_6$
30	Diazepam	Pharmaceutical	$C_{16}H_{13}ClN_2O$
31	Diazepam *N*-oxide	Pharmaceutical (metabolite)	$C_{16}H_{13}ClN_2O_2$
32	Diclofenac	Pharmaceutical	$C_{14}H_{11}Cl_2NO_2$
33	Diltiazem	Pharmaceutical	$C_{22}H_{26}N_2O_4S$

34	*N*-Desmethyldiltiazem	Pharmaceutical (metabolite)	$C_{21}H_{24}N_2O_4S$
35	Dimetridazole	Pharmaceutical	$C_5H_7N_3O_2$
36	Enalapril	Pharmaceutical	$C_{20}H_{28}N_2O_5$
37	Enalaprilat	Pharmaceutical	$C_{18}H_{24}N_2O_5$
38	Erithromycin	Pharmaceutical	$C_{37}H_{67}NO_{13}$
39	Famotidine	Pharmaceutical	$C_8H_{15}N_7O_2S_3$
40	Famotidine propanamide	Pharmaceutical (metabolite)	$C_8H_{13}N_5OS_2$
41	Famotidine sulfamoyl propanamide	Pharmaceutical (metabolite)	$C_8H_{14}N_6O_3S_3$
42	Fluoxetine	Pharmaceutical	$C_{17}H_{18}F_3NO$
43	Fluvastatin	Pharmaceutical	$C_{24}H_{26}FNO_4$
44	Furosemide	Pharmaceutical	$C_{12}H_{11}ClN_2O_5S$
45	Gemfibrozil	Pharmaceutical	$C_{15}H_{22}O_3$
46	Glibenclamide	Pharmaceutical	$C_{23}H_{28}ClN_3O_5S$
47	Hidrochlorothiazide	Pharmaceutical	$C_7H_8ClN_3O_4S_2$
48	Hydrocodone	Pharmaceutical	$C_{18}H_{21}NO_3$
49	Ibuprofen	Pharmaceutical	$C_{13}H_{18}O_2$
50	Indomethacine	Pharmaceutical	$C_{19}H_{16}ClNO_4$
51	Iopromide	Pharmaceutical	$C_{18}H_{24}I_3N_3O_8$
52	Irbesartan	Pharmaceutical	$C_{25}H_{28}N_6O$
53	Ketoprofen	Pharmaceutical	$C_{16}H_{14}O_3$
54	Piketoprofen	Pharmaceutical	$C_{22}H_{20}N_2O_2$
55	Levamisol	Pharmaceutical	$C_{11}H_{12}N_2S$
56	Loratidine	Pharmaceutical	$C_{22}H_{23}ClN_2O_2$
57	Lorazepam	Pharmaceutical	$C_{15}H_{10}Cl_2N_2O_2$
58	Losartan	Pharmaceutical	$C_{22}H_{23}ClN_6O$
59	Meloxicam	Pharmaceutical	$C_{14}H_{13}N_3O_4S_2$
60	Metformin	Pharmaceutical	$C_4H_{11}N_5$
61	Metoprolol	Pharmaceutical	$C_{15}H_{25}NO_3$
62	Metronidazole	Pharmaceutical	$C_6H_9N_3O_3$
63	Metronidazole-Oh	Pharmaceutical	$C_6H_9N_3O_3$
64	Nadolol	Pharmaceutical	$C_{17}H_{27}NO_4$
65	Naproxen	Pharmaceutical	$C_{14}H_{14}O_3$
66	Norfluoxetine	Pharmaceutical	$C_{16}H_{16}F_3NO$
67	Ofloxacin	Pharmaceutical	$C_{18}H_{20}FN_3O_4$
68	Olanzapine	Pharmaceutical	$C_{17}H_{20}N_4S$
69	Oxycodone	Pharmaceutical	$C_{18}H_{21}NO_4$

70	Noroxycodone	Pharmaceutical (metabolite)	$C_{17}H_{19}NO_4$
71	Paroxetine	Pharmaceutical	$C_{19}H_{20}FNO_3$
72	Phenazone	Pharmaceutical	$C_{11}H_{12}N_2O$
73	Piroxicam	Pharmaceutical	$C_{15}H_{13}N_3O_4S$
74	Piroxicam pivalic ester	Pharmaceutical	$C_{20}H_{21}N_3O_5S$
75	Pravastatin	Pharmaceutical	$C_{23}H_{36}O_7$
76	Propanolol	Pharmaceutical	$C_{16}H_{21}NO_2$
77	Propyphenazone	Pharmaceutical	$C_{14}H_{18}N_2O$
78	Ranitidine	Pharmaceutical	$C_{13}H_{22}N_4O_3S$
79	Ronidazole	Pharmaceutical	$C_6H_8N_4O_4$
80	Salbutamol	Pharmaceutical	$C_{13}H_{21}NO_3$
81	Sertraline	Pharmaceutical	$C_{17}H_{17}Cl_2N$
82	Sotalol	Pharmaceutical	$C_{12}H_{20}N_2O_3S$
83	Sulfamethoxazole	Pharmaceutical	$C_{10}H_{11}N_3O_3S$
84	Tamsulosin	Pharmaceutical	$C_{20}H_{28}N_2O_5S$
85	Tenoxicam	Pharmaceutical	$C_{13}H_{11}N_3O_4S_2$
86	Tetracycline	Pharmaceutical	$C_{22}H_{24}N_2O_8$
87	5a,11a-dehydrochlorotetracycline	Pharmaceutical (metabolite)	$C_{22}H_{21}ClN_2O_8$
88	4-aminoanhydrochlorotetracycline	Pharmaceutical (metabolite)	$C_{20}H_{17}ClN_2O_7$
89	Torasemide	Pharmaceutical	$C_{16}H_{20}N_4O_3S$
90	Trazodone	Pharmaceutical	$C_{19}H_{22}ClN_5O$
91	Trimethoprim	Pharmaceutical	$C_{14}H_{18}N_4O_3$
92	Desmethoxy-4-ethhoxy-trimethprim	Pharmaceutical (metabolite)	$C_{15}H_{20}N_4O_3$
93	Valsartan	Pharmaceutical	$C_{24}H_{29}N_5O_3$
94	Venlafaxine	Pharmaceutical	$C_{17}H_{27}NO_2$
95	Desvenlafaxine	Pharmaceutical (metabolite)	$C_{16}H_{25}NO_2$
96	Warfarin	Pharmaceutical	$C_{19}H_{16}O_4$
97	Xylazine	Pharmaceutical	$C_{12}H_{16}N_2S$
98	Estradiol 17-glucuronide	Hormone/Endocrine disruptor	$C_{24}H_{32}O_8$
99	Estradiole diacetate	Hormone / Endocrine disruptor	$C_{22}H_{28}O_4$
100	Dibromoestradiol	Hormone / Endocrine disruptor	$C_{18}H_{22}Br_2O_2$
101	Estriol	Hormone / Endocrine disruptor	$C_{18}H_{24}O_3$
102	Oxoestriol	Hormone / Endocrine disruptor	$C_{18}H_{22}O_4$
103	Nilestriol	Hormone / Endocrine disruptor	$C_{20}H_{24}O_3$
104	Ethynylestriol	Hormone / Endocrine disruptor	$C_{20}H_{24}O_3$
105	Estriol 16-glucuronide	Hormone / Endocrine disruptor	$C_{24}H_{32}O_9$

106	Estriol 3-sulfate	Hormone / Endocrine disruptor	$C_{18}H_{24}O_6S$
107	Estriol succinate	Hormone / Endocrine disruptor	$C_{26}H_{32}O_9$
108	Estriol tripropionate	Hormone / Endocrine disruptor	$C_{27}H_{36}O_6$
109	Estrone	Hormone / Endocrine disruptor	$C_{18}H_{22}O_2$
110	2-methoxyestrone 3-glucosiduronic acid	Hormone / Endocrine disruptor	$C_{25}H_{32}O_9$
111	2-methoxyestrone	Hormone / Endocrine disruptor	$C_{19}H_{24}O_3$
112	3-*O*-(Carboxymethyl)estrone	Hormone / Endocrine disruptor	$C_{20}H_{24}O_4$
113	Estrone quinone	Hormone / Endocrine disruptor	$C_{18}H_{20}O_3$
114	16α-hydroxyestrone	Hormone / Endocrine disruptor	$C_{18}H_{22}O_3$
115	Estradiol	Hormone / Endocrine disruptor	$C_{18}H_{24}O_2$
116	Estrone 3-glucuronide	Hormone / Endocrine disruptor	$C_{24}H_{30}O_8$
117	Estrone 3-sulfate	Hormone / Endocrine disruptor	$C_{18}H_{22}O_5S$
118	Ethinyl estradiol	Hormone / Endocrine disruptor	$C_{20}H_{24}O_2$
119	Diethylstilbestrol	Hormone / Endocrine disruptor	$C_{18}H_{20}O_2$
120	Caffeine	Stimulants	$C_8H_{10}N_4O_2$
121	Cocaine	Illicit drug / pharmaceutical	$C_{17}H_{21}NO_4$
122	Benzoylecgonine	Illicit drug (metabolite)	$C_{16}H_{19}NO_4$
123	Ecgonine-methyl-ester	Illicit drug (metabolite)	$C_{10}H_{17}NO_3$
124	Cocaethylene	Illicit drug (metabolite)	$C_{18}H_{23}NO_4$
125	4'-Fluorococaine	Illicit drug / pharmaceutical	$C_{17}H_{20}FNO_4$
126	Benzoylecgonine	Illicit drug (metabolite)	$C_{16}H_{19}NO_4$
127	LSD (lysergic acid diethylamide)	Illicit drug / pharmaceutical	$C_{20}H_{25}N_3O$
128	Lysergic acid	Illicit drug / pharmaceutical	$C_{16}H_{16}N_2O_2$
129	1-acetyllysergic acid diethylamide	Illicit drug	$C_{22}H_{27}N_3O_2$
130	Cannabidiol	Illicit drug / pharmaceutical	$C_{21}H_{30}O_2$
131	CBGA (cannabigerolic acid)	Illicit drug / pharmaceutical	$C_{22}H_{32}O_4$
132	Ephedrine	Illicit drug / pharmaceutical	$C_{10}H_{15}NO$
133	*N*-methylephedrine	Illicit drug derivative	$C_{11}H_{17}NO$
134	4-hydroxypehedrine	Illicit drug (metabolite)	$C_{10}H_{15}NO_2$
135	Mephedrone	Illicit drug	$C_{11}H_{15}NO_2S$
136	Methamphetamine	Illicit drug / pharmaceutical	$C_{10}H_{15}N$
137	Methylenedioxy-*N*,*N*-dimethylamphetamine	Illicit drug	$C_{12}H_{17}NO_2$
138	Morphine	Illicit drug / pharmaceutical	$C_{17}H_{19}NO_3$
139	Dibutirylmorphine	Illicit drug	$C_{25}H_{31}NO_5$
140	EDDP	Illicit drug (metabolite)	$C_{20}H_{23}NO_4$
141	Nicotine	Stimulant	$C_{10}H_{14}N_2$

142	3-Hydroxycarbofuran	Pesticide	$C_{12}H_{15}NO_4$
143	Acethochlor	Pesticide	$C_{14}H_{20}ClNO_2$
144	Alachlor	Pesticide	$C_{14}H_{20}ClNO_2$
145	Atrazine	Pesticide	$C_8H_{14}ClN_5$
146	Deisopropylatrazine	Pesticide (metabolite)	$C_5H_8ClN_5$
147	Desethylatrazine	Pesticide (metabolite)	$C_6H_{10}ClN_5$
148	Desethylhydroxyatrazine	Pesticide (metabolite)	$C_6H_{11}N_5O$
149	Deethyldeisopropylatrazine	Pesticide (metabolite)	$C_5H_8ClN_5$
150	Azinphos ethyl	Pesticide	$C_{12}H_{16}N_3O_3PS_2$
151	Azinphos methyl	Pesticide	$C_{10}PN_3H_{12}S_2O_3$
152	Burpofezin	Pesticide	$C_{16}H_{23}N_3OS$
153	Barbendazim	Pesticide	$C_9H_9N_3O_2$
154	Carbofuran	Pesticide	$C_{12}H_{15}NO_3$
155	Chlorfenvinphos	Pesticide	$C_{12}H_{14}Cl_3O_4P$
156	Chlorpyriphos	Pesticide	$C_9H_{11}Cl_3NO_3PS$
157	Diazinon	Pesticide	$C_{12}H_{21}N_2O_3PS$
158	Diclofenthion	Pesticide	$C_{10}H_{13}Cl_2O_3PS$
159	Dimetoate	Pesticide	$C_5H_{12}NO_3PS_2$
160	Diuron	Pesticide	$C_9H_{10}Cl_2N_2O$
161	Ethion	Pesticide	$C_9H_{22}O_4P_2S_4$
162	Fenitrothion	Pesticide	$C_9H_{12}NO_5PS$
163	Fenoxon	Pesticide	$C_{10}H_{15}O_4PS$
164	Fenthion	Pesticide	$C_{10}H_{15}O_3PS_2$
165	Fenthion Sulfone	Pesticide	$C_{10}H_{15}O_5PS_2$
166	Fenthion sulfoxide	Pesticide	$C_{10}H_{15}O_5PS$
167	Hexythiazox	Pesticide	$C_{17}H_{21}ClN_2O_2S$
168	Imazalil	Pesticide	$C_{14}H_{14}Cl_2N_2O$
169	Imidacloprid	Pesticide	$C_9H_{10}ClN_5O_2$
170	Isoproturon	Pesticide	$C_{12}H_{18}N_2O$
171	Isoproturon monodemethyl	Pesticide (metabolite)	$C_{11}H_{16}N_2O$
172	Isoproturon didemethyl	Pesticide (metabolite)	$C_{10}H_{14}N_2O$
173	Malathion	Pesticide	$C_{10}H_{19}O_6PS_2$
174	Methiocarb	Pesticide	$C_{11}H_{15}NO_2S$
175	Metoalachlor	Pesticide	$C_{15}H_{22}ClNO_2$
176	Molinate	Pesticide	$C_9H_{17}NOS$
177	Omethoate	Pesticide	$C_5H_{12}NO_4PS$

178	Parathio*N*-ethyl	Pesticide	$C_{10}H_{14}NO_5PS$
179	Parathio*N*-methyl	Pesticide	$C_8H_{10}NO_5PS$
180	Prochloraz	Pesticide	$C_{15}H_{16}Cl_3N_3O_2$
181	Propanil	Pesticide	$C_9H_9Cl_2NO$
182	Propazine	Pesticide	$C_9H_{16}N_5Cl$
183	Propazine 2-hydroxy	Pesticide (metabolite)	$C_9H_{17}N_5O$
184	Pyriproxyphen	Pesticide	$C_{20}H_{19}NO_3$
185	Simazine	Pesticide	$C_7H_{12}ClN_5$
186	Simazine 2-hydroxy	Pesticide (metabolite)	$C_7H_{13}ClN_5O$
187	Tebuconazole	Pesticide	$C_{16}H_{22}ClN_3O$
188	Terbumeton	Pesticide	$C_{10}H_{19}N_5O$
189	Terbumeto*N*-Desethyl	Pesticide	$C_8H_{15}N_5O$
190	Terbuthylazine	Pesticide	$C_9H_{16}ClN_5$
191	Terbuthylazine desethyl	Pesticide (metabolite)	$C_7H_{12}ClN_5$
192	Terbuthylazine-2 Hidroxy	Pesticide	$C_9H_{17}N_5O$
193	Terbuthylazine-desethyl-2-hydroxy	Pesticide (metabolite)	$C_7H_{13}N_5O$
194	Terbutryn	Pesticide	$C_{10}H_{19}N_5S$
195	Thiabendazole	Pesticide	$C_{10}H_7N_3S$
196	Tolclophos-methyl	Pesticide	$C_9H_{11}Cl_2O_3PS$
197	1H-Benzotriazole	Industrial organic	$C_6H_5N_3$
198	1-Chlorobenzotriazole	Industrial organic	$C_6H_4ClN_3$
199	Tolytriazol	Industrial organic	$C_7H_7N_3$
200	Nonylphenol monoethoxylate	Industrial organic	$C_{17}H_{28}O_2$
201	Octylphenol	Industrial organic	$C_{14}H_{22}O$
202	Octylphenol diethoxylate	Industrial organic	$C_{18}H_{30}O_3$
203	Octylphenol monocarboxylate	Industrial organic	$C_{16}H_{24}O_3$
204	Octylphenol monoethoxylate	Industrial organic	$C_{16}H_{26}O_2$
205	Tris(2-chloroethyl) phosphate	Industrial organic	$C_6H_{12}Cl_3O_4P$
206	Tris(1,3-dichloro-2-propyl)phosphate	Industrial organic	$C_9H_{15}Cl_6O_4P$
207	Tris(2,3-dibromopropyl) phosphate	Industrial organic	$C_9H_{15}Br_6O_4P$
208	Tris(butoxyethyl) phosphate	Industrial organic	$C_{18}H_{39}O_7P$
209	Tris(chloroisopropyl) phosphate	Industrial organic	$C_9H_{18}Cl_3O_4P$
210	Bisphenol A (BPA)	Industrial organic	$C_{15}H_{16}O_2$
211	Nonylphenol (NP)	Industrial organic	$C_{15}H_{24}O$
212	Nonylphenol diethoxylate	Industrial organic	$C_{19}H_{32}O_3$

213	Nonylphenol monocarboxylate	Industrial organic	$C_{17}H_{26}O_3$
214	4-Methylbenzylidene camphor	Personal care product	$C_{18}H_{22}O$
215	Benzophenone-3	Personal care product	$C_{14}H_{12}O_3$
216	Ethylhexyl methoxycinnamate	Personal care product	$C_{18}H_{26}O_3$
217	Octocrylene	Personal care product	$C_{24}H_{27}NO_2$
218	methoxybenzophenone	Personal care product	$C_{14}H_{12}O_2$
219	4,4'-Dihidroxybenzophenone	Personal care product	$C_{13}H_{10}O_3$
220	4-Hydroxybenzophenone	Personal care product	$C_{13}H_{10}O_2$
221	Benzophenone-1 (benzoresorcinol)	Personal care product	$C_{13}H_{10}O_3$
222	Benzophenone-2 (DJ1892000)	Personal care product	$C_{13}H_{10}O_5$
223	Ethyl 4-aminobenzoate	Personal care product	$C_9H_{11}NO_2$
224	Ethylhexyl dimethyl PABA	Personal care product	$C_{17}H_{27}NO_2$
225	Ethylparaben	Personal care product	$C_9H_{10}O_3$
226	Methylparaben	Personal care product	$C_8H_8O_3$
227	Benzylparaben	Personal care product	$C_{14}H_{12}O_3$
228	Propylparaben	Personal care product	$C_{10}H_{12}O_3$
229	Triclorocaraban	Personal care product	$C_{13}H_9Cl_3N_2O$
230	Triclosan	Personal care product	$C_{12}H_7Cl_3O_2$
231	Mefenamic acid	Pharmaceutical	$C_{15}H_{15}NO_2$
232	Clofibric acid	Pharmaceutical (metabolite)	$C_{10}H_{11}O_3Cl$
233	Mevastatin	Pharmaceutical	$C_{25}H_{38}O_5$
234	Lansoprazole	Pharmaceutical	$C_{16}H_{14}F_3N_3O_2S$
235	Loratadine	Pharmaceutical	$C_{22}H_{23}ClN_2O_2$
236	Erythromycin	Pharmaceutical	$C_{37}H_{67}NO_{13}$
237	Azythromycin	Pharmaceutical	$C_{38}H_{72}N_2O_{12}$
238	Propranolol	Pharmaceutical	$C_{16}H_{21}NO_2$
239	Ketamine	Pharmaceutical	$C_{13}H_{16}ClNO$
240	Hydroxynorketamine	Pharmaceutical (metabolite)	$C_{12}H_{14}ClNO_2$
241	Fentanyl	Illicit drug	$C_{22}H_{28}N_2O$
242	Benzylfentanyl	Illicit drug	$C_{21}H_{26}N_2O$
243	Acetylfentayl	Illicit drug	$C_{21}H_{26}N_2O$
244	Norfentanyl	Illicit drug	$C_{14}H_{20}N_2O$
245	4-Methoxybutyrfentanyl	Illicit drug	$C_{24}H_{32}N_2O_2$
246	Sucralose	Sweetener	$C_{12}H_{19}Cl_3O_8$
247	Azelaic acid	Personal care product	$C_9H_{16}O_4$
248	Suberic acid	Personal care product	$C_8H_{14}O_4$

Supplementary Table 3. Limits of quantification (LOQ) in drinking water (DW), limits of detection (LOD) in urine, and internal standards for target compounds

Per- and polyfluoroalkyl substances	DW LOQ (ng/L)	Urine LOD (pg/mL)	Internal Standard
Perfluoroalkyl carboxylates (PFCA)			
Perfluorobutanoate, PFBA (C4)	50	5.0	13C4-PFBA
Perfluoropentanoate, PFPeA (C5)	1.0	2.0	13C5-PFPeA
Perfluorohexanoate, PFHxA (C6)	10	0.8	13C5-PFHxA
Perfluoroheptanoate, PFHpA (C7)	1.0	1.7	13C4-PFHpA
Perfluorooctanoate, PFOA (C8)	10	1.8	13C8-PFOA
Perfluorononanoate, PFNA (C9)	5.0	1.4	13C9-PFNA
Perfluorodecanoate, PFDA (C10)	5.0	0.3	13C6-PFDA
Perfluoroundecanoate, PFUdA (C11)	5.0	0.3	13C7-PFUdA
Perfluorododecanoate, PFDoA (C12)	10	0.4	13C2-PFDoA
Perfluorotridecanoate, PFTrDA (C13)	50	1.0	13C2-PFDoA
Perfluoroalkyl sulfonates (PFSA)			
Perfluorobutane sulfonate, PFBS (C4)	5.0	0.2	13C3-PFBS
Perfluoropentane sulfonate, PFPeS (C5)	10	0.6	13C3-PFHxS
Perfluorohexane sulfonate, PFHxS (C6)	10	0.02	13C3-PFHxS
Perfluoroheptane sulfonate, PFHpS (C7)	5.0	0.04	13C8-PFOS
Perfluorooctane sulfonate, PFOS (C8)	10	0.02	13C8-PFOS
Perfluorononane sulfonate, PFNS (C9)	10	0.6	13C8-PFOS
Perfluorodecane sulfonate, PFDS (C10)	10	0.6	13C8-PFOS
Perfluorodecane sulfonate, PFUdS (C11)	10	0.6	13C8-PFOS
Perfluoroundecane sulfonate, PFDoS (C12)	10	0.6	13C8-PFOS
Perfluorotridecane sulfonate, PFTrDS (C13)	10	0.6	13C8-PFOS
Perfluorooctane sulfonamides			
PFOSA	50	0.33	13C8-PFOSA
N-MePFOSA	50	1.0	13C8-PFOSA
N-EtPFOSA	50	1.0	13C8-PFOSA
Fluorotelomer sulfonates (FTS)			
4:2 FTS	10	0.1	13C2-4:2 FTS
6:2 FTS	10	0.01	13C2-6:2 FTS
8:2 FTS	10	0.01	13C2-8:2 FTS
10:2 FTS	50	0.01	13C2-8:2 FTS
Fluoroalkylether compounds (ether-PFAS)			
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid, HFPO-DA	10	0.4	13C3-HFPO-DA
Perfluoro-4-oxapentanoic acid, PF4OPeA	10	1.3	13C3-HFPO-DA
Perfluoro-5-oxahexanoic acid, PF5OHxA	5.0	7.5	13C3-HFPO-DA
Perfluoro-3,6-dioxaheptanoic acid, 3,6-OPFHpA	5.0	1.7	13C3-HFPO-DA
Sodium dodecafluoro-3H-4,8-dioxanonanoate, NaDONA	1.0	0.7	13C3-HFPO-DA
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate, 9Cl-PF3ONS	10	0.01	13C3-HFPO-DA
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate, 11 Cl-PF3OUdS	10	0.01	13C3-HFPO-DA
Potassium perfluoro (2-ethoxyethane) sulfonate, PFEESA	50	0.5	13C3-HFPO-DA
Bisphenol A	10	-	
Nonylphenol	10	-	

Note: Isotope performance standards used in the urine analysis are 13C3-PFBA, 13C2-PFOA and 13C4-PFOS: 13C3-PFBA for PFBA; 13C2-PFOA for every PFCA, HFPO-DA, PF4OPeA, PF5OHxA, 3,6-OPFHpA and NaDONA; and 13C4-PFOS for all PFSAs, PFOSAs, FTSs, 9Cl-PF3ONS, 11 Cl-PF3OUdS and PFEESA, respectively.
The limit of quantification (LOQ) was considered the first level of the calibration curve. The limit of detection (LOD) was estimated as the concentration level that gives rise to a signal/noise ratio equal to three. No results were found in water samples with concentration levels <LOQ and >LOD, so we have considered the LOQ for water analysis. In contrast, for urine samples, the LOD has been taken as a reference.

Supplementary Methods

1) Reagents. All reagents were of liquid chromatographic (LC) grade.

PFAS analysed were supplied by Wellington Laboratories Inc. (Guelph, Canada): EPA-533PAR native analyte primary mix of 500 pg/µL in methanol, EPA-533ES isotope dilution standard mix of 500 (2000) pg/µL in methanol, EPA-533IS isotope performance standard mix of 1000 (3000) pg/µL in methanol, sodium 1H,1H,2H,2H-perfluorododecane sulfonate (10:2 FTS) of 50 ng/µL in methanol, perfluoro-1-octane sulfonamide (PFOSA) of 50 ng/µL in isopropanol, N-ethylperfluoro-1-octane sulfonamide (N-Et-PFOSA) of 50 ng/µL in methanol, N-methylperfluoro-1-octane sulfonamide (N-Me-PFOSA) of 50 ng/µL in methanol and perfluoro-1-[13C8]octane sulfonamide (M8PFOSA) of 50 ng/µL in isopropanol. EPA-533PAR is a native mixture that contains: carboxylates (C4-C12); sulfonates (C4-C7 linear, C6 and C8 linear and branched isomers); n:2 FTS (n: 4, 6 and 8); HFPO-DA; PF4OPeA; PF5OHxA; 3,6-OPFHpA; NaDONA; 9Cl-PF3ONS; 11Cl-PF3OUdS; and, PFEESA. EPA 533ES is a isotope dilution standars mix containing 13C4-PFBA, 13C5-PFPeA, 13C5-PFHxA, 13C4-PFHpA, 13C8-PFOA, 13C9-PFNA, 13C6-PFDA, 13C7-PFUdA, 13C2-PFDoA, 13C3-PFBS, 13C3-PFHxS, 13C8-PFOS, 13C2-4:2 FTS, 13C2-6:2 FTS, 13C2-8:2 FTS and 13C3-HFPO-DA. EPA-533IS is an isotope performance standard mix including 13C3-PFBA, 13C2-PFOA and 13C4-PFOS. Intermediate and calibration solutions were prepared weekly from the stock standard solution by appropriate dilution in methanol or acetonitrile and stored at -20 °C. Nitrogen (99.999% pure) and high-purity argon (Ar1) supplied by Air Liquide (Madrid, Spain) was used for the electrospray ionization (ESI) source and as a collision-induced dissociation (CID) gas in the TSQ Quantum triple quadrupole, respectively.

Nonylphenol solid, d8-NP of 100 ng/µL in acetone and d14-BPA 100 ng/µL in acetonitrile were acquired from Dr. Ehrenstorfer (LGC Standards, Teddington, UK). d5-NP of 100 ng/µL

in acetone was purchased at A2S Analytical Standard Solutions (Saint Jean d'Illac, France), and bisphenol A of 100 ng/µL in methanol was acquired at Neochema GmbH (Bodenheim, Germany). For GC–MS analysis, helium (He2) obtained by Air Liquide (Madrid, Spain) was employed as carrier gas.

2) Quality control. Quality control (blank spikes) and blank samples were extracted with every batch of sample. For water methodology, the compound recoveries range between 75 - 119% for all PFAS, with a median value of 85% and RSDs below 19% for reproducibility. On the other hand, for urine methodology, the compound recoveries range between 54 - 107% for all PFAS, with a median value of 76% and RSDs below 15% for reproducibility, with more favourable recoveries for PFAS with low-intermediate alkyl chain length (C4-C9). Two MRM transitions by LC–MS/MS or two ions by GC–MS were monitored for each compound included in the analyses, except for PFBA and PFPeA, one for quantification and one for confirmation according to the 2002/657/EC Commission Decision and relations between transitions or ions was calculated [3]. The fragmentation of PFBA and PFPeA yields a single fragment, respectively. Therefore, for these analytes, only one transition has been considered. Special care has been taken of identifying and quantifying PFBA and PFPeA, considering the retention time and peak shape of the respectively internal standard (13C4-PFBA and 13C5-PFPeA).

The quantification of PFAS, bisphenol A and nonylphenol was performed on the basis of the isotope dilution method, thus labelled internal standards have been added to each analysis. The following criteria were used for identification purposes: a) the ratio of the chromatographic retention time of the analyte to that of the internal standard should correspond to that of the calibration solution at a tolerance of ±2.5%, ±0.4 min, ±0.2 min for LC–MS/MS, NP and BPA by GC–MS/MS analysis, respectively; b) two m/z signals were confirmed for each analyte; c) as proposed in 2002/657/EC Decision, the ratio between the

two signals in the sample compared to ratio in the calibration curve should be in agreement with calibration curve average ± maximum permitted tolerances for relative ion intensities. The quantification of all other analytes was performed by internal calibration curve: the plot ratio of the most intensive peak area divided with the internal standard area against the ratio of concentrations. Branched and linear PFOS were summed for quantitation purposes.

Supplementary References

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3. European Commission. *Comission decission of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results (2002/657/EC)*. *Off. J. Eur. Comm.* (2002).