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

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A wide range of chemicals was measured in different types of drinking water and urine samples through target and non-target screening (NTS) to estimate human exposure. Tap water samples collected from 42 locations in Barcelona (August–October/2020, May/2021), tap water filtered with domestic activated carbon filters (AC, $N = 6$) and reverse osmosis (RO, $N = 5$), commercial bottled water ($N = 10$), and urine ($N = 39$) samples were included. 35 per- and polyfluoroalkyl substances (PFAS), bisphenol A, and nonylphenol were analyzed using LC–MS/MS and GC–MS/MS, and NTS using LC–HRMS. 9 PFAS were detected in unfiltered tap water of first sampling (79% samples, median = 30 ng/L), 6 in the second (69%, median = 9.8 ng/L), and 5 in 13% urine samples. NTS tentatively identified pharmaceuticals and other industrial chemicals in drinking water. PFAS were removed by RO and not by AC filters. Findings provide valuable information for exposure science and water quality monitoring of emerging drinking water contaminants.

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INTRODUCTION

The aquatic environment is threatened by an increasing number of chemicals used in consumer and industrial products, posing a human health hazard through drinking water exposure[1,2]. Endocrine disrupting chemicals such as per- and polyfluoroalkyl substances (PFAS) and phenols (e.g., bisphenol A, nonylphenol) are of high concern due to their large annual production and the difficulty of removal at drinking water treatment plants[2].

PFAS constitute a diverse group of anthropogenic substances produced since the 1950s for multiple industrial and consumer applications worldwide[3–5]. The unique properties of the carbon-fluorine bond make PFAS stable, resistant to degradation, and persistent, resulting in their ubiquitous presence in soil, surface and groundwater, food, and air[6]. Although the most widespread and toxic legacy compounds, perfluorooctane sulfonate (PFOS) and perfluorooctane carboxylate (PFOA), were phased out by manufacturers in most parts of the world, they are still present in the environment in line with replacement PFAS such as fluoroalkylether compounds (ether-PFAS; e.g., GenX, and ADONA) that are increasingly detected in the environment and organisms[7,8]. Strong epidemiological evidence shows associations with reduced birthweight, increased breast cancer risk, and impaired glucose tolerance[2]. Animal studies show adverse effects on the immune, liver, thyroid, and pancreatic function[6]. PFAS are water soluble, and elevated concentrations in drinking water have been reported near point sources contaminated by industrial activity or fire-fighting practices[9]. There is limited evidence about the occurrence of PFAS in bottled waters[10,11] and public drinking water supply of areas not impacted by contaminated sites, especially in Europe. Only a few studies assessed background levels of PFAS in treated drinking water in Canada[12], China[13], India[14], in the USA[15], and in European countries (France, Germany, Greece, Netherlands, Spain)[16–20]. Consequently, drinking water and food are considered the main pathways for PFAS entering the human body[7].

Bisphenol A has been widely used in the production of polycarbonate plastics and epoxy resins in the lining of metal products given its good thermal stability and resistance to oils and acids[21]. Although bisphenol A is not considered persistent due to its short half-life in the human body, it is widespread in the environment, including drinking water[21]. Epidemiological evidence showed that bisphenol A exposure is associated with adverse health effects such as impaired neurodevelopment, cardiovascular disease, and infertility[2]. Nonylphenol is used as an ingredient of personal care products, paints, detergents, polyvinyl chloride pipes; and it has been causally linked to altered hormone activities in humans[22,23].

There is limited evidence about the occurrence of bisphenol A and nonylphenol in different types of drinking water. Human exposure to drinking water is a serious concern, even low concentrations can lead to exposure in the general population due to bioaccumulation and persistence[9].

The public health concern by this exposure route is illustrated by the implementation of PFAS regulation and routine monitoring according to the recent EU Drinking Water Directive (EU DWD 2020/2184). Two maximum contaminant levels are defined, one for the sum of the totality of individual PFAS concentrations ('Total PFAS' at 500 ng/L), and one for the sum of 20 specific PFAS including C4-C13 carboxylates and sulfonates considered a concern with regard to water intended for human consumption ('Sum of PFAS' at 100 ng/L). In addition, a threshold (2500 ng /L) for bisphenol A is set[24]. Nonylphenol has been included in the first watch list of substances/compounds of concern in water intended for human consumption with a guidance value of 300 ng/L[25].

The present study aimed to assess residential exposure in the general population to selected chemicals of emerging concern in

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drinking water and urine samples from volunteers in the city of Barcelona (Spain) through target and non-target approaches. The specific objectives were: (1) to quantify the occurrence and distribution of 35 individual PFAS, bisphenol A, and nonylphenol through targeted analysis of different types of drinking water (tap, filtered tap, bottled); (2) to evaluate human exposure to PFAS through analysis in urine samples of study participants; (3) to tentatively identify emerging contaminants through non-target screening of tap water samples.

RESULTS AND DISCUSSION

Study population

A total of 39 volunteers participated in the study, including 24 women (60%), 14 men (37%), and 1 non-binary (3%), with an average age of 40.7 years (standard deviation (SD) = 10.2 years, range = 26–76 years). Educational level was university or more among 35 (90%) and a high school among 4 (10%). Average consumption of unfiltered tap, bottled, and filtered tap water were, respectively 0.6 (SD = 0.5, range = 0.1–1.5), 0.5 (SD = 0.4, range = 0.3–1.5), and 0.4 (SD = 0.5, range = 0.1–1.5) L/day, based on a self-reported water consumption questionnaire.

PFAS, bisphenol A, and nonylphenol in tap water

In total, 35 PFAS were analyzed in tap water, of which only perfluoroalkyl acids (PFAA; 7 carboxylates and 3 sulfonates) were above the quantification limits, mainly with a carbon chain length shorter than eight (≤C8); while C10, C11 and C12 carboxylates were only detected in one or two samples. Total PFAS detection rate for the first sampling was 79%, and 69% for the second sampling (Table 1). The most frequently detected (>50%) compounds during the first sampling were perfluoropentanoate (PFPeA) (64%; median = 3.3 ng/L), perfluorobutane sulfonate (PFBS) (64%; median = 9.2 ng/L), perfluoroheptanoate (PFHpA) (52%; median = 3.0 ng/L), perfluorohexanoate (PFHxA) (31%; median = 13.0 ng/L) and PFOS (52%; median = 12.5 ng/L), while the other PFAS showed detection frequencies lower than 12% (Table 1, Fig. 1). Similarly, the most prevalent compounds during the second sampling were PFPeA (62%; median = 4.0 ng/L) and PFBS (45%; median = 6.8 ng/L), whereas PFOS and PFHpA were present in 4.8% and 24% samples, respectively (Table 1, Fig. 1). The PFAS composition profile in the first sampling was dominated by PFBS (25.9%), PFOS (22.1%), PFPeA (17.6%), PFHxA (16.2%) relative to the total PFAS concentrations (Fig. 2). In the second sampling, high contributions to total PFAS concentrations were observed for PFPeA (45.7%), and PFBS (39.2%) (Fig. 2). To our knowledge, this was the first study analyzing ether-PFAS (e.g., GenX, and ADONA) in drinking water of the Barcelona region, showing non-detected levels.

Compared to previous studies conducted in Barcelona, replacement PFAS (PFPeA, PFHxA, PFBS) and PFHpA were the most predominant compounds detected in the tap water samples, with observed increasing concentrations over the last 10 years (Supplementary Table 1)[16,17].

This dominance of PFAS with fewer than eight carbons (<C8) in drinking water has been confirmed by other studies, following that the fluorochemical industry introduced "short-chain" alternatives to replace the "long-chain" legacy PFAS in formulations[26,27]. Initially, replacement PFAS were assumed safer given their lower bioaccumulative potential relative to legacy PFAS, however recent studies raised concerns about their high persistence, high mobility in the aquatic environment and adverse human health effects[26–29]. Notably, these compounds are less hydrophobic, having stronger polarity and lower adsorption potential to soil, which makes them more mobile and allows them to penetrate to deeper ground layers of water[30]. In addition, studies showed that conventional source water treatment technologies using activated carbon have been less effective to remove replacement PFAS[31,32].

For legacy compounds such as PFOA, perfluorononanoate (PFNA) and PFOS, a decreasing trend in concentrations in tap water was observed over the last 10 years in Barcelona compared to previous studies (Supplementary Table 1)[16,17]. PFAS composition profiles suggest that legacy compounds (PFOS, PFOA) still contribute to total PFAS concentrations, although not consistently across sampling events (Fig. 2). This may be explained by the high persistence and accumulation of legacy PFAS in the environment

Table 1. Number (%) of samples above the limit of quantification (≥LOQ), and concentrations (ng/L) of target compounds in unfiltered tap water samples collected in 42 locations in Barcelona, Spain, in repeated sampling campaigns (August–October 2020, and May 2021).

Analytes[a]	First sampling (*N* = 42)			Second sampling (*N* = 42)		
	N(%) ≥ LOQ	Min–Max	Median (IQR)	*N*(%) ≥ LOQ	Min–Max	Median (IQR)
Perfluoropentanoate, PFPeA (C5)	27 (64%)	<1.0–72.0	3.3 (2.0–4.6)	26 (62%)	<1.0–8.5	4.0 (3.2–5.2)
Perfluorohexanoate, PFHxA (C6)	13 (31%)	<10–62.0	13.0 (10.0–18.0)	0	<10.0	<10.0
Perfluoroheptanoate, PFHpA (C7)	22 (52%)	<1.0–12.5	3.0 (2.5–4.0)	10 (24%)	<1.0–3.5	1.6 (1.3–2.2)
Perfluorooctanoate, PFOA (C8)	5 (12%)	<10.0–21.0	11.0 (10.0 -12.0)	0	<10.0	<10.0
Perfluorodecanoate, PFDA (C10)	1 (2.4%)	6.0	6.0	1 (2.4%)	4.4	4.4
Perfluoro-n-undecanoate, PFUdA (C11)	1 (2.4%)	7.2	7.2	0	<5.0	<5.0
Perfluoro-n-dodecanoate, PFDoA (C12)	2 (4.8%)	<10.0–26.0	25.0 (23.8–25.3)	0	<10.0	<10.0
Perfluorobutane sulfonate, PFBS (C4)	27 (64%)	<5.0–51.8	9.2 (6.6–14.6)	19 (45%)	<5.0–13.0	6.8 (5.7–8.3)
Perfluorohexane sulfonate, PFHxS (C6)	0	<10.0	<10.0	1 (2.4%)	22.0	22.0
Perfluorooctane sulfonate, PFOS (C8)	22 (52%)	<10.0–17.0	12.5 (10.0 – 14.0)	2 (4.8%)	<10.0–13.0	11.5 (10.8–12.3)
Total PFAS[b]	33 (79%)	<1.0–180	30.0 (23.0–51.0)	29 (69%)	<1.0 – 34.0	9.8 (6.1–13.0)
Bisphenol A	0	<10.0	<10.0	—	—	—
4-Nonylphenol	0	<10.0	<10.0	—	—	—

N number of samples, *Min* minimum, *Max* maximum, *IQR* Interquartile Range (25th–75th percentile).
[a]The complete list of analytes is shown in Supplementary Table 3. Only those above the limit of quantification are shown here.
[b]According the EU DWD (2020/2184), two regulatory thresholds are set: "PFAS total" for the sum of the totality of individual PFAS (500 ng/L); and "sum of PFAS" for the sum of 20 specific PFAS being C4-C13 carboxylates and sulfonates (100 ng/L). In this study both thresholds resulted in the same levels and therefore we report results for total PFAS concentrations.

Fig. 1 PFAS concentrations (ng/L) in tap water. Unfiltered tap water samples were collected in 42 locations in Barcelona, Spain, in repeated sampling campaigns (August–October 2020, and May 2021). The line within the box marks the median, the boundaries of the box indicate the 25th to the 75th percentiles, and the dots denote observations (samples) corresponding to PFAS concentrations.

that can lead to human exposure long after being discontinued in global production[9].

Our results showed that median total PFAS concentrations were three times higher during the first sampling (30.0 ng/L) compared to the second (9.8 ng/L) (Table 1, Fig. 1). The second sampling was conducted after the rainy season in May whereas the first sampling was conducted in August-September during late-summer months. Differences in PFAS concentrations across sampling campaigns may be due to the seasonal variation of the quality of surface waters that supply the drinking water for Barcelona (Ter and Llobregat rivers). Indeed, a study conducted in Catalonia (Spain)[33] found seasonal variation over 3 sampling campaigns of untreated water from the Ebro river for PFPeA (autumn = 30%, winter = 17%, spring/summer = 66%) and PFOS (autumn = 22%, winter = 4%, spring/summer = 86%). Seasonal changes in PFAS concentrations of surface and groundwater have been observed in different countries[34,35]. For instance, Nguyen et al. (2022) investigated the catchment of a river in Sweden at a sampling site impacted by the use of PFAS-containing aqueous fire-fighting foams (AFFFs), where they found higher PFAS concentrations due to the high water flow season (i.e. spring). Additionally, they also found inverse seasonal trends in PFAS concentrations at sampling sites that were less impacted by point sources, that can possibly be explained by the effect of dilution during high flow events without extra inputs of pollution[34]. In another study, Tokranov et al., (2021) found lower concentrations of PFAS in the summer and higher concentrations during the winter months within the surface water/groundwater boundary and in downgradient groundwater of a lake (Massachusetts, USA) driven by natural biogeochemical fluctuations associated with surface water/groundwater boundaries. Taken together, seasonal differences in PFAS levels of source water have been documented with different underlying mechanisms, therefore it is important to note that seasonal changes may have an influence on drinking water quality.

The results of spearman correlation coefficients between individual PFAS are summarized in Fig. 3. The correlations did not reach statistical significance, however strong positive correlations were observed between PFBS and Total PFAS ($r = 0.6$; p value = 0.4) and moderate correlations between PFPeA and Total PFAS ($r = 0.4$; p value = 0.7); PFPeA and PFBS ($r = 0.4$; p value = 0.8); PFOS and Total PFAS ($r = 0.5$; p value = 0.7) in the first sampling. Regarding the second sampling, PFPeA was highly correlated with Total PFAS (= 0.8; p value = 0.4) and moderately with PFBS ($r = 0.5$; p value = 0.4). Our results are in line with a previous study showing moderate or high correlations between individual PFAS in treated water that have been explained by their similar sources[36]. A limitation of the correlation analysis was the number of samples above the limit of quantification only a few compounds were included for this analysis for the compounds.

Policies to manage PFAS contamination are being implemented at EU level, including the recent EU DWD[24], that regulates PFAS as a class to be routinely monitored in drinking water starting in 2023. In this study, the sum and total PFAS concentrations as defined by the EU DWD were identical as only carboxylates and sulfonates C4-C12 were detected. The observed median sum/total of PFAS concentration in the first sampling (30.0 ng/L) was lower than the EU DWD regulatory limits, except for one sample (180 ng/L) that exceeded the parametric value for the "sum of PFAS" (Fig. 4). In this sample, PFPeA, PFBS, PFOA, PFOS, PFHpA and PFHxA were quantified at concentrations of 72, 52, 21, 13, 12, and 10 ng/L, respectively, and the sum of carboxylates represents 64% of total concentration level. The corresponding sum/total PFAS concentration of the second sampling (7.6 ng/L) was considerably lower and below the EU parametric value (Fig. 4).

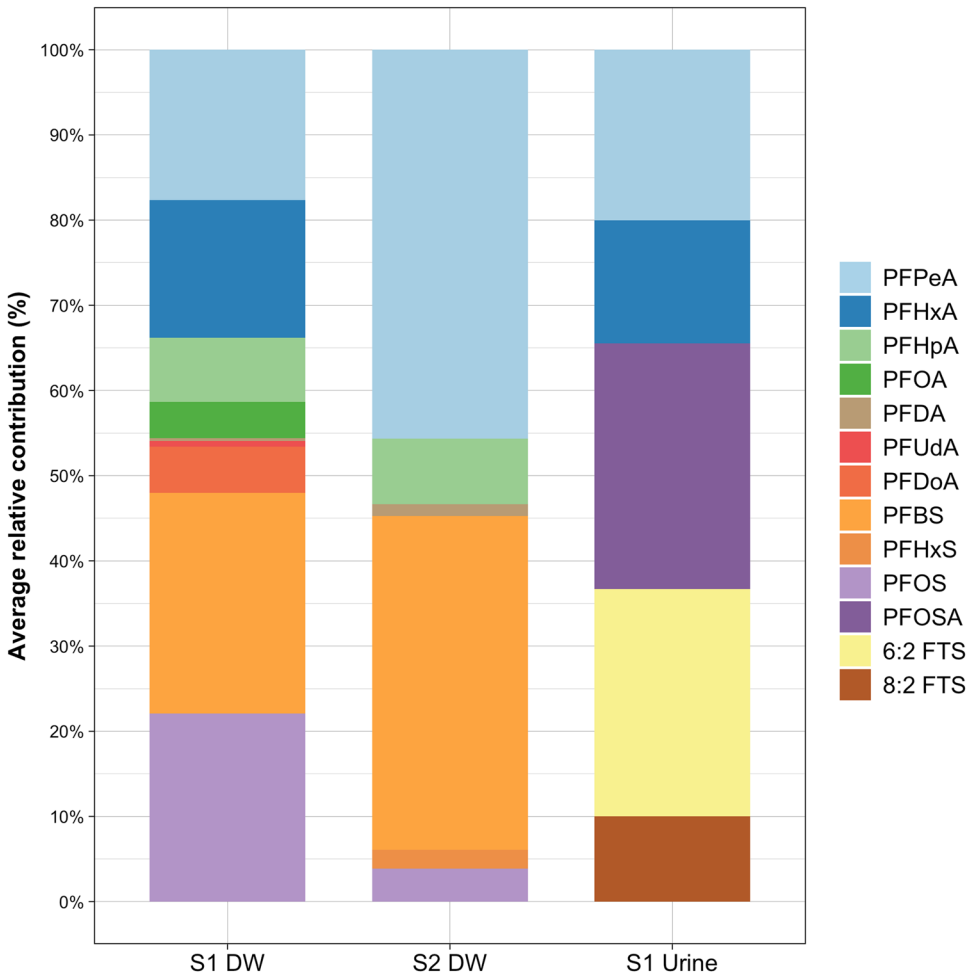

Fig. 2 Average percentage contributions of individual PFAS concentrations relative to total PFAS concentrations detected in drinking water samples. First sampling ($N = 42$; S1 DW), second sampling ($N = 42$; S2 DW), and urine samples of the first sampling ($N = 39$; S1 Urine).

Bisphenol A and nonylphenol were not detected in tap water samples (Table 1).

Results are representative of urban settings supplied with surface water with diffuse source contamination by PFAS and other industrial chemicals.

PFAS, bisphenol A, and nonylphenol in filtered and bottled water

In this study, the activated carbon (AC) pitcher filtered samples showed similar PFAS levels as the respective tap water samples before filtering. Median concentrations were 32.0 ng/L in non-filtered, and 33.0 ng/L after AC filtration (Table 2). Some samples showed slightly higher PFAS concentrations after AC filtering. Given that the AC filters remove contaminants through adsorption process, we hypothesize that domestic AC filters in real-life working conditions do not efficiently adsorb PFAS when highly loaded and clogged, and thus having the potential to release PFAS to the filtered water. PFAS breakthrough of AC filter has been observed when AC media was not regenerated to renew adsorptive capabilities[37]. Flores et al. (2013) previously showed the importance of the loading of granular AC filters to guarantee the efficient removal of PFAS in drinking water potabilization processes. On the other hand, removal efficiency of PFAS by AC pitcher filters from drinking water was recently evaluated by Herkert et al., (2020) reporting that 85% of activated carbon filters significantly removed PFAS by ~50% in drinking water, with increased removal efficiency for legacy PFAS. Overall, evidence shows that carbon filters can effectively remove PFAS, only if properly maintained[37].

Reverse osmosis (RO) technology for water treatment has been effective to remove contaminants by pushing water through a semipermeable membrane and provide consistent removal for longer period (6–12 months)[37]. Our results show that RO filters reduced median PFAS concentrations from 38.0 to 1.0 ng/L (97% reduction) (Table 2). Consistently, previous studies showed that domestic RO filters removed more than 90% of PFAS from tap water[38], as well as effectively removed PFAS during potabilization process at a drinking water plant[32]. Particularly, RO filters have been proven for their ability to remove both replacement and legacy PFAS to below detection limits, due to the membrane performance attributable to the small size of pores[37].

In the current study, PFAS were not detected in bottled water, consistently with previous studies that did not detect PFAS in 4 Spanish bottled water brands[17] and in 20 Japanese and international bottled water brands[10]. On the contrary, Ericson et al. (2008) found low PFAS concentrations (<1 ng/L) in three Spanish bottled water brands, and Schwanz et al. (2016) quantified PFAS in 10 Spanish bottled water brands with median concentrations of 11 ng/L for the sum of PFAS. Moreover, other studies reported the occurrence of PFAS (slightly above LOQ) in mineral water samples from Europe[11,20] and from the United States[39].

Bisphenol A and nonylphenol were not detected in filtered and bottled water samples.

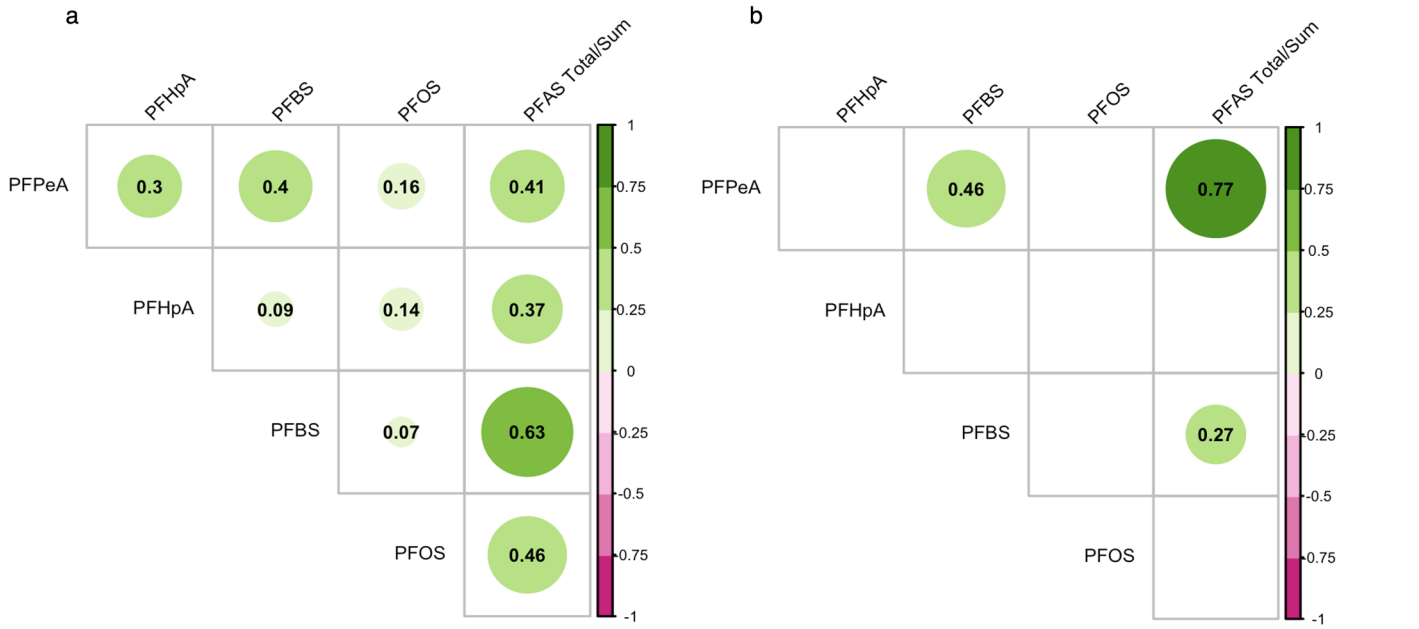

Fig. 3 Spearman correlation coefficients between PFAS measured in unfiltered tap water. a First sampling (August–October 2020). **b** Second sampling (May 2021). Correlations were calculated for compounds detected in at least 45% of the samples. *P* value was <0.05 for all correlations shown.

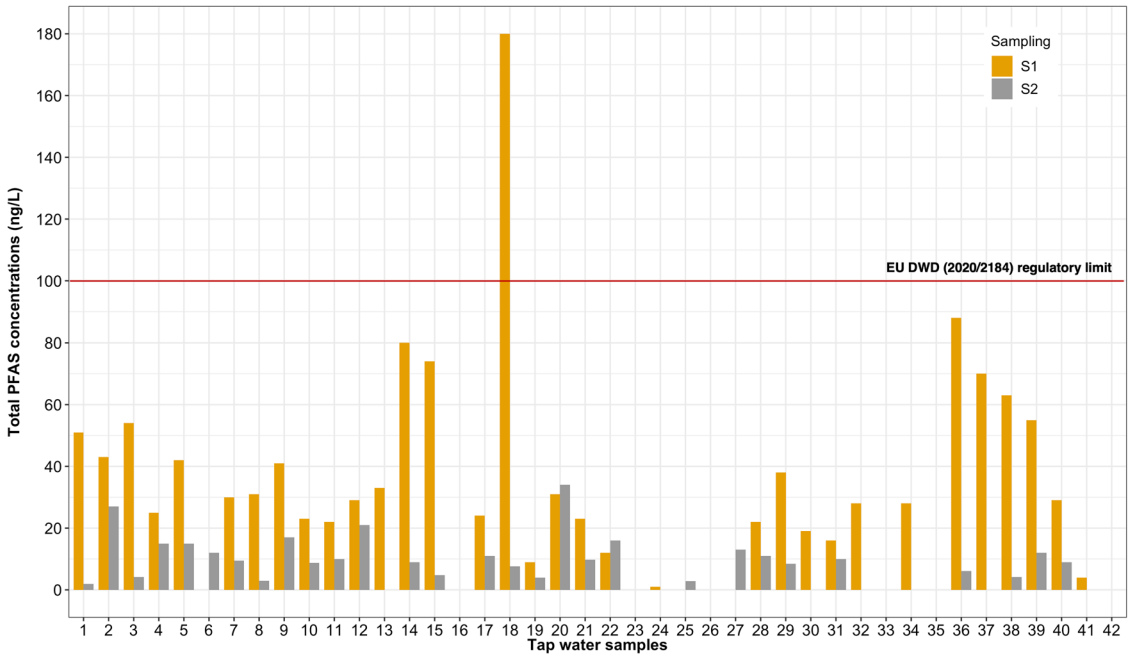

Fig. 4 Total PFAS concentrations (ng/L) in unfiltered tap water samples collected in residential locations (*N* = 42). S1, first sampling (August–October 2020); S2, second sampling (May 2021). PFAS were below the quantification limit for the following locations 16, 23, 26, 33, 35, 42 (in S1 and S2); 25, 27 (in S1); and 24, 32, 34, 41 (in S2).

Occurrence of PFAS in urine

We detected 5 distinct PFAS, one each in 5 out of 39 urine samples (Fig. 2): PFPeA (0.018 ng/mL; 65.9 ng/g creatinine), PFHxA (0.013 ng/mL; 325 ng/g creatinine), 6:2 FTS (0.024 ng/mL; 11.6 ng/g creatinine), 8:2 FTS (0.009 ng/mL; 4.3 ng/g creatinine) and PFOSA (0.026 ng/mL; 10.8 ng/g creatinine). A previous study conducted in Barcelona (*N* = 30) found 8 PFAS in urine (PFBA, PFHxA, PFHpA, PFOA, PFDA, PFUdA, PFBS, PFHxS) above detection limits, of which PFBA (median = 337.0 ng/mL) was detected in 100% of the samples[40]. Recent studies are in line with our results showing that PFAS are detected in urine at lower concentrations compared to urinary concentrations detected for communities that work or live close to polluted sites or occupationally exposed[41–43]. Calafat et al. (2019) showed that 67.5% of the US general population did not have detectable urinary PFAS concentrations. In the current study, three of the detected PFAS in urine samples (6:2 FTS, 8:2 FTS, PFOSA) have not been present in drinking water. Two participants with detectable 6:2 FTS or

Table 2. Total PFAS concentrations (ng/L) in tap water samples before and after using domestic filters.

	Before	After	Change	% change
Activated carbon filter				
Sample 1 (ng/L)	51.0	74.0	23	45
Sample 2 (ng/L)	<LOQ	<LOQ	0	0
Sample 3 (ng/L)	32.0	33.0	1	3
Sample 4 (ng/L)	33.0	5.0	−28	−85
Sample 5 (ng/L)	24.0	13.0	−11	−46
Sample 6 (ng/L)	23.0	65.0	42	183
Median	32.0	33.0	1	3
Reverse osmosis				
Sample 7 (ng/L)	43.0	1.0	−42	−98
Sample 8 (ng/L)	18.0	<LOQ	−18	−100
Sample 9 (ng/L)	10.0	<LOQ	−10	−100
Sample 10 (ng/L)	1.0	1.0	0	0
Sample 11 (ng/L)	38.0	1.0	−37	−97
Median	18.0	1.0	−37	−97

Samples were collected in Barcelona (Spain) in August–October 2020. *N* number of samples, *LOQ* limit of quantification. Change is the difference in concentration after minus before filtering. The percentage change is relative to 'before filtering' concentration.

PFOSA concentrations reported consuming bottled water (where PFAS were undetected), and three out of five urine samples with detectable levels of PFPeA, PFHxA, or 8:2 FTS were from participants reporting AC filtered water consumption. Altogether, findings suggest that drinking water might be responsible for PFPeA and PFHxA urinary levels, while exposure sources other than drinking water explain the urine concentrations of 6:2 FTS, 8:2 FTS, and PFOSA. Our results are consistent with Zhang et al. (2013) regarding the detection of replacement PFAS in urine (PFPeA, PFHxA) that have shorter half-lives in humans, thus urine is considered a suitable biospecimen for PFAS that are rapidly cleared from the human body[44]. On the other hand, PFAS can bind to blood protein and the body burden is reflected by serum levels of PFAS that can affect the transfer efficiency to urine[45]. A limitation of the present study is that it involved spot urine samples instead of a repeated sampling method.

Non-target screening in drinking water

A summary of tentative results regarding non-target screening is shown in Table 3. A total of 16 out of 248 analytes were detected in at least one water sample, with occurrence frequency varying substantially between types of drinking water (Table 3, Supplementary Table 2). Non-filtered tap water presented the highest number of compounds including 12 micropollutants and 4 metabolites. The highest detection rates were found for carbamazepine (a recalcitrant pharmaceutical compound used as anticonvulsant and mood stabilizer), tris(chloroisopropyl) phosphate (a high-volume production chemical included in polymer formulations because of its flame retardant potential), suberic, and azelaic acids (saturated linear dicarboxylic acids used in plastic manufacturing personal care products), and terbuthylazine (herbicide). These were detected, respectively, in 100%, 83%, 78%, 56%, and 56% of unfiltered tap water samples (Table 3).

Tap water filtered with AC showed lower detection frequency relative to unfiltered tap water, but more than twice compared as RO filtered water. Notably, personal care products (suberic and azelaic acids) were detected in all types of drinking water (non-filtered tap, filtered tap, and bottled). However, interpretation of findings should be cautious. According to the confidence levels of non-target analysis in high resolution mass spectrometric analysis we could confirm 4 out of 5 levels, i.e., level 2 according to Schymanski et al. (2014), specifically: (a) the mass of interest; (b) the unequivocal molecular formula but insufficient structural evidence; (c) the tentative candidate compounds by identifying the suspect, substructure, and class; (d) the probable structure by library diagnostic evidence[46]. In this study, we could not confirm probable structure by a reference standard and validate the results nor could we quantify the concentrations of suspects. Hence, we only reported instrumental response (a.u = arbitrary units) or, in other words, the presence and frequency of suspect contaminants.

Table 3. Occurrence frequency (%) of chemicals tentatively identified through non-targeted screening in unfiltered tap water ($N = 42$), filtered tap water with activated carbon (AC, $N = 6$), and reverse osmosis (RO, $N = 5$), and bottled water samples ($N = 10$).

Chemical and chemical class	Unfiltered tap water (%)	Filtered tap water		Bottled water (%)
		AC (%)	RO (%)	
Pharmaceuticals and metabolites				
Carbamazepine	100	83	0	0
Desmethylcitalopram	10	0	0	0
Desmethylvenlafaxine	12	0	0	0
Pesticides and metabolites				
Desethylatrazine	20	33	40	0
Desethylhydroxyatrazine	7	17	20	0
Terbuthylazine	56	50	0	0
Terbumeton	49	50	0	0
Industrial organic				
Benzotriazole	46	0	0	0
Chlorobenzotriazole	29	0	0	0
Tris(butoxyethyl) phosphate	12	17	20	0
Tris(chloroisopropyl) phosphate	83	67	0	70
Illicit drug/pharmaceutical				
Ephedrine	20	17	0	0
CBGA (cannabigerolic acid)	15	17	0	0
Personal care product				
Azelaic acid	56	100	80	40
Suberic acid	78	83	80	80
Hormones/endocrine disruptors				
Hydroxyestrone	7	0	0	0

Samples were collected in Barcelona (Spain) in August–October 2020.

METHODS

Study area and population

Barcelona is a densely populated city in the North-East of Catalonia (Spain). The public water supply is a mixture of sources, mainly surface water from the Llobregat and Ter rivers, followed by groundwater from local aquifers and desalinated water. These distinct sources differ in their raw water quality[47–49], and the city receives a varying proportion of the different sources. In particular, the Llobregat water course is characterized by intensive industrial activity and densely populated areas, thus receiving urban and

Table 4. Samples collected and chemicals analyzed in the first (August–October 2020) and second (May 2021) sampling campaigns.

	Tap water	Filtered tap water	Bottled water	Urine
	Sampling 1 (August–October 2020)			
# samples	$N = 42$	$N = 11$	$N = 10$	$N = 39$
Chemicals analyzed	35 PFAS	35 PFAS	35 PFAS	35 PFAS
	Bisphenol A	Bisphenol A	Bisphenol A	
	Nonylphenol	Nonylphenol	Nonylphenol	
	NTS	NTS	NTS	
	Sampling 2 (May 2021)			
# samples	$N = 42$	—	—	—
Chemicals analyzed	35 PFAS	—	—	—

NTS non-target screening, *PFAS* Per- and polyfluoroalkyl substances.

industrial effluents that contribute to chemical contamination[49]. To account for the geographical variability of Barcelona, we aimed to identify 42 sampling points (one per postal code) in homes from volunteers that were recruited via social media. Eligible subjects were screened through an online questionnaire based on the (1) postal code of residence; (2) type of water consumed (tap, bottled, filtered tap water); and (3) a balanced gender distribution. Selected study subjects provided information on socio-demographics and water consumption through a structured questionnaire. Participants provided written informed consent prior to voluntary participation in the study. This study was approved by the ethical committee of Parc de Salut Mar.

Sampling campaigns and procedures

Sampling 1. Between August 31st and October 16th of 2020, we conducted home visits to collect tap water samples from homes and first-morning void urine samples from study participants living in Barcelona city. We enrolled 39 volunteers, including a subset of 11 domestic filter users ($N =$ five reverse osmosis (RO), $N = 6$ activated carbon (AC)) and bottled water users ($N = 10$) (Table 4). Study subjects for 3 postal codes were not found and we collected tap water samples from public fountains in order to obtain tap water samples at all 42 postal codes from Barcelona city.

Filtered and unfiltered tap water samples were collected in three containers after leaving cold water running for 2 min approximately: (1) 500 mL polypropylene bottle for PFAS analysis; (2) 2.5 L glass bottle for bisphenol A and nonylphenol analysis; (3) 2.5 glass bottle for non-target analysis containing ascorbic acid as quenching agent to prevent chlorine reactions and allow parallel analysis of disinfection by-product[50]. Prior to the visit, participants were provided with a sterile plastic container (70 mL) and instructions to collect and preserve a first-morning void urine sample on the day of the home visit. The urine sample was kept in the refrigerator until the scheduled appointment. Urine and tap water samples (filtered and unfiltered) were transported to the research center in a portable cooler with ice packs to keep the temperature at 4 °C. Tap water samples were stored at 4 °C until shipment to the laboratory (within 2 days after sampling), and urine samples were stored at −20 °C until shipment to the laboratory at the end of the study. Additionally, 10 popular brands of bottled natural mineral water were selected, and one 1.5 L polyethylene terephthalate (PET) bottle of each brand was purchased from local supermarkets and transported at room temperature to the laboratory.

Sampling 2. Water samples were collected at the same locations in May 2021 to evaluate the seasonal variation of PFAS in tap water (Table 4). Samples were collected in 500 mL polypropylene bottles for PFAS analysis. The shipment and storage procedures were identical to the first sampling.

Target analytes

We analyzed 35 PFAS in the whole set of drinking and urine samples including 10 perfluoroalkyl carboxylates (C4-C13), 10 perfluoroalkyl sulfonates (C4-C13), 3 perfluorooctane sulfonamides (PFOSA, N-MeFOSA, N-EtFOSA), 4 fluorotelomer sulfonates (FTS n:2, n = 4, 6, 8 and 10) and 8 ether-PFAS, including HFPO-DA (2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid [Gen X]), ADONA (dodecafluoro-3H-4,8-dioxanonanoate) and chlorinated PFAS (Table 4, and Supplementary Table 3). In addition, bisphenol A and nonylphenol were analyzed in drinking water samples in the first sampling campaign (Table 4). Detection and/or quantification limits for PFAS, bisphenol A, and nonylphenol are shown in Supplementary Table 3. Information of reagents and quality control measures according to the 2002/657/EC Commission Decision[51] are detailed in the Supplementary Methods.

Analytical procedure

PFAS. Drinking water samples were pre-concentrated by online solid phase extraction (SPE) followed by LC–MS/MS for the analysis of PFAS[8,17,42]. Labeled internal standards were added prior to analysis (Supplementary Table 3). For all tandem mass spectrometry coupled to liquid chromatography (LC–MS/MS) analyses, a TSQ quantum triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (Thermo Fisher Scientific, San Jose, CA, USA) was used. The analyses were carried out in negative ion electrospray and multiple reaction monitoring acquisition mode (MRM). The spray voltage was chosen at 3.0 kV and the tube lens voltage and collision energy were optimized for each transition. The argon gas collision-induced dissociation was used with a pressure of 1.5 millitorr (mTorr). Data acquisition was performed with Xcalibur 2.0.7 software (Thermo Fisher Scientific). The chromatographic separation was performed on a reversed-phase Kinetex XB-C18 column (100 × 2.1 mm, 2.6 µm) preceded by an C18 guard column (2 × 2.1 mm, 2.6 µm) both from Phenomenex (Torrance, CA, USA) inside an oven at 40°C. Samples were homogenized, and an aliquot of 1 mL was directly processed using a Thermo Electron's EQuan environmental quantitation system that consists of two Surveyor LC and MS pumps with a preconcentration column, an analytical column, a PAL autosampler (CTC Analytics, Zwingen, Switzerland) and one switching device unit. The entire system was connected to a TSQ quantum triple quadrupole mass spectrometer. To minimize background contamination throughout the procedure, all known sources of contamination, including accessible polytetrafluoroethylene (PTFE) and other fluoropolymer materials of instruments and apparatus, have been eliminated. Blanks and white-fortified blanks have been used as quality controls. In addition, a column (Hypersil GOLD C18, 20 × 2.1 mm and 12 µm from Thermo Fisher Scientific, Franklin, MA) to capture PFAS was used after the LC pump and before the injection valve and a by-pass of the degasser was made in MS pump. The trapping column improved the LOQ especially for PFHxA and PFOA. The used SPE columns were a combination of mixed-mode Strata-X cartridge (2.0 × 20 mm, 25 µm particle size; Phenomenex, Torrance, CA, USA) and plus Hypersil GOLD C18 (2.1 × 20 mm, 12 µm particle size; Thermo Fisher Scientific, Franklin, MA). After enrichment at 1 mL/min, analytes were transferred to the analytical column for their separation by switching the MS valve into loading mode. The mobile phase was composed of water as solvent A and methanol as solvent B at a flow rate of 300 µL/min using a linear gradient. The total run time was 15 min. The ion transfer tube temperature was set at 300 °C. Nitrogen was used as

a sheath gas, ion sweep gas an auxiliary gas at flow rates of 40 psi, 0, and 10 arbitrary units (a.u.), respectively.

Urine samples were pre-concentrated by off-line SPE. Initially, labeled EPA-533ES mix and 13C8-FOSA were added to 3.5 mL of urine samples as extraction internal standard. Each sample was sonicated (20 min) and centrifuged (3000 rpm, 10 min) to eliminate solid residue. The supernatant was diluted with 7 mL of water and 4.6 µL of formic acid. Oasis-HLB SPE cartridge, 200 mg/6 mL (Waters Corporation, Milford, MA), was conditioned with 5 mL of methanol and 5 mL of acidified water (0.1% formic acid). Then, the diluted urine was loaded onto the conditioned SPE cartridge. Finally, PFAS were eluted twice with 5 mL of MeOH:H2O 20:80. The extracts were evaporated to dryness and reconstituted with acidified MeOH:H2O 70:30 (0.1% HCOOH) and labeled EPA-533IS mix as injection internal standard until 200 µL. Prepared samples were stored at −20°C before analysis. The mobile phase was composed of solvent A (0.1% formic acid in water) and solvent B (0.1% formic acid in acetonitrile) using a linear gradient. The mobile phase flow rate was 200 µL/min. The total duration of the method was 25 min. The sample volume injection was 10 µL. The ion transfer tube temperature, sheath and auxiliary gas flow rates were set at 250 °C, 65 psi and 15 arbitrary units (a.u.), respectively.

Bisphenol A and nonylphenol. Analysis was performed by liquid-liquid extraction (LLE) with dichloromethane and gas chromatography coupled to triple quadrupole mass spectrometer EVOQ GC–TQ (Bruker, Fremont, CA, USA) according to the U.S. EPA 1625 method[52,53]. Chromatographic separation was achieved with a DB 5 capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) from J&W using helium as the carrier gas in a GC–MS/MS instrument. The temperature program was from 70 °C (held 1 min) to 310 °C (held 15 min) at 10 °C/min. Injector and interphase temperatures were 280°C. Injection mode was splitless for 1 min and injection volume was 1 µL. Mass spectrometry was performed using the electron ionization mode at 70 eV of ionization energy. Ion source temperature was set to 250 °C. Acquisition was carried out in Selected Ion Monitoring (SIM) mode.

Non-target screening

Tap water samples were extracted following a custom method adapted from Dittmar & Koch (2006). Briefly, 2.0 L sample aliquots were acidified at pH 2.5 with formic acid to extract the maximum of compounds that could be negatively charged at neutral pH, and extracted with Bond Elut PPL cartridges (500 mg, 3 mL, Agilent Technologies). The cartridges were loaded, washed with 3 mL of formic acid 0.1%, dried under vacuum, and eluted with 2.0 mL of methanol. Extracts were stored at −20 °C until their analysis. A procedural blank (2.0 L of quenched and acidified ultrapure water) was extracted in parallel with every batch of samples following the exact same procedure. Methanol extracts were diluted with ultrapure water 1:1 and analyzed by high-performance liquid chromatography coupled to high resolution mass spectrometry (LC–HRMS). Each extract was injected once as a single replicate. LC was performed with an Acquity UPLC System (Waters) and separation was achieved with a ZORBAX Eclipse XDC18 column (150 × 4.6 mm, 5 m particle size; Agilent Technologies) and acetonitrile/ammonium formiate (0.01 M, pH 3.0) as mobile phases (0.5 mL/min). The ionization was performed with electrospray (ESI) in positive and negative polarity. Acquisition was performed in data-dependant scan mode with a Q Exactive™ mass spectrometer (Thermo Fisher Scientific). The main full scan event was acquired from *m/z* 70 to 1000 at a resolution of 70,000 FWHM (measured at *m/z* 200), while data-dependent MS^2 events were performed on the five most abundant ions (Res = 17,500 FWHM, normalized collision energy = 30%).

Chromatogram smoothing, chromatogram alignment, peak deconvolution, and peak integration were performed with Thermo Compound Discoverer version 3.1 (Thermo Fisher Scientific). Chromatograms were aligned with a *m/z* tolerance of 5 ppm and according to the integrated "adaptative curve model". Peaks were built with at least five scans/peak and a mass tolerance of 5 ppm, considering the quasi-molecular ion and potential sodium/potassium adducts. Once the peak list was obtained, a suspect screening was conducted for 248 selected organic micropollutants and their related metabolites (Supplementary Table 2). The occurrence of these compounds was confirmed or discarded on the basis of (i) the accurate mass measurement (*m/z* error tolerance of ±5 ppm) and (ii) the coherency of their experimental MS2 spectra. To this end, MS2 spectra were compared to MassBank entries, when these were available; MS2 fragments were tentatively identified and scored using the FISh assignation algorithm (Thermo Fischer Scientific); and the likelihood of MS2 fragmentation was scored and ranked using the Metfrag webtool. The chromatographic peaks of those compounds that had been tentatively identified were integrated, sample by sample, using Xcalibur. Integration took in consideration the quasi-molecular ion and, when possible, the presence of additional ESI fragmentation ions and their intensities ratio. Results were reported as an instrumental response (peak areas, in arbitrary units, a.u.). The confidence level of such annotation corresponds to level 2 according to Schymanski et al. (2014).

Statistical analysis

Descriptive statistics of individual chemicals were based on the samples with concentrations >LOQ following a previous study[17]. The total or sum of PFAS concentrations was based on levels >LOQ of individual compounds. The distribution of the variables was explored with Q–Q plots and the Shapiro–Wilk test for normality. Spearman rank correlation coefficients were calculated to evaluate the degree of correlations between the concentrations of individual chemicals (>LOQ) that were detected in >45% of the samples, with $p < 0.05$ regarded as significant. To assess the removal efficiency of the filters, paired *t* tests were used to compare concentrations before/after filtration. The homogeneity of the variances was studied for each variable and included in the paired *t* test. The average percentage change was calculated as the increment or reduction in the concentration relative to the average concentration before filtration. Analyses were carried out using R software (version 4.1.1)[54].

DATA AVAILABILITY

All of the data supporting the findings of this study are available in the article and/or in its Supplementary Information.

CODE AVAILABILITY

Code is available from the corresponding author upon request.

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AUTHOR CONTRIBUTIONS

C.M.V., C.F., J.C., M.J.F., and J.S. conceptualized the study and designed the methodology and D.C.S. and P.E.R.H. collected the drinking water samples. A.B., A.P., C.F., D.C.S., E.M.H., M.J.F., J.S., and P.E.R.H. conducted the analytical measurements and A.B., C.F., M.J.F., and J.S. validated the data. D.C.S. and P.E.R.H. carried out data analysis and drafted the manuscript, which was reviewed and edited by C.M.V., C.F., M.J.F., J.C., and J.S. C.M.V., M.J.F., and C.F. administered the project and acquired the financial support. D.C.S. and P.E.R.H. are co-first authors.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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