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Human Exposure to Perfluorinated Compounds in Catalonia, Spain: Contribution of Drinking Water and Fish and Shellfish

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ABSTRACT: In this study, the concentrations of 15 perfluorinated compounds (PFCs) were analyzed in 30 water samples collected in Catalonia (Spain) at three stages of the drinking water treatment process in several water purification plants. In addition, the concentrations of 13 PFCs were determined in samples of fish and shellfish collected from coastal areas of Catalonia. The intake of PFCs through both pathways, drinking water intake and fish and shellfish consumption, was also estimated. In water samples, the highest mean concentrations corresponded to perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) (1.81 and 2.40 ng/L, respectively), whereas perfluorodecanosulfonate (PFDS) and perfluorotetradecanoic acid (PFTDA) were under their respective limits of detection in all analyzed samples. The results show that although the current treatment processes caused slight reductions in PFC concentrations, these processes did not mean significant changes in the amounts of PFCs already contained in the raw water. Among the analyzed PFCs in fish and shellfish, only seven compounds could be detected in at least one composite sample. PFOS showed the highest mean concentration (2.70 ng/g fw), being detected in all species with the exception of mussels. With regard to PFOA (mean, 0.074 ng/g fw), the highest concentrations were detected in prawn and hake (0.098 and 0.091 ng/g fw, respectively). The current exposure to PFCs through consumption of fish and shellfish indicates that it should not be of concern for the consumers. The amounts ingested are well below the recommended tolerable daily intakes, at least for those PFCs for which information is available.

KEYWORDS: *perfluorinated compounds, drinking water, fish and shellfish, human exposure, Catalonia (Spain)*

INTRODUCTION

Perfluorinated compounds (PFCs) are a group of fluorinated chemicals with surface-active properties, which have been manufactured for over 50 years. They have been widely used in consumer products. Due to their extensive applications, PFCs have been released to the environment, where they persist and may bioaccumulate through the food chain.[1] In recent years, a number of studies have reported a ubiquitous distribution of PFCs in human tissues.[2] Although the relative importance of the routes of human exposure to these compounds is not quite established yet,[3,4] recent investigations have shown that food intake and packaging,[5−7] water,[8−10] and house dust and indoor air[11−13] are all potentially significant sources. Among these sources, water consumption has been identified as one of the most important routes of human exposure.[8,14−16] However, dietary intake is probably the main route of exposure to PFCs, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the most extensively investigated PFCs.[3,17−19] Among the different foodstuffs, fish and shellfish seem to make the highest contribution to dietary PFC exposure.[19−22]

In recent years, we initiated a wide surveillance program aimed at analyzing the levels of a number of PFCs in environmental, human, and food samples in Catalonia (Spain).[8,14,21,23,24] Because of the potential implications for public health, a follow-up of the levels of PFCs in drinking water and foodstuffs is being performed since 2008. Although the most well-known PFCs, PFOS and PFOA, have been detected in tap water from a number of countries,[9−11,15,22,25] very few studies have examined the fate, especially removal or addition, of PFCs in drinking water treatment processes.[25,26]

On the basis of the results of our previous studies,[8,14] we wished to know whether PFCs could accumulate or, by contrast, be removed in the water supply network, or if they were already included in the raw water from their sources of origin. In the present study, we analyzed the concentrations of various PFCs in water samples collected in Catalonia at three stages of the drinking water treatment process in several water purification plants, which employ advanced water treatment technologies. Accordingly, this study was designed considering three different stages through the drinking water distribution: (a) at the place of abstraction (raw water); (b) after the purification process, which transforms raw water into drinkable water; and (c) in the places of consumption (public fountains). On the other hand, and taking into account the importance of the dietary intake of PFCs (and particularly that derived from fish and shellfish consumption) in human exposure, the concentrations of various PFCs were also determined in samples of fish and shellfish collected from coastal areas of

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Figure 1. Sampling points of drinking water (yellow), as well as fish and shellfish (red).

Catalonia. Finally, the intake of PFCs through both pathways, drinking water intake and fish and shellfish consumption, was also estimated.

MATERIALS AND METHODS

Sampling. In December 2009, water samples were collected at 3 points in each of 10 municipal water supply networks of Catalonia, making a total of 30 samples for analysis of PFCs. Sampling points corresponded to the five areas in which Catalonia is divided for health purposes: Barcelona, Girona, Lleida, Tarragona, and Terres de l'Ebre. One-third of those samples (drinking water for human consumption) were collected in public fountains from 10 different Catalan locations (Figure 1). The remaining 20 samples were collected within the supply network, before and after the purification process to make the water drinkable. Duplicate water samples were collected and kept refrigerated at 4 °C in 0.75 L polyethylene bottles. Moreover, samples of seven species of fish and shellfish were obtained from the following representative coastal areas of Catalonia: (a) Tarragona-Cambrils (Tarragona Province), (b) Vilanova i la Geltrú-Barcelona (Barcelona Province), and (c) Palamós-Roses (Girona Province). Sardine, tuna, red mullet, hake, cuttlefish, mussel, and prawn were the selected species. They had all been caught at the indicated areas and were acquired in/from local markets. For each species, three composite samples were prepared as follows: for composites of small species (sardine, mussel, and prawn) a minimum of 21 units was used, whereas for the remaining species the composite samples were formed by at least 12 units of each species. In total, 21 composite samples of fish and shellfish were analyzed. Samples were freeze-dried at −80 °C with a Cryodos Telstar lyophilizer for 24 h and then stored at −20 °C until analysis of PFCs.[8,14,21] The PFCs analyzed in this study are shown in Table 1.

Analytical Procedure. Water samples (500 mL) were filtered through glass microfiber filters (GF/B, Whatman) before extraction using Oasis WAX (6 cm^3/150 mg, Waters, Milford, MA, USA). Before addition of the internal standard mixture, the pH was adjusted to 4.0. The WAX cartridges were conditioned before a vacuum was used to run through the water samples at a flow rate of approximately 1 drop/s. Sodium acetate buffer (4 mL, pH 4, 25 mM) and methanol/water (1:1, 4 mL) were added. Both eluates were discarded. After the cartridges had been dried using vacuum suction, the analytes were eluted with 2 mL of 2% NH_4OH/methanol solution at a rate of 1 drop/s. The eluates were collected, filtered, and evaporated to a suitable volume with a gentle stream of nitrogen gas. Recovery standards ($^{13}C_8$-PFOA, $^{13}C_8$-PFOS, 7*H*-perfluoroheptanoic acid (7*H*-PFHpA)) and 2 mM ammonium acetate were added to the final extract. Extraction and field blank samples were prepared with ultrapure laboratory-produced water. They were treated exactly as the remaining samples.

Table 1. PFCs Analyzed in Drinking Water and Fish and Shellfish Samples

compound	abbreviation	molecular formula
perfluorobutanoic acid[a]	PFBA	$C_3F_7CO_2H$
perfluoropentanoic acid[a]	PFPeA	$C_4F_9CO_2H$
perfluorobutanesulfonate	PFBuS	$C_4F_9SO_3^-$
perfluorohexanesulfonate	PFHxS	$C_6F_{13}SO_3^-$
perfluorooctanesulfonate	PFOS	$C_8F_{17}SO_3^-$
perfluorodecanosulfonate	PFDS	$C_{10}F_{21}SO_3^-$
perfluorohexanoic acid	PFHxA	$C_5F_{11}CO_2H$
perfluoroheptanoic acid	PFHpA	$C_6F_{13}CO_2H$
perfluorooctanoic acid	PFOA	$C_7F_{15}CO_2H$
perfluorononanoic acid	PFNA	$C_8F_{17}CO_2H$
perfluorodecanoic acid	PFDA	$C_9F_{19}CO_2H$
perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}CO_2H$
perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}CO_2H$
perfluorotridecanoic acid	PFTrDA	$C_{12}F_{25}CO_2H$
perfluorotetradecanoic acid	PFTDA	$C_{13}F_{27}CO_2H$

[a]Determined only in drinking water.

Thawed fish and shellfish samples were ground. From the homogenate, 1 g of each sample was used for the analytical procedure. Internal standard mixture was added before 0.4 mL of a 0.2 M NaOH (in methanol) solution, and the samples were left for 30 min. Extraction was performed using 4 mL of acetonitrile, followed by ultrasonication for 15 min and shaking for 15 min. The samples were neutralized and centrifuged; after removal of the supernatant, the extraction was repeated once more, and the two extracts were combined. Cleanup was performed with extraction (three times) with *n*-hexane (corresponding to a volume of 2:1 sample extract/hexane) and shaking with a mixture of 50 mg of dispersive carbon (Supelclean ENVI-Carb (20/400 mesh), Supelco, Bellefonte, PA, USA) and 100

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μL of glacial acetic acid. After filtration and evaporation, the recovery standards (RS) 7*H*-PFHpA, $^{13}C_8$-PFOS, and $^{13}C_8$-PFOA were added together with 2 mM ammonium acetate. Blank samples (extraction blanks) and field blanks were performed in parallel with each batch of samples and treated exactly as the other samples.

Chemical Analysis and Quality Assurance. Analysis was performed using an Acquity UPLC coupled to a Quattro Premier XE MS/MS (Waters Corp., Milford, MA, USA) with an atmospheric electrospray interface operating in negative ion mode (ES-MS/MS). Multiple reaction monitoring was used monitoring product ions. Concentration of the analytes in the samples was calculated using internal standard quantification. The internal standard closest in retention time was used for those compounds that did not have a corresponding labeled internal standard. Separation was performed on an Acquity BEH C18 2.1 × 50 mm, 1.7 μm, kept at 50 °C. An extra guard column (PFC isolator, Waters Corp.) was inserted between the pump and injector to trap contaminants originating from the LC system. The injection volume was 10 μL, and the flow rate was set to 400 μL/min. A gradient program was employed delivering mobile phases that consisted of 2 mM ammonium acetate in methanol and 2 mM ammonium acetate in water.

The limit of detection (LOD) was set to 3 times the signal in the extraction blank. Two transitions were measured for most of the compounds, and the ratio between the qualifier and quantifier ions was calculated; samples with more than 50% difference were not quantified with the exception of PFOS in fish for which the *m*/*z* 80 transition could not be used due to interferences from the fish matrix. The recoveries of the internal standards were monitored, and native compounds were spiked to clean matrices. Acceptable recoveries were 50−150%. Results with less certainty were obtained and reported with a notification (20−50% recovery). Matrix effects such as ion suppression were seen for samples with low recovery. The internal standard adjustment for this suppression, however, as compared to a recovery standard with different chain length, results in low recovery values. The results with obtained recoveries below 2% were not included.

Repeated injections of calibration standard solutions to the UPLC system covering a concentration range of 0.2−40 ng/mL showed good linearity, with $R^2 > 0.99$ for all compounds (PFCAs, C5−C14, C16, and C18; and PFSA, C4, C6, C8, and C10), except for PFBA ($R^2 = 0.987$), and repeatability, with RSD values ranging from 2.6 to 17% (for PFOS and PFTeDA, respectively). The only exception was C_{18}-PFCA, which presented an RSD of 37%. A fish sample was quantified for each extraction batch, assuring reproducibility and accuracy. For water analysis, the quality was assured by spiking native compounds to a laboratory-produced water sample in each extraction batch. Finally, the successful participation of the laboratory in the 2009 worldwide interlaboratory study on PFCs in fish muscle and water reaffirms the quality control/quality assurance of the analytical determinations.[8]

Statistics. Statistical analysis of the data was performed using the software package SPSS 17.0. The Levene test was applied to establish whether the data followed a normal distribution. Subsequently, ANOVA or the Kruskal−Wallis test, depending on the homogeneity of the differences, was used. To obtain comparable results with data from the literature, as well as with those from of our previous surveys, undetected values were assumed to be half of the respective limit of detection (LOD) (ND = $^1/_2$ LOD).

RESULTS AND DISCUSSION

A summary of the concentrations of PFCs in the 30 water samples collected at different sampling points of Catalonia is shown in Table 2. The highest mean concentration corresponded to the two most investigated PFCs, PFOS and PFOA (1.81 and 2.40 ng/L, respectively). In contrast, PFDS and PFTDA were under their respective LOD in all 30 analyzed samples. In general terms, the most polluted samples were found in municipalities belonging to the Barcelona area (data not shown), which is by far the most industrialized area of Catalonia. This is in agreement with the results of our previous study.[8] The current mean concentration of PFOS in Barcelona was 3.16 ng/L, a level that is >3 times higher than the concentrations found in the remaining four areas ($p < 0.05$). In turn, the mean PFOA concentration in water samples from Barcelona was 4.21 ng/L, a value that is at least 4 times higher than the levels detected in the other four areas ($p < 0.01$). With the exception of PFDS, PFDoDA, and PFTDA, which in the Barcelona area were below their respective LODs, all of the remaining PFCs showed higher values in the waters of that highly industrialized area, the differences of PFPeA, PFBuS, and PFHpA being significant ($p < 0.05$), in addition to PFOS and PFOA. The results of a recent study having as its main goal the examination of the occurrence of 11 PFCs in several wastewater treatment plants from Japan and Thailand[27] indicated that certain industries using PFCs in manufacturing processes could be the principal point source of PFCs, whereas domestic activities could be releasing PFCs at detectable levels causing environmental concern.

The concentrations of PFCs in each of the 30 individual water samples here analyzed are shown in Table 2. Outlier levels of 32.8 ng/L for PFOS and 20.2 ng/L for PFOA were observed in samples collected in Ripoll and St. Joan Despí, respectively. We assumed that it was probably due to a specific point pollution problem and, therefore, these values were excluded from the statistical evaluation. There were no significant differences in PFC concentrations depending on the specific sampling point of the distribution network in which the respective samples were collected (Figure 2). This indicates that PFCs are neither removed nor incorporated during the treatment process or during the transport through the distribution network, but they would be already present in the raw water. However, with the exception of PFBA, it was noted that all PFCs showed lower concentrations after the purification process of the raw water, suggesting that, to a greater or lesser extent, the current treatment processes would reduce the levels of PFCs, with removal rates ranging between 3 and 53% for PFNA and PFDA, respectively. This finding agrees with the results of Shivakoti et al.[27] and Eschauzier et al.,[28] who reported a certain elimination of some PFCs in the process of water filtration with granular activated carbon (GAC). In turn, Eschauzier et al.[29] recently found that hydrophilic shorter chain compounds, such as PFBA, were not removed by GAC, in agreement with our results. After comparing the concentrations of PFOS and PFOA in raw and tap water, Takagi et al.[25,26] observed that water treatment processes did not completely remove PFOS and PFOA. The removal of PFOS and PFOA in advanced water treatment (including ozonation and activated carbon filtration) was found to be incomplete. As in the present study, the concentrations of PFOS and PFOA in raw water should influence the residue levels in tap water. In tap water samples from some water purification plants, Takagi et al.[26] also noted that the concentrations of PFOS and PFOA were higher than those found in raw water.

To assess the temporal trend of the concentrations of PFCs in drinking water from Catalonia, the results of the present study were compared with those obtained in our previous surveys.[8,14] Despite the differential characteristics of the samples, some trends were noted (Figure 3). Thus, in the last period (2008−2009), an important decrease in PFC levels was detected, with reductions of 48 and 47% for PFOS and PFOA, respectively. Generally, the current levels of PFCs in

Table 2. Individual PFC Concentrations (Nanograms per Liter) in Each of the 30 Water Samples Collected in Catalonia[a]

	no.	PFBA	PFPeA	PFBuS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDS	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA
Flix (Terres de l'Ebre)	1A	1.90	0.59	0.33	*b*	0.70	0.49	1.40	<0.25	0.48	<0.40	<0.30	<0.24	0.12	<0.50	<0.50
	1B	<0.33	<0.33	0.15	0.67	<0.41	0.25	0.72	0.15	0.38	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	1C	<0.33	<0.33	0.16	0.83	<0.41	0.26	0.83	0.22	0.60	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
Tàrrega (Lleida)	2A	<0.33	<0.33	<0.10	0.19	<0.41	<0.10	0.79	0.22	0.24	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	2B	<0.33	<0.10	<0.10	0.29	0.47	<0.10	0.70	<0.10	<0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	2C	<0.33	<0.10	<0.10	<0.10	0.44	<0.10	<0.40	<0.10	<0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
Ripoll (Girona)	3A	<0.33	<0.10	<0.10	0.82	1.60	<0.10	32.8[c]	0.19	<0.05	*b*	0.68	<0.10	0.16	<0.10	<0.29
	3B	<0.33	<0.10	<0.10	<0.10	<0.41	<0.10	<0.40	<0.10	<0.05	<0.10	<0.10	<0.10	*<0.10*	*b*	*b*
	3C	<0.33	<0.10	<0.10	<0.10	<0.41	<0.10	<0.40	<0.10	<0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
Torroella de Montgrí (Girona)	4A	<0.33	<0.10	0.26	<0.10	<0.41	0.57	<0.40	<0.10	2.30	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	4B	0.61	<0.10	0.24	<0.10	<0.41	0.51	<0.40	<0.10	2.20	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	4C	0.57	<0.10	0.33	<0.10	<0.41	0.58	<0.40	<0.10	1.70	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
Palafolls (Barcelona)	5A	2.10	2.50	0.38	3.60	4.40	0.74	9.50	8.90	6.00	*b*	3.80	1.40	<0.10	<0.10	<0.29
	5B	3.10	1.90	0.38	2.80	4.10	0.85	9.20	8.20	3.70	*b*	2.10	1.50	<0.10	<0.10	<0.29
	5C	1.30	1.70	0.33	2.20	3.30	0.66	7.90	9.60	5.10	*b*	3.70	3.20	<0.10	<0.10	<0.29
Reus (Tarragona)	6A	0.65	0.39	<0.10	0.24	<0.41	<0.10	0.43	<0.10	<0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	6B	0.65	0.26	<0.10	0.34	<0.41	<0.10	<0.40	<0.10	0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
	6C	0.19	0.27	<0.10	0.29	<0.41	<0.10	<0.40	<0.10	0.05	*b*	<0.13	<0.10	<0.10	<0.10	<0.29
Olost (Barcelona)	7A	0.49	0.16	<0.10	0.12	0.47	<0.50	<0.72	*0.04*	0.18	<0.13	*<0.20*	0.17	*<0.10*	*0.06*	*<0.50*
	7B	1.20	<0.10	<0.10	0.23	0.32	<0.50	<0.72	*b*	0.26	<0.13	<0.20	<0.10	<0.10	0.05	<0.50
	7C	0.33	*<0.10*	<0.10	0.23	<0.30	<0.50	<0.72	*b*	0.43	<0.13	<0.20	<0.10	<0.10	0.02	<0.50
Abrera (Barcelona)	8A	0.97	1.10	0.31	2.00	1.10	0.53	3.10	*b*	1.40	<0.13	*b*	*0.17*	*<0.10*	*0.04*	*<0.50*
	8B	1.70	0.96	0.31	1.20	1.20	0.31	2.50	*1.10*	1.40	<0.13	*<0.20*	0.15	*<0.10*	*0.04*	*<0.50*
	8C	0.24	<0.10	<0.20	<0.20	<0.30	<0.50	9.60	<0.30	<0.50	<0.40	<0.20	<1.0	*b*	*b*	*b*
St. Joan Despí (Barcelona)	9A	3.40	1.60	9.90	2.60	2.90	1.20	4.70	*b*	20.2[c]	<0.40	0.44	<0.24	<0.10	<0.50	<0.50
	9B	4.40	2.10	10.10	2.70	2.50	0.70	4.10	0.87	6.60	<0.40	<0.30	<0.24	<0.10	<0.50	<0.50
	9C	4.30	1.70	9.60	*b*	2.50	0.73	3.70	0.67	6.20	<0.40	*0.27*	*<0.24*	<0.10	<0.50	<0.50
El Prat de Llobregat (Barcelona)	10A	1.40	1.10	1.30	<1.6	3.10	1.60	5.00	0.40	*6.00*	*<0.40*	*<0.20*	*b*	*b*	*b*	*b*
	10B	0.81	*b*	0.47	<1.6	0.31	<0.50	1.80	*0.41*	*1.60*	*<0.40*	*<0.20*	*b*	*b*	*b*	*b*
	10C	1.00	0.39	4.60	<1.6	0.44	<0.50	1.00	*<0.30*	*5.10*	*<0.40*	*b*	*b*	*b*	*b*	*b*
mean		1.09	0.61	1.33	0.86	1.08	0.40	2.40	1.23	1.81	nd[d]	0.46	0.31	0.06	0.08	nd
SD		1.23	0.76	3.01	1.03	1.31	0.37	3.08	2.85	2.28	*b*	1.01	0.69	0.03	0.08	
median		0.63	0.17	0.20	0.32	0.38	0.25	0.79	0.15	0.48	*b*	0.10	0.05	0.05	0.05	

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Table 2. continued

	no.	PFBA	PFPeA	PFBuS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDS	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA
min		<0.33	<0.10	<0.10	<0.10	<0.30	<0.10	<0.40	<0.10	<0.05	*b*	<0.10	<0.10	<0.10	<0.10	
max		4.4	2.5	10.1	3.6	4.4	1.6	9.6	9.6	6.6	*b*	3.8	3.2	0.16	0.25	
no. nondetected		9	15	13	12	13	15	11	17	7	30	24	24	28	25	30

[a]Recovery = 50−150%. Samples with a recovery <50% are shown in italics. Samples: A, raw water; B, after purification; C, drinking water. [b]Samples with a recovery either <20 or >150%. [c]Outliers. [d]nd, non-detected.

water samples from Catalonia are similar to those reported by other authors. However, it must be noted that the reported range of reference values is notably wide.[9−11,26,30,31]

Assuming an intake of 2 L of tap water per day,[32] the mean exposure to PFOS for the adult population of Catalonia was estimated at 3.9 ng/day, whereas that of PFOA was estimated at 4.8 ng/day. The calculations for the sampling points carried out using the highest concentrations of PFOS (St. Joan Despí) and PFOA (Abrera) (6.2 and 9.6 ng/L, respectively) showed a maximum intake of 12.4 ng/day of PFOS in a worst-case scenario, whereas that of PFOA was estimated at 19.2 ng/day. Both intakes are notably lower than those obtained in our previous study (119 and 112 ng/day for PFOS and PFOA, respectively).[8] Moreover, the mean concentrations of PFOS and PFOA in water samples from Catalonia, 1.81 and 2.40 ng/L, respectively, are considerably lower than the health-based concentrations of 20 and 40 ng/L (for PFOS and PFOA, respectively) recommended by the U.S. EPA ($^1/_{10}$ of the provisional health advisory recommended by the U.S. EPA[33]). In turn, the current values are also notably lower than those recommended by the U.K. Health Protection Agency (HPA), advising that the maximum acceptable concentration of PFOS in drinking water is 300 ng/L, whereas that for PFOA is 10000 ng/L.

The levels of PFCs in samples of fish and shellfish from Catalonia are summarized in Table 3. Among the analyzed PFCs, only seven compounds could be detected in at least one composite sample. PFBuS, PFHxA, PFHpA, PFDS, PFDA, and PFTDA were undetected in all samples. PFOS was, by far, the PFC showing the highest mean concentration in fish and shellfish (2.70 ng/g of fresh weight (fw)), being detected in all species with the exception of mussels. High PFOS levels were found in sardine and red mullet (8.32 and 7.24 ng/g fw, respectively). With regard to PFOA (mean level = 0.074 ng/g fw), the highest concentrations were detected in prawn and hake (0.098 and 0.091 ng/g fw, respectively).

No significant differences in PFC concentrations were observed when the results depending on the respective coastal area of collection were compared. However, notably higher levels of PFOS, PFOA, and PFUnDA were observed in samples collected in the south (Tarragona Province) and midcoastal (Barcelona Province) areas, in comparison with those from the northern area (Girona Province). In a previous study,[21] we determined the levels of some PFCs in a few food samples acquired in Catalan markets and supermarkets. Among the studied food items, white fish, seafood, tinned fish, and blue fish were separately selected. In that study, PFOS, PFOA, and PFHpA were the only PFCs that could be detected in foodstuffs. Recent studies around the world have reported that fish and seafood are generally the foodstuffs with the highest PFC concentrations.[3,19,22,34,35] In one of the first studies focused on determining the levels of PFCs in food, Tittlemeir et al.[6] analyzed the levels of these compounds in various Canadian foods, including fresh fish, canned fish, and seafood. PFOS was the only PFC that could be detected, with values ranging between 1.3 and 2.6 ng/g of fresh weight. Recently, Noorlander et al.[19] reported that lean fish was an important contributor to the dietary PFOS intake in The Netherlands. In freshwater species, Hölzer et al.[30] found median concentrations of PFOS as high as 96 and 77 ng/g in perch and eels, respectively, from the Lake Möhne (Germany). More information on the levels of PFCs in foodstuffs in general and in fish and shellfish in particular, as well as on human

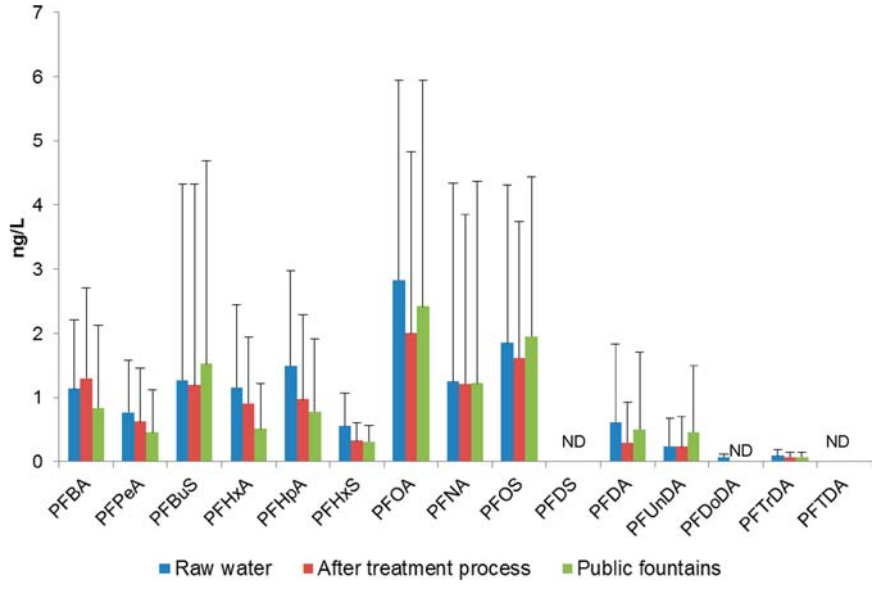

Figure 2. Mean PFC concentrations (ng/L) in samples of raw water and drinking water. ND, not detected.

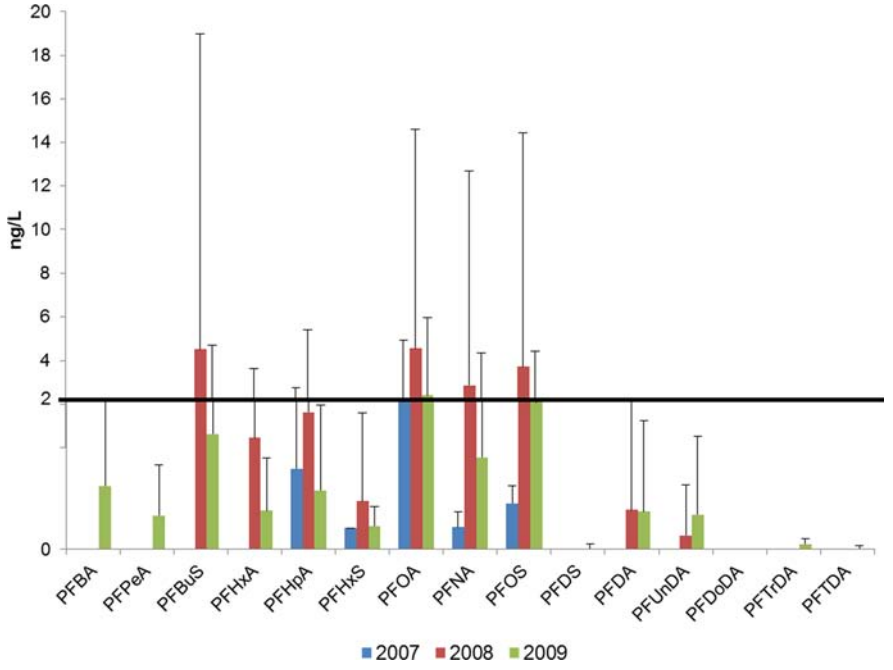

Figure 3. Temporal trend of PFCs in drinking water.

Table 3. Concentrations of PFCs (Nanograms per Gram Fresh Weight) in Samples of Fish and Shellfish from Catalonia, Spain[a]

species	PFBuS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDS	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA
sardine	<0.076	<0.076	<0.076	0.037	<0.076	0.11	8.32	<0.050	*b*	0.71	0.24	0.46	<0.13
tuna	<0.070	<0.070	<0.070	<0.035	0.039	0.031	0.56	<0.046	<0.046	0.32	*b*	*b*	*b*
hake	<0.082	<0.082	<0.082	0.032	0.091	0.074	1.71	<0.055	<0.055	0.34	<0.11	0.15	<0.14
red mullet	<0.050	<0.050	<0.050	0.030	0.071	0.51	7.24	<0.033	<0.033	0.36	0.11	0.15	<0.083
cuttlefish	<0.078	<0.078	<0.078	<0.039	<0.078	0.26	0.54	<0.052	<0.052	*b*	*b*	*b*	*b*
mussel	<0.068	<0.068	<0.068	<0.034	<0.068	0.030	<0.045	<0.045	<0.045	<0.045	*b*	*b*	*b*
prawn	<0.073	<0.073	<0.073	<0.036	0.098	0.17	0.48	<0.049	<0.049	0.22	0.20	0.35	<0.12
mean	nd[c]	nd	nd	0.035	0.074	0.171	2.70	nd	nd	0.342	0.164	0.278	nd

[a]Three composite samples were analyzed for each species. [b]Samples showing recoveries either <20 or >150%. [c]nd, nondetected.

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dietary intake of PFCs for a number of countries, can be found in recent extensive reviews on these issues.[3,7,34]

On the basis of the current data, we estimated the human exposure to PFCs through consumption of fish and shellfish. For this purpose, consumption data of the analyzed foodstuffs were obtained from the ENCAT survey.[36] Considering the whole set of PFCs, and assuming values of half of the detection limit for the undetected compounds (ND = $^1/_2$ LOD), the mean intake of PFCs due to fish and shellfish consumption for the adult population of Catalonia was estimated at 97.0 ng/day. PFOS showed the largest contribution, with a mean level of 71.3 ng/day (73% of the total). This would be due to the high intake of PFCs derived from the consumption of sardine and red mullet (31.4 and 27.4 ng/day, respectively). This value is considerably lower than the tolerable daily intake (TDI) recommended by the EFSA[38,39] for PFOS, 150 ng/kg/day. In turn, the maximum intakes of PFOS and PFOA through drinking water for an adult subject (based on a 70 kg body weight), 0.18 and 0.27 ng/kg/day, respectively, are well below the provisional oral reference doses (RfDs) for PFOS and PFOA, which were estimated on the basis of a rat chronic carcinogenicity study and a rat multigenerational study, respectively.[37] On that basis, the provisional oral RfD values are 25 and 333 ng/kg/day for PFOS and PFOA, respectively. Overall, PFOS intake, including that from drinking water (worst-case scenario), 12.4 ng/day, would be 83.7 ng/day, or 1.20 ng/kg/day for an adult of 70 kg body weight.

In our previous survey,[21] PFC intake was 34.1 ng/day, when we considered the intake of PFCs through fish and shellfish consumption only. However, it must be remarked that important procedure differences exist between both surveys, which make rather difficult the comparison. In any case, the data confirm that PFOS is the PFC with the highest concentrations in marine species. In Norway,[22,35] fish and shellfish were also the major dietary sources of PFCs, contributing 38 and 81% of the estimated dietary intakes of PFOA and PFOS, respectively.

From the above results, some interesting conclusions can be drawn. With regard to water samples, although the current treatment processes showed slight reductions in PFC concentrations, these purification processes did not mean significant changes in the amounts of PFCs already contained in the raw water. Despite this, human exposure to PFCs through municipal drinking water in Catalonia is not expected to pose health risks based on the recommendations of various international organizations. With respect to exposure to PFCs through the consumption of fish and shellfish, comprising the food group potentially containing the highest PFC concentrations, the results of the present study indicate that the current consumption should not be of concern. The amounts ingested are well below the recommended TDIs, at least for those PFCs for which information is currently available. Finally, the results of the present study agree with those of previous papers indicating that in Catalonia, drinking water is a minor source of human exposure to PFCs in comparison to dietary intake under normal intake scenarios.

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Notes

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