REGIONAL AND RURAL-URBAN DIFFERENCES OF PFOS AND PFOA IN BLOOD OF THE GENERAL POPULATIONS IN CHINA

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Introduction

Perfluoroalkyl acids (PFAAs), featured with perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been manufactured and employed as surfactants and surface protectors in various domestic and industrial products, since their initial commercialization over half a century ago[1]. It has become well-known that the extremely strong C-F bonds of PFAAs result in their resistance to environmental and biological degradation, chemical and thermal stability, and both hydrophobicity and oleophobicity[2], contributing to their global distribution[3], bioaccumulation[4], and various toxicities[5]. As a result, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009, calling for restricted use worldwide[6].

Research on the PFAA load in the non-occupationally exposed general populations in different areas of China has been carried out since 2006[7-9]. PFOS was determined as the predominant PFAA in the whole blood samples from donors in nine cities of China[7]. In addition, Jin et al found an overall increasing trend in serum PFOS and PFOA levels in residents of Shenyang from 1987 through 2002[8]. A recent study showed that PFOA was the dominant PFAA in serum samples from residents in Fuxin, resulting from a fluorochemical plant for the production of polytetrafluoroethylene (PTFE) located there[9]. However, little is known about the influence of geographical factors on serum PFOS and PFOA concentrations of the general populations in China.

The present study aimed to investigate the serum PFOS and PFOA levels in the general populations from two coastal and two inland cities of China, and to determine the regional and rural-urban differences of the serum PFOS and PFOA concentrations in the Chinese general populations.

Materials and methods

Potassium salt of heptadecafluorooctane sulfonate (PFOS, 98%) was acquired from Fluka (Steinheim, Germany). Pentadecafluorooctanoic acid (PFOA, 95%) was purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrabutylammonium hydrogensulfate (TBAHS) of HPLC grade and anhydrous extra pure sodium carbonate (Na_2CO_3, 99.5%) were obtained from Acros Organics (Geel, Belgium). HPLC grade ammonium acetate was obtained from Dikma Technology (Richmond, VA). HPLC grade methyl tert-butyl ether (MTBE), methanol, and acetonitrile were obtained from Tedia (Fairfield, OH). Milli-Q water was cleaned using Waters Oasis HLB Plus (225 mg) cartridges (Milford, MA) to remove the potential residue of PFCs. Mixed stock PFOS and PFOA standard solution was prepared in methanol. All reagents were used as received.

As Figure 1 shows, 1437 serum samples were collected from the general populations living in urban and rural areas of one coastal city (Dalian) and two inland cities (Shenyang and Chongqing) in China, and those living in urban area of another Chinese coastal city (Shenzhen). In detail, 406 samples were from Dalian, 388 samples were from Shenyang, 416 samples were from Chongqing, and 227 samples were from Shenzhen. The serum samples were stored in 2 mL methanol-rinsed polypropylene (PP) vials at -20 ^{o}C until extraction. The sample collection was approved by the Medical Ethics Committee at China Medical University in China.

Serum samples were extracted following a method developed by Hansen et al[10]. Two milliliters of 0.25 M Na_2CO_3 and one milliliter of 0.5 M TBAHS were added to 0.5 mL of serum and then extracted twice with MTBE. The combined MTBE extracts were brought to dryness under a gentle stream of high purity nitrogen, and reconstituted in 1 mL mixture of methanol and 10 mM ammonium acetate (2:3, v/v) before final filtration with a 0.22 µm nylon filter. The extracts were analyzed via high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). Chromatography was performed by an Agilent 1100 HPLC system (Palo Alto, CA), and the HPLC system was interfaced to an Agilent 6410 Triple Quadrupole (QQQ) mass spectrometer (Santa Clara, CA) operated with electrospray ionization (ESI) in negative mode.

Statistical analysis was performed with the software SPSS 16.0. During the analysis, values of serum samples that lower than the LOQ were set to one half of the LOQ, and those of samples that lower than the LOD were assigned as values of the LOD / $\sqrt{2}$. Correlations between age and serum PFOS and PFOA concentrations, regional and rural-urban differences of serum PFOS and PFOA levels in terms of gender and age were assessed via Spearman rank correlation test and Mann-Whitney test. Statistical correlations and differences were considered to be significant at $p < 0.05$.

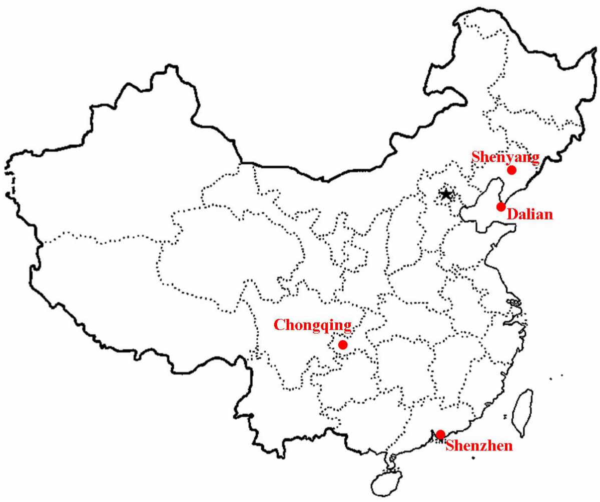

Figure 1. Sampling locations in China

Results and discussion

As Table 1, geometric means (GMs) of serum PFOS and PFOA in the general populations of China were 4.25 and 3.64 ng/mL, respectively. Statistically, PFOS and PFOA concentrations showed a good mutual correlation, suggesting a similar source of human exposure in China. In addition, a significant positive correlation was observed between age and serum concentrations of PFOS and PFOA with both genders. Although there were marginal differences between GMs of PFOS and PFOA in male and female populations, no significant differences were found between serum concentrations of each compound in both genders. However, serum PFOS and PFOA in adults > 14 years were much higher than those in children < 14 years (p = 0.000 and 0.000).

Table 1. Serum PFOS and PFOA concentrations in the general populations of China (ng/mL)

		N	PFOS		PFOA	
			Geometric Mean (95% CI)	**Median**	**Geometric Mean (95% CI)**	**Median**
Gender	**Male**	**737**	**4.67 (4.10-5.32)**	**6.20**	**3.71 (3.34-4.12)**	**5.15**
	Female	**700**	**3.85 (3.31-4.49)**	**6.29**	**3.57 (3.21-3.98)**	**4.72**
Age	**< 14**	**659**	**2.58 (2.22-3.00)**	**4.45**	**3.20 (2.87-3.56)**	**4.10**
	> 14	**778**	**6.48 (5.70-7.36)**	**10.58**	**4.10 (3.70-4.54)**	**5.62**
Total		**1437**	**4.25 (3.85-4.70)**	**6.24**	**3.64 (3.38-3.92)**	**4.96**

Table 2. Serum PFOS and PFOA levels in the general populations from different regions of China (ng/mL)

Region		N	Variable	PFOS		PFOA	
				Geometric Mean (95% CI)	Median	Geometric Mean (95% CI)	Median
Urban	Dalian	206	Male	9.08 (7.59-11.0)	10.1	4.40 (3.63-5.37)	4.57
			Female	8.69 (7.41-10.2)	9.47	5.44 (4.47-6.61)	5.64
			< 14	7.09 (6.03-8.51)	7.84	4.62 (3.72-5.75)	5.47
			> 14	10.9 (9.12-12.9)	12.2	5.09 (4.27-6.17)	5.16
			Total	8.89 (7.94-10.0)	9.70	4.86 (4.27-5.62)	5.24
	Shenyang	196	Male	17.3 (13.8-21.4)	21.8	6.04 (4.79-7.59)	8.34
			Female	20.6 (16.2-25.7)	28.0	5.47 (4.37-6.92)	6.56
			< 14	8.73 (6.92-11.0)	9.41	3.15 (2.34-4.27)	4.28
			> 14	35.3 (30.9-39.8)	40.4	9.38 (8.32-10.5)	8.81
			Total	18.8 (16.2-21.9)	25.4	5.75 (4.90-6.76)	7.46
	Chongqing	200	Male	4.46 (3.47-5.75)	5.08	0.95 (0.74-1.23)	0.99
			Female	5.43 (4.37-6.76)	6.09	1.09 (0.87-1.35)	1.05
			< 14	3.92 (3.24-4.68)	4.59	1.01 (0.79-1.29)	0.85
			> 14	6.15 (4.79-7.94)	7.80	1.04 (0.81-1.32)	1.15
			Total	4.97 (4.17-5.89)	5.51	1.02 (0.87-1.20)	1.00
	Shenzhen	227	Male	2.07 (1.55-2.75)	1.88	6.41 (5.50-7.41)	6.53
			Female	2.28 (1.62-3.24)	2.39	6.33 (5.25-7.76)	7.64
			< 14	0.87 (0.68-1.10)	0.58	5.23 (4.57-5.89)	6.02
			> 14	4.64 (3.47-6.17)	8.13	7.55 (6.31-9.12)	9.86
			Total	2.15 (1.74-2.69)	2.07	6.38 (5.62-7.24)	6.72
	Total	829	Male	5.75 (5.01-6.61)	7.52	3.86 (3.39-4.37)	5.12
			Female	6.86 (5.89-7.94)	8.40	3.62 (3.16-4.07)	4.56
			< 14	3.64 (3.16-4.17)	5.15	3.00 (2.63-3.39)	3.80
			> 14	10.0 (8.71-11.5)	13.6	4.52 (3.98-5.13)	5.96
			Total	6.26 (5.62-6.92)	8.07	3.74 (3.39-4.07)	4.88
Rural	Dalian	200	Male	8.47 (6.46-11.0)	11.0	6.62 (5.01-8.71)	9.61
			Female	6.75 (5.01-9.12)	10.5	5.31 (4.07-6.92)	7.61
			< 14	6.03 (4.07-8.91)	9.01	4.33 (2.95-6.31)	7.44
			> 14	8.59 (6.76-11.0)	12.3	7.07 (5.75-8.71)	9.43
			Total	7.56 (6.17-9.33)	11.0	5.93 (4.90-7.24)	8.51
	Shenyang	192	Male	11.8 (9.33-15.1)	14.3	5.46 (4.27-7.08)	8.42
			Female	9.03 (7.59-11.0)	9.35	5.15 (3.98-6.76)	8.36
			< 14	8.75 (7.24-10.5)	9.46	5.67 (4.47-7.24)	8.57
			> 14	12.2 (9.77-15.5)	13.9	4.97 (3.80-6.61)	8.16
			Total	10.4 (8.91-12.0)	11.9	5.31 (4.47-6.31)	8.39
	Chongqing	216	Male	0.50 (0.35-0.72)	0.96	1.25 (0.91-1.70)	2.14
			Female	0.14 (0.09-0.19)	0.15	1.76 (1.23-2.51)	3.09
			< 14	0.15 (0.10-0.22)	0.18	1.91 (1.35-2.69)	3.20
			> 14	0.45 (0.31-0.65)	0.91	1.15 (0.83-1.58)	1.97
			Total	0.26 (0.20-0.34)	0.49	1.48 (1.17-1.86)	2.70
	Total	608	Male	3.51 (2.75-4.47)	4.93	3.47 (2.88-4.17)	5.27
			Female	1.80 (1.35-2.40)	3.06	3.53 (2.95-4.27)	4.82
			< 14	1.61 (1.20-2.14)	2.72	3.44 (2.82-4.17)	4.66
			> 14	3.54 (2.95-4.57)	5.05	3.66 (2.95-4.27)	5.39
			Total	2.52 (2.09-3.02)	4.24	3.50 (3.09-3.98)	5.00

Table 2 summarizes serum PFOS and PFOA concentrations in the general populations from both urban and rural areas of different regions in China. Serum PFOS concentration in Shenyang had the highest GM at 14.0 ng/mL, which was considerably higher than those in the other three cities (p = 0.000, 0.000, and 0.000). In addition, serum PFOS concentration with a GM of 8.21 ng/mL in Dalian was also significantly higher than those in Chongqing and Shenzhen (p = 0.000 and 0.000). Although serum PFOA concentration in Shenzhen with a GM of 6.38 ng/mL was higher than those of the other three cities, a significant difference was only found between serum PFOA concentrations between Shenzhen and Chongqing (p = 0.000).

Rural-urban differences of serum PFOS and PFOA concentrations in Dalian, Shenyang, and Chongqing were also evident in Table 2. For instance, serum PFOS concentrations in urban areas of Shenyang and Chongqing were significantly higher than those in rural areas of the two cities (p = 0.000 and 0.000). However, serum PFOA concentrations in urban areas of Dalian and Chongqing were much lower than those in rural areas of the two cities (p = 0.000 and 0.000), which could result from the significant differences between serum PFOA concentrations in urban and rural adults > 14 years of Dalian as well as those in urban and rural children < 14 years of Chongqing (p = 0.000 and 0.000). Significant positive correlations between age and serum PFOS and PFOA concentrations were found in the urban populations of Shenyang, Chongqing, and Shenzhen, while only serum concentration of PFOS was significantly correlated with age of the urban populations in Dalian. Age and serum PFOS concentration showed a significant positive correlation in the rural populations of Chongqing only, whereas a considerable negative correlation was observed between age and serum PFOA concentration in the rural populations there, suggesting high PFOA exposure in rural infants and toddlers of Chongqing.

Overall, serum PFOS concentrations in both genders and two age groups of the urban populations were observed to be much higher than those of the rural populations (p = 0.017, 0.000, 0.008, and 0.000). As a result, serum PFOS concentrations in the urban populations were significantly higher than those in the rural populations (p = 0.000). In addition, serum PFOA concentrations in urban children < 14 years were significant lower than those in rural children with the same ages (p = 0.002). Significant positive correlations were observed between age and serum PFOS concentrations in the urban and rural populations, while serum PFOA concentrations were only significantly correlated with age of the urban populations.

As above, significant differences presented in serum PFOS and PFOA concentrations in the general populations from urban and rural areas in coastal and inland cities of China, demonstrating regional and rural-urban differences in the human exposure pathways to PFOS and PFOA in China. Further investigations would be required to determine the potential sources of PFOA exposure for rural children in Chongqing.

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