

AN INITIAL STUDY ON PERFLUORINATED COMPOUNDS IN TAP WATER FROM SELECTED CITIES IN CHINA

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Introduction

Due to the anionic functional groups and non-polar perfluoroalkyl chains that can repel both water and oil, perfluorinated compounds (PFCs), including perfluoroalkyl sulfonates (PFASs) and perfluoroalkyl carboxylates (PFCAs) have been widely used as surface protectors, surfactants, and in aqueous fire fighting foams and fluoropolymers for more than fifty years^{1,2}. However, they have been shown to be persistent, bioaccumulative and toxic³ and have thus prompted concern about their presence in the environment. One PFAS, perfluorooctane sulfonate (PFOS), is now being proposed for inclusion on the list of emerging persistent organic pollutants (POPs)⁴.

In recent decades, China has become the world's factory, and the coastal environment has been polluted by various human activities⁵. Many studies have shown that PFCs are present in surface waters like the Yangtze River and Pearl River at the ng/L level⁵. River water, from which tap water may originate, is one of the possible sources of drinking water. Even though raw river water is purified before becoming tap water, polar pollutants like PFCs might still remain⁶ and a direct correlation has been shown between PFOS and PFOA concentrations in tap water and in surface water⁷. In China, people drink tap water both with and without boiling, and thus they may be at risk from exposure to PFCs. To date, studies related to PFC contamination in tap water are limited⁶⁻¹¹. In addition, most of these studies mainly focused on the detection of PFOS and PFOA. Other PFASs and PFCAs, however, were not identified because of their relatively low concentrations and a lack of sensitive analytical methods until the recent development of a new method for trace analysis of shorter chain compounds¹². In order to construct a more complete composition profile of PFCs in tap water, twenty PFCs were identified and quantified in Chinese tap water.

Materials and Methods

Thirteen tap water samples were collected from Wuhan ($n=3$), Nanjing ($n=1$), Shanghai ($n=3$), Xiamen ($n=2$) and Hong Kong ($n=4$) during 2006-2008. They were stored in 1 L polypropylene (PP) bottles with narrow mouths and screw caps at 4 °C before extraction. Duplicate tap water samples were analyzed for each sampling location. Five hundred mL tap water samples were used for extraction using Oasis[®]WAX (6 cc) solid phase extraction (SPE) cartridges (Waters Corp., Milford, USA). The extraction procedure was described in detail elsewhere¹³. Twenty PFCs, including six PFASs (perfluorodecane sulfonate (PFDS), PFOS, perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), perfluoropropane sulfonate (PFPrS), and perfluoroethane sulfonate (PFEtS)), two FOSAs (perfluorooctane sulfonamide (PFOSA) and *N*-ethyl perfluorooctane sulfonamidoacetate

(*N*-EtFOSAA)) and twelve PFCAs (perfluorooctadecanoic acid (PFOcDA), perfluorohexadecanoic acid (PFHxDA), perfluorotetradecanoic acid (PFTeDA), perfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnDA), perfluorodecanoic acid (PFDA), perfluorononanoate (PFNA), PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutanoic acid (PFBA)), were quantified. Separation, identification and quantification of the analytes was performed by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) operated in the electro-spray negative mode. A 10 µL aliquot of extract was injected onto both a Keystone Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 µm, 100Å pore size, endcapped) with 2 mM ammonium acetate and methanol as the mobile phases for the quantifications of C6-C18 PFCs, and a RSpak JJ-50 2D (2.0 mm i.d. x 150 mm length, 5 µm; Shodex, Showa Denko K.K., Kawasaki, Japan) with 50 mM ammonium acetate and methanol as the mobile phases for the quantifications of C2-C5 PFCs, separately. The details of the conditions for the LC-MS/MS were reported elsewhere^{12,13}. Procedural blanks and recoveries were conducted with every extraction batch. All procedural blanks were below corresponding limits of quantification (LOQs) and the procedural recoveries of individual PFCs ranged from 79-128%. Matrix spike recoveries were carried out and the recoveries ranged from 44-123% (Table 1). The measured concentrations were not corrected for recovery.

Results and Discussion

Thirteen tap water samples from Wuhan, Nanjing, Shanghai, Xiamen and Hong Kong were analyzed, and 13 PFCs were detected in these samples. In general, the dominant PFAS present in Chinese tap water was PFOS (mean: 4.07 ng/L), followed by PFBS (mean: 3.72 ng/L). PFOS was found at the greatest levels in tap water from Shanghai (6.81 ng/L), Xiamen (0.526 ng/L) and Hong Kong (6.67 ng/L), whereas PFBS was the predominant PFAS in Wuhan (12.6 ng/L) and Nanjing

(1.55 ng/L) tap water. All of the longer chain PFCAs (PFUnDA, PFDoDA, PFTeDA, PFHxDA, PFOcDA) were absent in tap water from Wuhan, Nanjing, Shanghai, Xiamen and Hong Kong, except for PFUnDA (0.500 ng/L), which was present in Shanghai tap water. In Chinese tap water, PFOA (mean: 14.0 ng/L) and PFBA (mean: 4.69 ng/L) were detected at the greatest concentrations. The predominant PFCA in samples from Shanghai was PFOA (54.8 ng/L); however, PFBA was predominant in tap water from Wuhan (8.95 ng/L) and Nanjing (2.82 ng/L). Although the overall mean concentration of PFPeA in Chinese tap water was low (1.72 ng/L), it was the most prevalent PFCA in tap water from Xiamen (2.45 ng/L) and Hong Kong (2.25 ng/L).

	Blank (<i>n</i> =5) (ng/L)	Procedure Recovery (<i>n</i> =5) (%)			Matrix Spike (<i>n</i> =2) (%)		
		Mean	S.D.	Range	Mean	S.D.	Range
PFASs							
PFDS	<0.1	101	7	95-110	89	0	88-99
PFOS	<0.1	101	4	99-107	95	3	93-97
PFHxS	<0.1	100	4	95-105	102	2	100-103
PFBS	<0.1	95	4	91-100	94	2	93-95
PFPrS	<0.4	101	3	98-105	82	4	79-84
PFEtS	<0.4	95	3	91-100	116	3	114-118
PFOSA	<0.004	86	6	79-94	89	1	88-89
<i>N</i> -EtFOSAA	<0.1	103	10	94-115	86	2	85-87
PFCAs							
PFOcDA	<0.1	97	6	87-102	88	2	86-89
PFHxDA	<0.1	79	3	76-83	44	1	44-45
PFTeDA	<0.1	97	9	86-108	100	7	95-104
PFDoDA	<0.1	104	5	100-111	100	7	95-105
PFUnDA	<0.1	109	6	102-118	97	4	94-100
PFDA	<0.1	117	7	111-128	102	6	98-106
PFNA	<0.1	128	5	122-134	123	2	121-124
PFOA	<0.1	99	6	95-108	99	8	94-105
PFHpA	<0.1	114	7	104-122	78	2	77-79
PFHxA	<0.1	112	10	99-127	98	0	98
PFPeA	<0.4	87	8	80-100	81	5	78-84
PFBA	<0.4	79	12	63-96	117	1	116-117
13C4-PFOS	<0.1	97	2	94-98	89	4	86-91
13C2-PFDA	<0.1	98	3	93-102	85	5	82-88
13C5-PFNA	<0.1	120	14	103-138	117	9	110-123
13C4-PFOA	<0.1	97	7	89-108	84	2	83-86

Table 1 Procedural blanks, procedural recoveries and matrix spikes recoveries

Levels of total PFASs, PFCAs, and PFCs are shown in Figure 1. Concentrations of total PFCAs were much higher than those of PFASs in most of the tap water samples analyzed, with the exception of samples from Hong Kong, which contained comparable levels of total PFASs and total PFCAs. The greatest and least mean total PFC concentrations were measured in tap water from Shanghai (range: 123-131 ng/L) and Xiamen (5.69-9.53 ng/L), respectively. The presence of PFCs in all of the tap water samples shows that Chinese people are exposed to PFCs via drinking tap water from these sources.

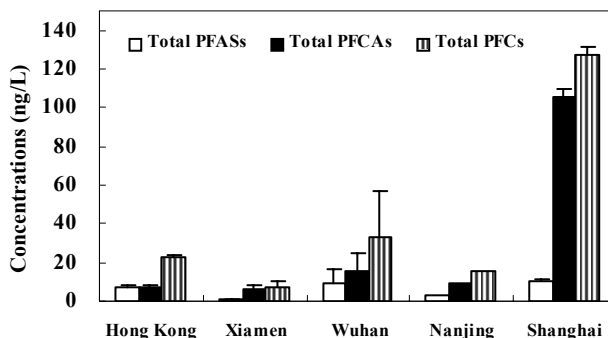


Figure 1 Concentrations of total PFASs, PFCAs and PFCs

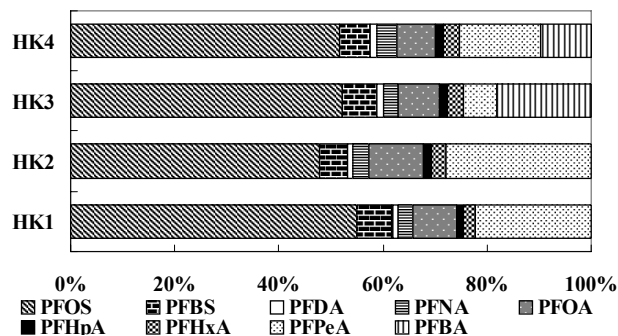


Figure 2 Composition profiles of PFCs in Hong Kong tap water

The composition profiles of PFCs in the tap water samples from Wuhan, Nanjing, Shanghai, Xiamen and Hong Kong were generally different, suggesting different origins of the PFC contamination. There are several possible causes of PFC contamination in tap water, such as contamination of the water source to differing degrees, or contamination during transportation or storage of the tap water, since the components of pipelines or water tank may be made up of materials containing fluoropolymers. Tap water in China can originate from river water, rainwater, and/or groundwater and it varies from place to place. The infrastructure and facilities for the transport of tap water in these cities might also vary. It is difficult to identify precisely the possible reasons for this contamination. In Hong Kong, the major source of tap water is the Dongjiang River. If the PFC contamination was only due to a contaminated water source, the composition profiles of PFCs in all tap water samples from Hong Kong should be more or less the same. Even though the composition profiles of PFCs in tap water samples from this region (Figure 2) were similar, in samples HK3 and HK4, PFBA contributed 10-15% of the total PFCs whereas it was absent in sample HK1 and HK2. Samples HK1 and HK2 were of domestic origin, whereas HK3 and HK4 were from a commercial shopping centre and our laboratory, indicating that the small difference in PFC composition might be partly due to different water transportation systems in buildings that contain integral parts made up of different PFCs, and that PFC contamination might not originate from water sources alone.

A global comparison was carried out on PFOS and PFOA only since most of the studies mainly focused on the detection of these two compounds in tap water samples (Figure 3). Although the concentrations of PFOS in tap water from Shanghai (mean: 6.81 ng/L) and Hong Kong (mean: 6.67 ng/L) were relatively high among five cities in China, they were still less than those from Lake Maggiore (8.10 ng/L)⁶ in Italy and Osaka (12.0 ng/L)¹⁰ in Japan. However, the concentration of PFOA in tap water from Shanghai (54.8 ng/L) was the second highest when compared with other countries.

Besides PFOS and PFOA, these results indicated that other PFASs (such as PFBS) and PFCAs (such as PFBA or PFPeA) were significant in some cities. Further work should focus on these shorter chain compounds in addition to these two well-known PFCs. These results are only an initial report on PFC contamination in tap water in selected Chinese cities. A more extensive sampling campaign has been initiated to collect tap water samples from different cities in China for a better understanding of the degree of PFC contamination in this medium. A human health risk assessment will also be conducted on these tap water samples in the future.

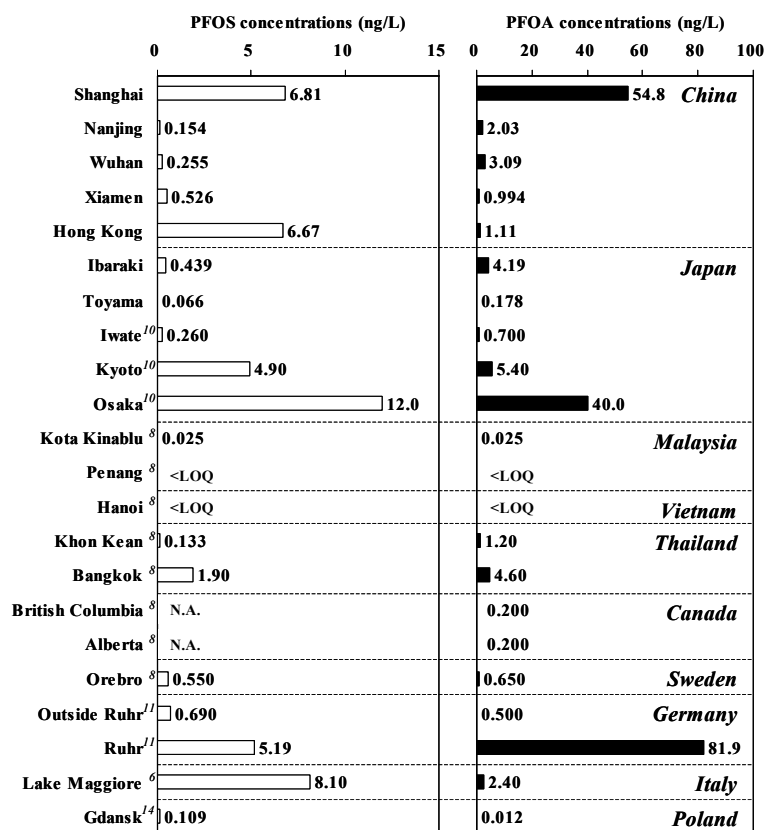


Figure 3 Global comparisons of PFOS and PFOA in tap water

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