A PILOT STUDY OF PERFLUORINATED COMPOUNDS IN RIVER WATER, SEA WATER, TAP WATER AND WASTE WATER SAMPLES FROM SOUTH INDIA

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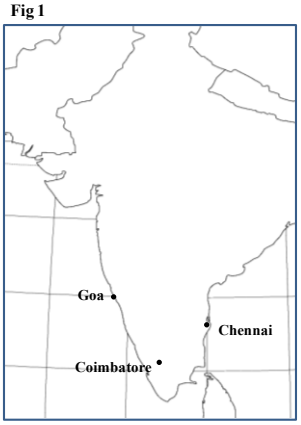
Introduction

Perfluorinated compounds (PFCs), a group of persistent organic compounds, have received worldwide attention in recent years. Perflurooctanesulfonate (PFOS) and perflurooctanoate (PFOA) are the two typical candidates representing this group of chemicals as they are frequently found in different environmental matrices from open ocean water to foodstuffs[1-3]. More importantly, PFCs have also been found in human blood at ng/mL levels[4]. Furthermore, studies have documented potential carcinogenicity of PFCs[5-7], and PFOS has been proposed as a candidate POP for regulations under Stockholm Convention.

Surface water and wastewater samples collected from several countries have been shown to contain PFCs. PFOS concentrations ranged from 74.8 to 144ng/L in the Tennesse River[8] (U.S.), 15-121 ng/L in Lake Ontario[9], 0.7-157 ng/L in the Tama River (Japan)[10]. The most highly contaminated water bodies were near from the use of aqueous film forming foam (AFFF) or military bases where PFOS concentrations in ground water as high as 2210000 ng/L (in Ectobicoke Creek, Canada)[11], and as high as 2300000 ng/L (in Tyndall Air Force Base)[12] have been reported. In developing countries, such as China PFOS concentrations were: 0.90-99 ng/L in the Pearl River and <0.01-14 ng/L in the Yangtze River[13]; PFOS levels in Korean coastal water were 2.24-651 ng/L in Lake Shihwa[14]. These data suggested lack of marked difference in PFOS concentrations between developed and developing countries.

In contrast, India is an agricultural country. Blood PFOS concentrations of Indians were relatively lower than the concentrations reported for other countries[4] which might suggest PFC pollution in India may be low. A recent report of survey of PFCs[1] in oceans showed that the concentrations in the Indian Ocean were much lower than the PFC levels found in the Atlantic and Pacific Oceans. All these findings initiated the investigation of PFCs in different water bodies in India to evaluate the degree of PFC contamination. Three sampling locations were chosen for this pilot study; they were Goa, a highly populated area with only primary production (agricultural and fishing); Coimbatore, a cosmopolitan city with textile and agricultural industries; and Chennai, a typical modern urban city with different industries. Water samples originated from different sources such as rivers, coastal sea, lakes, tap water, and waste water (sewage). The results of PFC analysis are presented to understand the magnitude of contamination in India based on the analysis of water.

Fig 1



Material and Methods

Water samples were collected in January and February, 2008, from three locations (Goa, Coimbatore, and Chennai) in South India (Fig 1). River water, lake water, coastal sea water, tap water, well water, and waste water samples were collected and were stored in 500 mL polypropylene (PP) bottles (Table 1). All samples were stored at 4°C before extraction.

All water samples (300mL) were extracted using Oasis WAX (6cc) solid phase extraction (SPE) cartridges[15] (Waters Corp., Milford, USA). Perfluorinated compounds (PFCs), including perfluorodecanesulfonate (PFDS), PFOS,

Table 1. Sample description

No	Location	Sample ID	Sample type	Origin
1	Goa	GMD	River water	Mandovr River, Downstream
2		GMU	River water	Mandovr River, Upstream
3		GNB	Seawater	Colangute Beach
4		GW	Waste water	Domestic, household
5		GZU	River water	Zuari River, Upstream
6		GZD	River water	Zuari River, Downstream
7		GSB	Seawater	Colva Beach
8		GT	Tap water	Guest house
9	Coimbatore	CmU	River water	Bhavani River, upstream
10		CmM	River water	Bhavani River, Middle stream
11		CmK	River water	Kallar River
12		CmW	Waste water	Village house
13		CmL	Lake water	Ooty Lake
14		CmT	Tap water	Village tap
15	Chennai	ChR	River water	Cooum River
16		ChG	Ground water	Well water
17		ChB	Seawater	Marina Beach
18		ChT	Tap water	Shopping mall

perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluoropropanesulfonate (PFPrS), perfluoroethanesulfonate (PFEtS), 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), perfluorobutanoic acid (PFBA), perfluorooctane sulfonamide (PFOSA), N-ethyl perfluorooctane sulfonamide (N-EtFOSA), N-ethyl perfluorooctane sulfonamidoacetate (N-EtFOSAA) were determined by HPLC-MS/MS. Separation 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 electrospray negative ionization mode. A 10 µL aliquot of the 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 phase for the quantification 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 phase for the quantification of C2-C5 PFCs, separately. The details of the LC-MS/MS conditions have been reported elsewhere[15,16].

Table 2. Procedural blanks and recoveries.

	QA/QC		
Volume (mL)	300	300	
Final vol (mL)	0.5	0.5	
	Blk n=5 (ng/L)	**Recovery (%) n=5**	**S.D.**
PFDS	<0.0833	99	7
PFOS	<0.0833	94	7
PFHS	<0.0833	101	4
PFBS	<0.0833	95	8
PFPrS	<0.0833	96	8
PFEtS	<0.0833	88	7
PFOSA	<0.0333	86	4
N-EtFOSA	<0.0333	68	9
N-EtFOSAA	<0.0833	97	14
PFOcDA	<0.0167	105	8
PFHxDA	<0.0167	95	2
PFTeDA	<0.0167	98	7
PFDoDA	<0.0167	111	5
PFUnDA	<0.0167	115	5
PFDA	<0.0833	118	5
PFNA	<0.0833	116	7
PFOA	<0.0167	99	7
PFHpA	<0.0833	119	8
PFHxA	<0.0833	119	3
PFPeA	<0.0833	102	5
PFBA	<0.0833	101	1

Procedural blanks were analyzed with every batch of samples and procedural recoveries were conducted to check the accuracy of the methods. PFC levels in all procedural blanks were below the corresponding LOQs and the procedural recoveries ranged from 68 to 119% (Table 2). Samples were analyzed in duplicate when possible. PFC concentrations in samples were not corrected for the recoveries.

Results and Discussion

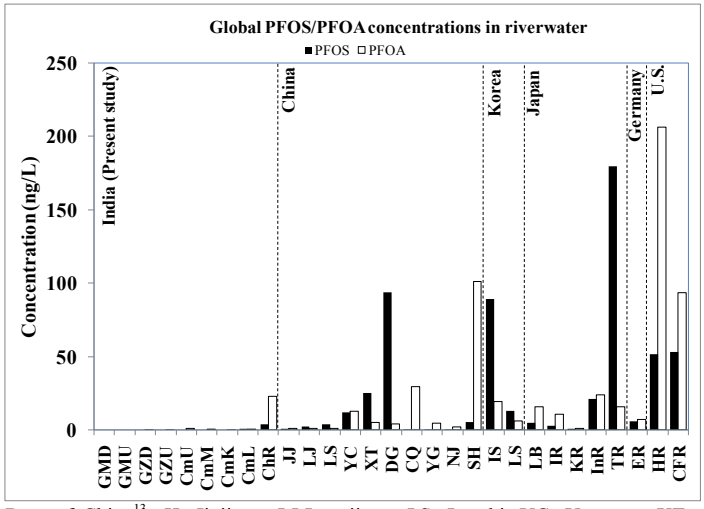
In total, 19 water samples from 5 different sources (rivers, lakes, sea water, tap water, well water, and waste water) were analyzed. Among 21 PFCs determined, only 11 of them could be detected in some of the samples. None of the perfluorosulfonates (PFDS, PFOS, PFHxS, and PFBS) could be found in water samples from Goa (<0.083-<0.167 ng/L), and only one water sample (Ooty lake) from Coimbatore contained 0.692 ng/L PFOS. For water samples from Chennai, one sample from Marina beach coastal water did not contain either PFOS or PFHxS, whereas all the other water samples from Chennai contained both PFOS (ChR: 3.13 ng/L; ChG: 3.13 ng/L; ChT: 8.29 ng/L) and PFHxS (ChR: 0.776 ng/L; ChG: 0.522 ng/L; ChT: 81.2 ng/L). In addition, water from the Cooum River (primarily receiving sewage) contained 0.251 ng/L N-EtFOSAA.

As for perfluorocarboxylates (PFCAs), no long chain PFCs (C11-18) could be detected in any of the water samples (<0.083-<0.167 ng/L). Seawater sample from Chennai contained trace amount of PFOA (0.691 ng/L), whereas seawater from Goa did not contain any PFCAs. Wastewater from Goa and Chennai only contained trace amount of PFHpA (0.74-2.52 ng/L). PFOA was the most abundant PFCA and it was found in 88% of the river water/lake water samples (<0.0833-23.1 ng/L), 75% of the tap water/ground water samples (0.0833-2.36 ng/L), 33% of the seawater samples (<0.083-0.691 ng/L). Other PFCAs such as PFDA, PFPeA and PFHxA were found in only 17% (<0.083-0.306 ng/L), 22% (<0.083-3.31 ng/L), and 11% (<0.083-2.07 ng/L) of the samples. For PFBA, it was found in all tap water/ground water samples (3.33-27.9 ng/L) and the Cooum River water (0.526 ng/L).

Among the river water samples, the Cooum River in Chennai was the most contaminated, whereas the lowest PFC concentrations were found in Goa. In general, PFOS concentrations of river water samples from India were lower than those reported for other countries (Fig 2). PFOA concentrations in river water samples from Goa and Coimbatore were lower than in other countries, but concentrations in the Cooum River in Chennai were comparable or lower than in other countries (Fig 2). Concentrations of other PFCAs such as PFDA and PFNA, in Indian river water samples (PFDA: <0.083-0.306 ng/L; PFNA: <0.083 -0.192) were much lower than those of the US (PFDA: 16.7-92 ng/L; PFNA: 57.2-146 ng/L), and lower than in other countries such as China (PFDA: <0.13-1.37 ng/L; PFNA: <0.13-3.7 ng/L), Japan (PFDA: 0.18-3.00 ng/L; PFNA: 2.25-26.7 ng/L), Korea (PFDA: 0.73-1.98 ng/L;

PFNA: 1.32-3.26 ng/L) and Germany (PFDA: 0.537 ng/L; PFNA: 1.13 ng/L). Nevertheless, PFHpA concentrations in waters from the Coum River, Chennai (2.52 ng/L), were comparable to those reported for other countries (0.25-72.1 ng/L).

Fig 2. A global comparison on PFOS/PFOA concentrations in riverwater



Data of China[13]- JJ: Jiujiang, LJ:Longjiang, LS: Lanshi, YC: Yuancun, XT: Xintang; DG: Dongguan; CQ: Chongqing; YG: YG, NJ: Nanjing; SH: Shanghai; Korea[14]– IS: Inland stream, LS: Lake Shihwa; Japan (Taniyasu et al. Unpublished data) – LB: Lake Biwa, IR: Ibi River, KR: Kitami River, InR: Ina River, TR: Tsurumi River[17]; Germany[18]– ER: Elbe River; U.S[19]– HR: Haw River, CFR: Cape Fear River.

For tap water, most studies reported only PFOA and PFOS concentrations, and our results for the samples from Chennai showed PFOS (3.13-8.29 ng/L) and PFOA (0.386-2.04 ng/L), which were comparable to those reported for European countries[20] (PFOS: 0.550-8.10 ng/L; PFOA: 0.30-2.4 ng/L), Thailand[21] (PFOS: 0.130-1.90 ng/L; PFOA:1.2-4.6 ng/L), Japan[22] (PFOS: 0.260-17.8 ng/L; PFOA: 0.12-40 ng/L).

The three sampling locations in India could be characterized by different degrees of developments. For example, Goa is a highly populated urban area, but the major industries are agriculture and fisheries. Coimbatore and its vicinity have higher elevations (over 2000 m from sea level) with agriculture and textile and dyeing industries. Chennai is also a highly populated, urbanized area with different types of industries such as automobile, technology, hardware manufacturing, and healthcare. In the present study, two wastewater samples from Goa and Coimbatore were analyzed and the results showed that only PFHpA could be detected at 0.763 and 2.36 ng/L respectively. This suggests that domestic or household waste is not a major source of PFC contamination in these locations. However, tap water from these three locations contained relatively high concentrations of PFBA (40-100%), although PFOS and PFOA concentrations were low (0.386-2.04 ng/L). The source of PFBA might be from water storage facilities or the use of water pipelines made up of fluoropolymers. Further studies are needed to clarify this point.

There were no general patterns of PFC composition among the water samples analyzed, and this might be due to the low concentrations and different sources of trace levels of contamination. Different types of PFCs have been used in different industries from chip-making to metal treatment, from food packing to fire-fighting. The uses of PFCs are likely to differ from country to country depending on the manufacturing processes that occur in each nation or region. Ratios of PFOS/PFASs and PFOA/PFCAs in river water were calculated (Table 3). PFOS and PFOA were chosen for this calculation because they have been often detected and reported in water samples. Ratios of PFOA/PFCAs and PFOS/PFASs differed among countries. PFOS/PFASs ratios ranged from 0.69 to 1 in India, Japan, and Germany, whereas only 1 in China, and 0.86 to 0.91 in the USA. For the ratios of PFOA/PFCAs, a large variability was observed. However, there were still some patterns that could be observed. For example, PFOA was still a major PFCA or less proportion of other –PFCAs were found in Asian countries except for Japan. Besides, except for China, other countries appear to use other perfluorosulfonyl-based compounds. Further studies are needed to confirm these observations from the pilot study.

Table 3. Ratios of PFOA/PFCAs and PFOS/PFASs in riverwater from different countries

		PFOA/PFCAs	PFOS/PFSAs
India	GZD	N/A	N/A
	GZU	N/A	N/A
	GMD	0.53	N/A
	GMU	0.50	N/A
	CmU	0.69	N/A
	CmM	0.62	N/A
	CmK	1.00	N/A
	CmL	1.00	1.00
	ChR	0.94	0.83
China	JJ	0.77	1.00
	LJ	0.87	1.00
	LS	0.59	1.00
	YC	0.63	1.00
	XT	0.63	1.00
	DG	0.83	1.00
	CQ	0.99	1.00
	YG	0.92	1.00
	NJ	0.81	1.00
	SH	0.92	1.00
Korea	IS	0.71	0.89
	LS	0.68	0.91
Japan	LB	0.50	0.91
	IR	0.49	0.95
	KR	0.24	1.00
	InR	0.44	0.69
	TR	0.32	1.00
Germany	ER	0.67	0.93
US	HR	0.40	0.86
	CFR	0.47	0.91

PFCA: C4-C10; PFASs: C4-C8

The results of our global open ocean survey showed that the Indian Ocean is less polluted with PFCs relative to other oceans[1]. The low concentrations of PFCs in samples from India might suggest the reason

for low levels of PFCs in the Indian Ocean.

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