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A survey of perfluorinated compounds in surface water and biota including dolphins from the Ganges River and in other waterbodies in India

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ABSTRACT

Despite the reports of the occurrence of perfluorochemicals (PFCs) in industrialized nations, information on PFCs in less industrialized countries is meager. In the present study, concentrations and profiles of PFCs were investigated in surface waters (rivers, lakes, coastal seas and untreated sewage; $n = 42$) including the Ganges River water, and biota such as shrimp ($n = 2$), fish ($n = 28$), and Ganges River dolphin (*Platanista gangetica*; $n = 15$). PFOS was the dominant PFC found in most of the samples analyzed including water samples except untreated sewage (water: <0.04–3.91 ng L^{-1}; biota: 0.248–27.9 ng g^{-1} ww). Long-chain (C11–C18) perfluorocarboxylates (PFCAs) were not detected in the water samples (<0.2 ng L^{-1}), although PFDA (0.061–0.923 ng g^{-1} ww) and PFUnDA (0.072–0.998 ng g^{-1} ww) were found in biological samples The arithmetic mean PFOS concentration found in the liver of Ganges River dolphin was 27.9 ng g^{-1} ww. Bioconcentration and biomagnifications factors of PFCs were estimated in the Ganges River basin food web. The highest concentration of PFOA, 23.1 ng L^{-1}, was found in untreated sewage samples. Overall, concentrations of PFCs of water and biological samples from India are lower than the concentrations reported for other countries so far. PFC profiles in Indian waters are dominated by PFOS, followed by PFOA, which is different from the pattern reported for other countries such as Korea, Japan and USA, where PFOA was the predominant compound in waters. The flux estimates for PFOS, PFOA and PFNA from the Ganges River in India to the Bay of Bengal were in the range of several hundreds of kilograms per year.

1. Introduction

Perfluorinated compounds (PFCs) have received worldwide attention in recent years. Several of the PFCs have been used as surfactants, surface protectors and in aqueous film-forming foams (AFFF) for the past five decades. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two typical perfluorochemicals representing this group of chemicals, and they are frequently found in different environmental matrices from open ocean water to foodstuffs (Gulkowska et al., 2006; Yamashita et al., 2008). PFCs have also been found in human blood at ng mL^{-1} levels (Kannan et al., 2004; Yeung et al., 2006). PFOS has been proposed as a candidate persistent organic pollutant (POP) for regulation under the Stockholm Convention (http://chm.pops.int/Convention/POPsReviewCommittee/Meetings/POPRC3/tabid/278/mctl/ViewDetails/EventModID/871/EventID/6/xmid/884/language/en-US/Default.aspx). Further regulations on PFOS and related compounds have been implemented in the EU (Directive 76/769), Canada (http://canadagazette.gc.ca/partII/2008/20080611/html/sor178-e.html), USA (the New Jersey, the Department of Environmental Protection), and Japan (under the Rule of Regulation and Manufacture of Chemical Substances).

Surface water and wastewater collected from several countries have been shown to contain PFCs. PFOS concentrations in surface water ranged from tens to hundreds of ng L^{-1} concentration (Rostkowski et al., 2006; Guruge et al., 2007; Nakayama et al., 2007; So et al., 2007; Murakami et al., 2008; Loos et al., 2009); while for those wastewater, PFOS could reach up to thousands of ng L^{-1} concentrations (Bossi et al., 2005; Murakami et al., 2008).

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India is an agricultural country that is undergoing rapid industrialization and economic development in recent years. However, no baseline information is available on the current status of environmental contamination by PFCs. A recent study indicated that concentrations of PFOS in blood samples from India were the lowest among the ten countries studied (Kannan et al., 2004). The Ganges River is one of the largest rivers in the world, which supports the lives of millions of people in the Indian subcontinent in various ways, including irrigation, drinking, and fishing. The Ganges originates from the melting snow and glacial ice of the Himalayas (the Gangotri glacier at Gomukh – 4100 m altitude). The Yamuna River is one of the major tributaries to the Ganges River. The Yamuna River originates from the Yamunotri glacier in the Himalayas and runs for over 1300 km parallel to the Ganges before joining the Ganges River at Allahabad. The Ganges River passes through Kolkatta and discharges into the Bay of Bengal. The Ganges is polluted with pesticides, manure, and sewage discharge (Öry et al., 1996; Sankararamakrishnan et al., 2005; Hamner et al., 2006). Pollution due to the discharge of industrial wastes has been of concern (Öry et al., 1996). Information regarding PFC contamination in the Ganges River is not available.

One of the top predators in the Ganges River ecosystem is the endemic Ganges River Dolphin (*Platanista gangetica*) (IUCN, 2006). The population of Ganges dolphins is declining in recent

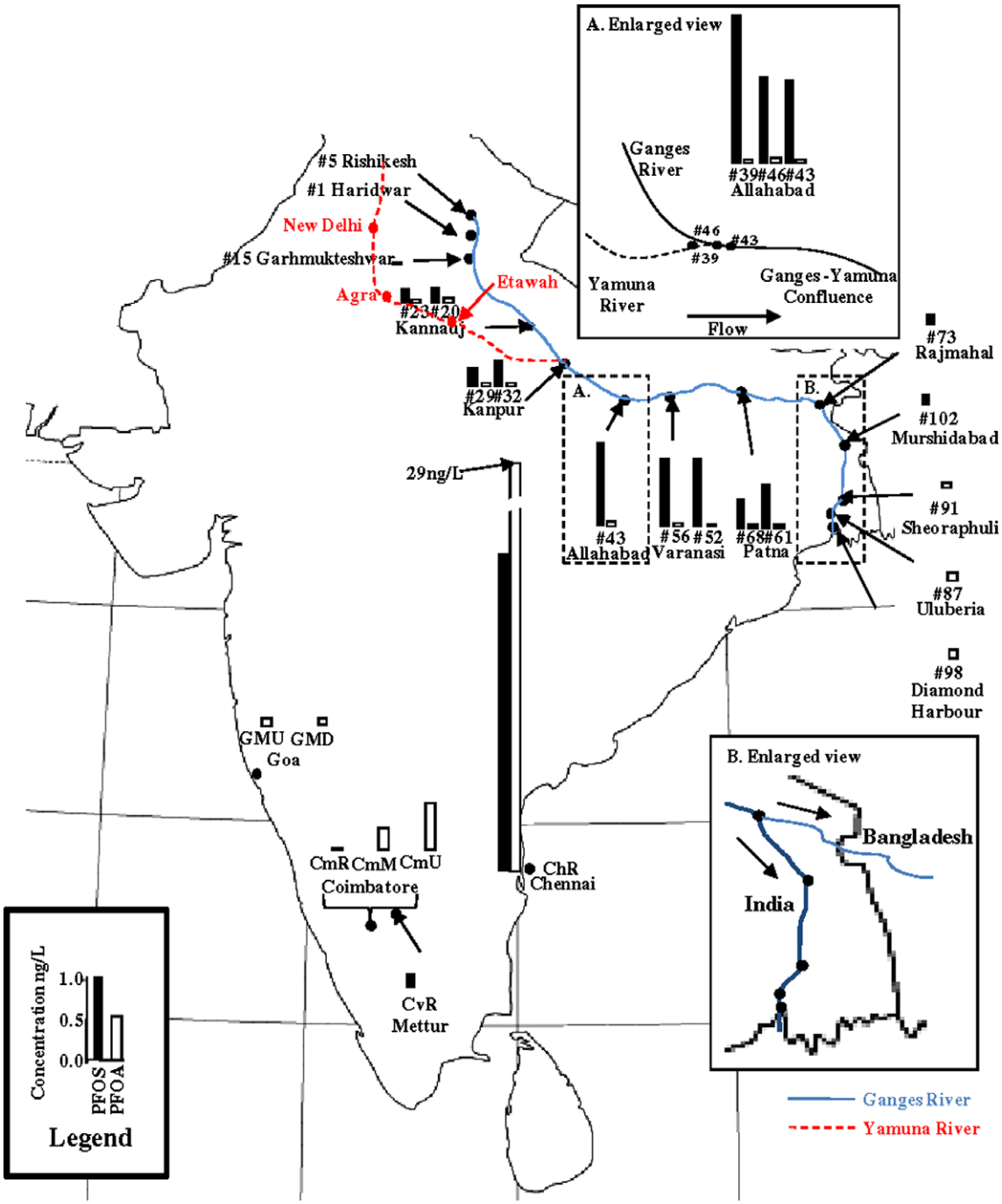


Fig. 1. Distribution of PFOS and PFOA in river water samples (ng L^{-1}) from India. No bar is shown for values below the LOQ (i.e. CvR: 0.06 ng L^{-1}, Goa and Coimbatore: <0.08 ng L^{-1}, Ganges River: <0.04 ng L^{-1}).

years and the current population is estimated to be 1200–1800 individuals (IUCN, 2006). The dolphin has been listed as a most endangered species in India. Elevated concentrations of some traditional POPs such as PCBs, DDTs, and TBT were observed in the Ganges River Dolphin from India (Kannan et al., 1993, 1997). Investigation of PFCs in Ganges River Dolphin would provide information of the status of contamination and potential risks posed due to PFCs.

The objectives of the present study were: first, to determine PFC concentrations in different environmental samples (i.e. surface water, shrimp, fish, and dolphins) to establish baseline information of PFCs in the Indian environment; second, to estimate fluxes of PFCs into the Bay of Bengal (from the Ganges River discharges); and finally, to determine the biomagnification and bioconcentration of PFCs in the freshwater ecosystem of Ganges dolphins.

2. Material and methods

2.1. Sample collection

Water samples ($n = 42$) were collected from January to August, 2008 in Southern India and in 13 locations along the Ganges River in Northern India (Fig. 1). The water samples from Northern India were collected during April–May, 2008, prior to the monsoon season (Supporting Information Table S1). Water samples were collected and stored in 500 mL polypropylene (PP) bottles. All samples were stored at 4 °C before extraction.

Shrimp ($n = 2$p, representing 2 composite samples of which each composite sample consisted of 30 individuals) and fish samples ($n = 28$) that originated from the Ganges River near Patna, were purchased in local fish markets in Patna in August 2008. Dolphins were found entangled in fishing nets or stranded (from 1993 to 2007); livers were taken from archived dolphin samples at Patna University, India (Supporting Information Table S1). Livers of dolphins and fish and wholebody homogenates of shrimp were analyzed.

2.2. Chemicals and reagents

The target analytes included perfluoroalkylsulfonates (C2, 3, 4, 6, 8, 10), perfluorocarboxylates (C3–C18), perfluorooctanesulfonamide, *N*-ethyl perfluorooctane sulfonamide, *N*-ethyl perfluorooctane sulfonamidoacetate (Supporting Information and Table S2). Details of the chemicals and reagents used in the present study are given in Supporting Information. Unfiltered water samples were extracted using solid phase extraction (SPE) using WAX cartridges as described elsewhere (Taniyasu et al., 2005, 2008; ISO25101, 2009). Biological samples were extracted using the ion-pairing method and the extract was purified by SPE prior to instrumental analysis, as described elsewhere (Hansen et al., 2001; Taniyasu et al., 2005). Further details of the analysis are given in Supporting Information.

2.3. Instrumental analysis

Separation of the target analytes was performed using 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 an ion exchange column, RSpak JJ-50 2D (2.0 mm i.d. × 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 (Taniyasu et al., 2008). PFC concentrations were further confirmed by injecting the extracts onto a Keystone Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm, 100 Å pore size, endcapped) with 2 mM ammonium acetate and methanol as the mobile phase for the quantification of C6–C12 PFCs, and the coefficient of variation was less <10% (Taniyasu et al., 2005). The desolvation gas flow and temperature were kept at 610 L h^{-1} and 450 °C, respectively. The collision energies, cone voltages and MS/MS parameters for the instrument were optimized for individual analytes, and were similar to those reported elsewhere (Taniyasu et al., 2005, 2008).

2.4. Quality assurance and quality control

The quality assurance and control measures including field blank and travel blank, the limit of quantification (LOQ), calibration curve, procedural blank, procedural and matrix spike recoveries are given in Supporting Information. The procedural and matrix spike recoveries of PFCs ranged from 68% to 119% and 44–123%, respectively for water analysis (Supporting Information Table S2). For biotic sample analysis, the procedural recoveries for all native compounds ranged from 70% to 103%, while matrix spike recoveries for native compounds ranged from 62% to 99%, and 13C-labeled compounds ranged from 70% to 98% (Supporting Information Table 2b). PFC concentrations in samples were not corrected for the recoveries.

2.5. Statistical analyses

One-way ANOVA was used to assess significant differences in the mean PFC concentrations among the dolphin samples and Pearson correlation statistics were used to evaluate any significant correlations among PFCs, if the data were normally distributed. Otherwise, non-parametric analyses including Kruskal–Wallis H tests and Spearman rank correlation analyses were applied. The significance level was set at $\alpha = 0.05$.

3. Results and discussion

This is the first comprehensive study of PFC pollution in the Ganges River and includes results from various environmental compartments (water, shrimp, fish, and dolphin). In addition, surface waters from other regions in India have also been analyzed. PFC concentrations measured in 42 water samples from rivers, lakes, coastal seas, and untreated sewage, whole body homogenates of shrimp ($n = 2$), and liver samples of 12 species of fish ($n = 28$) and Ganges River Dolphin ($n = 15$) are shown in Supporting Information (Tables S3).

Among the 20 PFCs analyzed, only 12 compounds were detected in the water samples. Perfluoroalkylsulfonates other than PFOS (i.e., PFDS, PFBS, and PFPrS) were not detected in the samples (LOQs ranged from 0.04 to 0.20 ng L^{-1}). The greatest PFOS concentrations were found in water samples from the Cooum River (ChR: 3.91 ng L^{-1}) and in untreated sewage (ChW: 12.0 ng L^{-1}), both from Chennai (Fig. 1, Supporting Information Table S2). As for the biological samples, only PFOS was detected (0.151–83.9 ng g^{-1} ww) in almost all of the samples. Only one fish sample (i.e. *Catla catla*) contained trace levels of PFBS (0.093 ng g^{-1} ww); PFOSA was found in three Ganges River Dolphins (<0.5–5.73 ng g^{-1} ww) (Supporting Information Table S3b).

None of the long-chain (C11–C18) perfluorocarboxylates (PFCAs) were detected in water samples (LOQs ranged from 0.04 to 0.2 ng L^{-1}). PFOA was found in 55% of the water samples; PFDA, PFNA, PFPeA and PFHxA were found in 10%, 40%, 38%, and 43%, respectively, of the water samples analyzed (Supporting Information Table S3a). As for the biological samples, none of the C4–C7 perfluorocarboxylates was found (<0.025 ng g^{-1} ww for fish and

shrimp and <0.25 ng g^{-1} ww for Ganges dolphins). Nevertheless, PFUnDA, PFDA, PFNA, and PFOA were found in 75%, 92%, 33%, 75%, respectively, of the fish samples analyzed. In Ganges River Dolphins, PFUnDA, PFDA, and PFNA were found in 80%, 87%, and 53% of the samples analyzed (Supporting Information Table S3b). Neither PFOA (C8) nor PFDoDA (C12) was found in shrimp (<0.025 ng g^{-1} ww) and dolphin (<0.25 ng g^{-1} ww) samples. No fluorotelomer carboxylates could be detected in the samples. Only PFOSA, the precursor compound of PFOS, was detected in the dolphin. PFC concentrations increased from lower trophic level (i.e. shrimp) to higher trophic level organisms (i.e. from shrimp, fish to dolphins) (Supporting Information Fig. 1 and Supporting Information Table S3b). The PFC composition profiles among the shrimp (whole body homogenate), fish and dolphin (liver), investigated were similar to each other that PFOS was the dominant compound, followed by either PFUnDA or PFDA (Supporting Information Fig. 2).

In general, PFOS concentrations of river water samples from India were lower than the concentrations reported for other countries (Nakayama et al., 2007; Murakami et al., 2008) (Fig. 2). In India, the highest concentrations of PFOS and PFOA were found in the Cooum River in Chennai (PFOS: 3.91 ng L^{-1}; PFOA: 23.1 ng L^{-1}), whereas the lowest concentrations were found in waters from Goa (PFOS/PFOA: <0.083–<1 ng L^{-1}). PFCAs such as PFDA and PFNA in the Indian river water samples were found at sub ng L^{-1} levels, which are one to two orders of magnitude lower than the levels reported in other countries such as the USA, Sri Lanka, China, Japan, and Korea (Rostkowski et al., 2006; Guruge et al., 2007; Nakayama et al., 2007; So et al., 2007; Murakami et al., 2008).

Water samples collected from 13 locations along a 2200-km distance of the Ganges River showed (Fig. 3) not detectable PFOS (<0.04 ng L^{-1}) in samples collected at the river's origin at Rishikesh, where the water originates from the glaciers and groundwater recharge in the Himalayas. PFC levels gradually increased downstream; the degree of contamination was relatively low until its confluence with the Yamuna River in Allahabad. PFOS concentrations increased considerably after confluence with the Yamuna River, indicating the presence of contamination sources in the Yamuna River. PFOS concentrations declined gradually due to dilution, as the water mass increased downstream of Varanasi, Patna, and Rajmahal. After Rajmahal, the waters of the Ganges River branched into several tributaries at Farakka Barrage, with the major flow as the Gorai River in Bangladesh, and as the Bhagirathi River, which flows into the Hooghly River in India. The sampling location, Murshidabad, was on the Bhagirathi River and three more samples were collected at Sheoraphuli, Uluberia and Diamond Harbor of the Hooghly River.

PFC levels and profiles in the Ganges River provided some important insights. First, a major source of PFOS could be identified as the Yamuna River confluence at Allahabad. The Yamuna River is one of the largest tributaries of the Ganges River (Dalai et al., 2002), and is one of the most polluted river in the world, especially around New Delhi, where approximately 57% of the city's wastes are discharged into the river. There are approximately 45 major industries, including coal-based thermal power plants, fertilizer, food processing, textiles, insecticide manufacturing, and electroplating located along the river (Karn and Harada, 2001). Since the Yamuna River discharges about one and half times the volume of water of the Ganges River at Allahabad (Rao, 1975), it

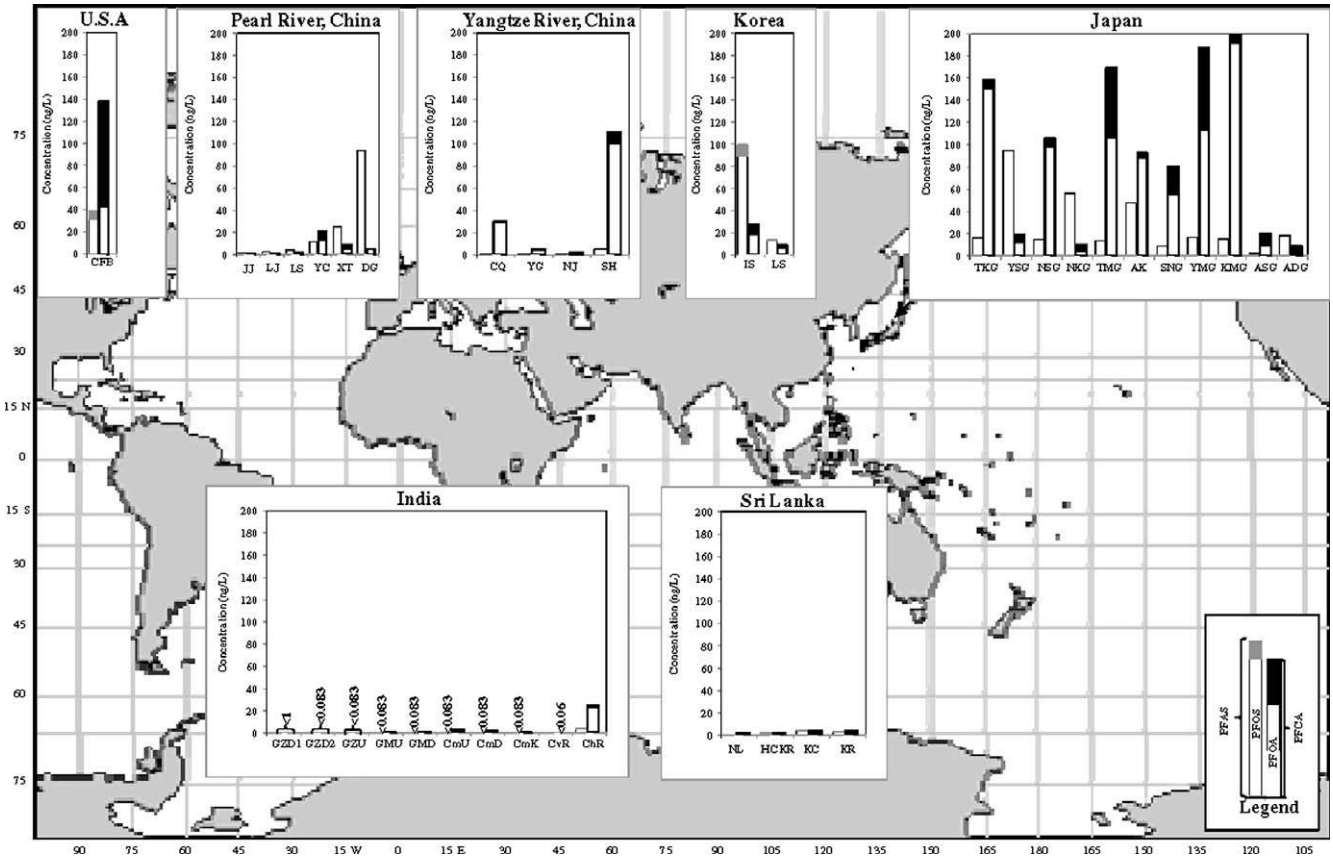


Fig. 2. Global comparison of PFOS (PFAS) and PFOA (PFCA) concentrations (ng L^{-1}) in river waters. Data sources: *India were present study*; USA from reference Nakayama et al. (2007); China from reference So et al. (2007); Korea from reference Rostkowski et al. (2006); Japan from reference Murakami et al. (2008); Sri Lanka from reference Guruge et al. (2007).

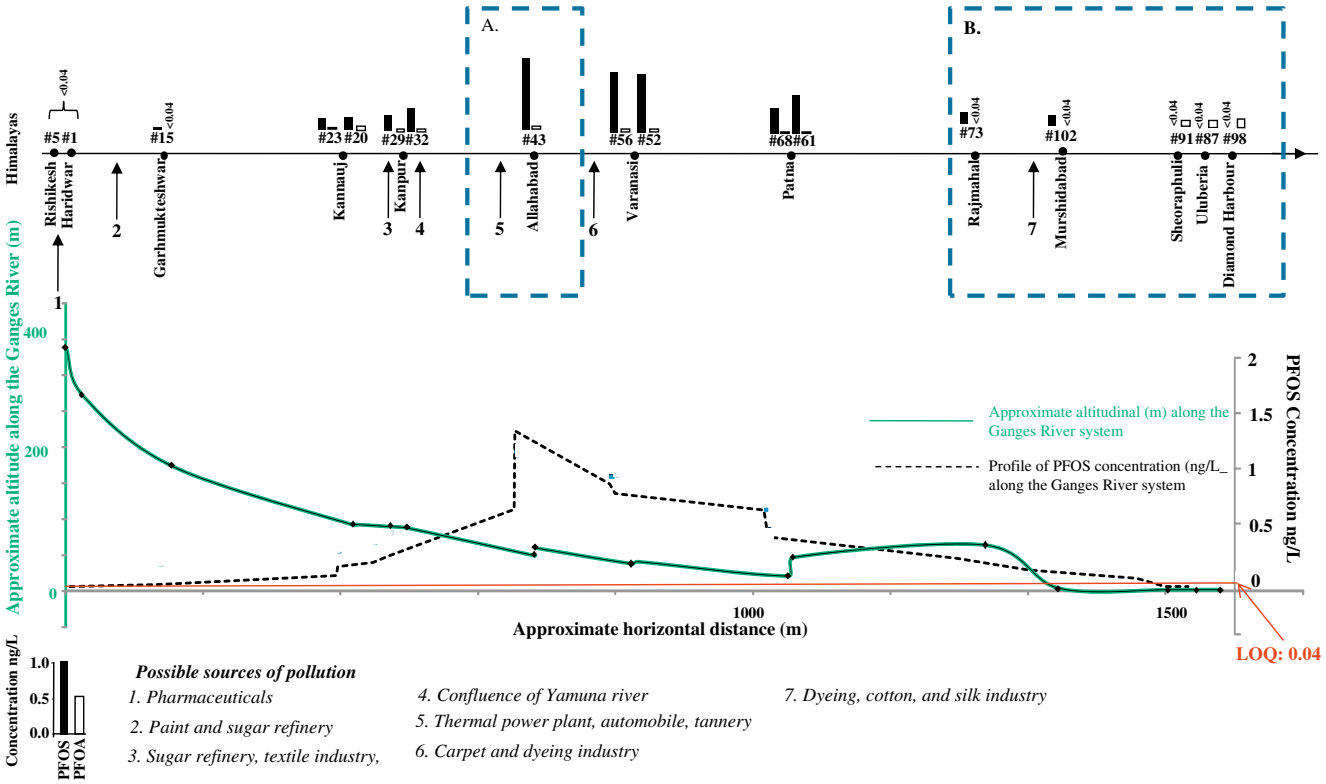


Fig. 3. PFOS/PFOA concentrations in water (ng L^{-1}), altitude (m) and possible industrial sources along the Ganges River system in India.

is conceivable that the Yamuna River is the major source of PFOS in water samples collected after the confluence. Secondly, perfluorocarboxylate levels are low throughout the Ganges River system. PFHxA and PFPeA were found in the entire stretch from Rishikesh to Murshidabad, and the composition of these two compounds was relatively uniform (Supporting Information Fig. 3a) suggesting the existence of low but diffuse sources of these two compounds; further studies are needed to identify the sources of these two short-chain PFCAs (Supporting Information Fig. 3b). Thirdly, PFOA and PFNA were detected throughout the Ganges River after Kannauj (site #23) and before the branching of the river at Rajmahal (site #73), and a significant correlation (Pearson $R^2 = 0.57$, $p < 0.01$, $n = 9$, Supporting Information Fig. 4) was found between these two chemicals, suggesting that they originate from similar sources and a potential source of contamination is near Kannauj.

Wastewater has been demonstrated to be a major source of PFC contamination in the rivers (Sinclair and Kannan, 2006). In India, there is no integrated sewage collection system for the treatment of industrial, municipal, domestic and hospital wastes, and in most cases, the untreated sewage waters drain directly into rivers. Of the nine untreated sewage/wastewater analyzed, those from Chennai contained PFOA and PFOS at levels greater than those found in the Cooum River, which receives discharges from sewage (Supporting Information Table S3a). However, PFOS and PFOA were either below the corresponding LOQs (<0.083 ng L^{-1}) or occurred at trace levels in other wastewater samples. Although some industries are located along the Ganges River from Rishikesh to Diamond Harbour (Fig. 3), PFOS concentrations were elevated only at Allahabad, and no other PFCs were detected. Further studies are needed to evaluate the sources of PFCs in India, with an emphasis on the industries located along the Yamuna River.

PFC concentrations in the Ganges River were lower than the concentrations found in water samples from Southern India. However, comparisons based solely on concentrations may be misleading because of the dilution effects from the large water mass of the Ganges River. For comparison of PFCs in the Ganges River with other rivers in the world, average annual fluxes were estimated based on the volume of water discharged and the concentrations of PFCs measured (Table 1). Total water discharges for these rivers were obtained from the nearest monitoring stations to the PFC measurements. The discharge data used for flux calculations for the Ganges and Yamuna Rivers were from the UNESCO and other publications (Rao, 1975; UNESCO, 1971) and the seasonal variation in the discharges was considered. It should be noted that the PFC flux estimated for the Ganges River at Farakka represents only a small portion of the discharges of the Ganges River to the Bay of Bengal, because discharges of the Ganges from Bangladesh were not taken into account. The total global historical PFC emissions (direct + indirect) were estimated to be 3200–7300 tonnes from 1960 to 2004 (see reference Prevedouros et al. (2006) for details). The percentage of emission based on the flux calculated at Patna (#68) was 0.01–0.03% of the total global historical emission. Based on the annual flux estimates, it was evident that the large rivers such as the Ganges in India and the Yangtze in China contained relatively low PFOS/PFOA/PFNA concentrations, but, due to the high water discharge rates, these rivers contribute significant PFC fluxes to the oceans. Although the PFC concentrations in the Ganges River were in the low ng L^{-1} range, the flux from the Ganges is comparable to those of rivers with great PFC concentrations. An important point that should be noted is that the sources and the mass of the Ganges River water are greatly influenced by the annual monsoon. During the pre-monsoon season (March–June), the water is sustained by groundwater seepage, whereas during the monsoon season (July–September), the major source of water in the river is precipitation. As a result, the greatest flow of the Ganges is from September (25%), and much lower flow rates occur during April (1.5%) and May (2%) (Tomy et al., 2004; Gulkowska et al., 2006).

Table 1
Comparison of PFC flux estimates (kg yr^{-1}) in selected rivers from several countries.

Name	Discharge (m^3 s^{-1})	PFOS		PFOA		PFNA		Source for discharge data
		Concentration (ng L^{-1})	Flux (kg yr^{-1})	Concentration (ng L^{-1})	Flux (kg yr^{-1})	Concentration (ng L^{-1})	Flux (kg yr^{-1})	
Ganges River, India	12400	0.363	142	0.0616	24.1	0.0589	23.0	UNESCO (1971)
Yamuna River, India	2950	1.81	168	0.0947	8.81	0.0673	6.26	Sarin et al. (1989)
Yangtze River, China	47000	0.36	534	2.55	3780	0.160	237	Chen et al. (2001)
Cape Fear River, North Carolina, USA	27	56.3	47.9	6.84	5.82	31.2	26.6	http://www.nwis.waterdata.usgs.gov/nc/nwis/uv?02105769 (accessed on 15 Oct 2008)
Tamagawa, Kanto, Japan	13.4	143	60.4	107	45.2	53.0	22.4	Murakami et al. (2008)
Yoneshirogawa, Tohoku, Japan	94.8	6.9	20.6	13	38.9	2.30	6.88	Murakami et al. (2008)
Kelani River, Sri Lanka	16.2	2.7	1.38	1.7	0.869	0.300	0.153	http://www.adb.org/Documents/Environment/sri-kelanitissa.pdf (accessed on 15 October 2008)
Europe	–	–	–	–	14300	–	260	Mclachlan et al. (2007)

PFC data for the Ganges River was from sampling location #68; for the Yamuna River, sampling location #39 (present study); for the Cape Fear River, station 10 (Nakayama et al., 2007); for the Yangzte River, Nanjing station (So et al., 2007); for the Tamagawa River, station 3 and Yoneshirogawa, Japan (Murakami et al., 2008); for the Kelani River, station H4 (Guruge et al., 2007); for the data of Europe were from 14 rivers from several European countries (Mclachlan et al., 2007). "–", not given in the literature. References for the discharge data are given in Supporting Information.

Studies focused on sampling before and after the monsoon are needed to evaluate the influence of seasonal flooding on the loading and fluxes of PFCs in the Ganges River. The Indian population (around 1.1 billion – second largest) only contributed to less than 0.03% of the total global PFC emission implying that the degree of PFC pollution was not related to the size of the population but to the manufacture and the use of PFCs.

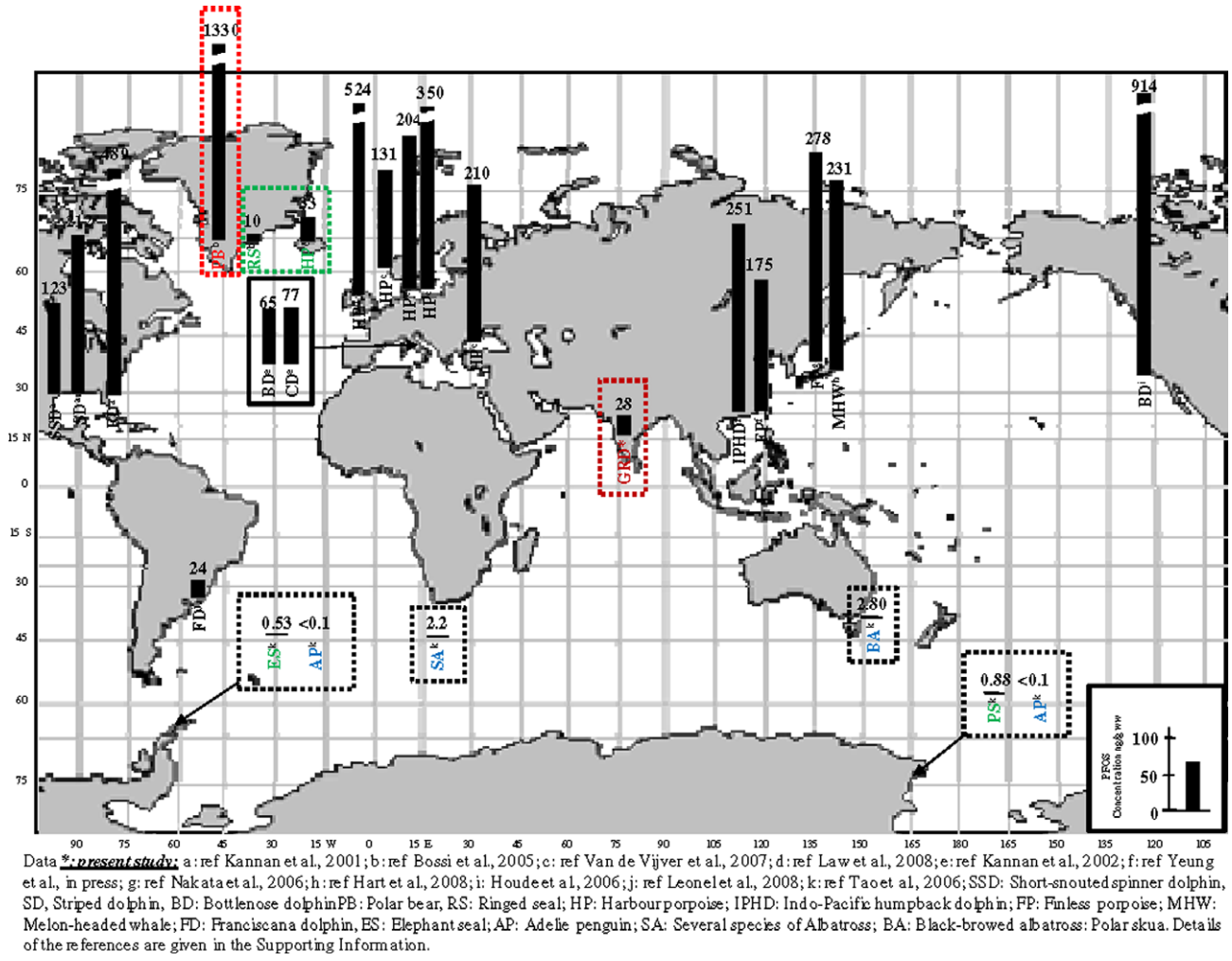
Biological samples collected in the Ganges River contained lower concentrations of PFCs than those reported in other studies elsewhere. PFOS concentrations found in shrimp from Patna were similar to those reported for the eastern Arctic (Tomy et al., 2004), but at least 2 to 56-fold lower than the concentrations reported from China (Gulkowska et al., 2006), and at least 76–2000 times lower than the concentrations reported from the North Sea (De Vijver et al., 2003). PFUnDA concentrations in Ganges River shrimp were lower than the concentrations reported for shrimp from China (Gulkowska et al., 2006). PFOS was the dominant PFC found in fish livers from the Ganges River. Neither PFUnDA nor PFDA showed significant difference among the 12 species of fish ($p > 0.05$, Kruskal–Wallis H test, $n = 12$), except that PFOA concentrations in *C. mrigala* (mean: 1.35 ng g^{-1} ww) and *T. tilapia* (mean: 1.18 ng g^{-1} ww) were at least 5-times higher than in other fish species. PFOS was the only PFAS detected in the Ganges River fish, whereas PFOSA, PFBS, and PFHxS were reported to occur in fish from other studies (Falandysz et al., 2006; Dorneles et al., 2008). PFOS concentrations in the Ganges River fish were similar to those reported for Greenland fish (occur at sub ng g^{-1} to low ng g^{-1} levels), but two to three orders of magnitude lower than those from Poland (Falandysz et al., 2006), USA (Kannan et al., 2005), and Belgium (Hoff et al., 2005). The concentrations of PFCAs (i.e. PFUnDA, PFDA, PFNA, and PFOA) in the Ganges River fish were lower than those reported for fish from the Canadian Arctic (Tomy et al., 2004).

PFOS was the predominant PFC found in dolphin liver samples, and was present at levels 20 times higher than those of PFUnDA and PFDA. No correlations were found between the size (i.e. length and weight) of the dolphins and PFOS/PFDA/PFUnDA concentrations ($R^2 < 0.05$, $n = 12$, $p > 0.05$), which was similar to those reported for melon-headed whales (*Peponocephala electra*) in Japan (Hart et al., 2008) and Tucuxi dolphins (*Sotalia fluviatilis*) from Brazil (Leonel et al., 2008). The PFOS concentrations measured in the Ganges River Dolphins were similar to or slightly higher than those in Sub-Antartic fur seals from Brazil (Bossi et al., 2005) and in ringed seals (*Pusa hispida*) and harbor porpoises (*Phocoena phocoena*) from the Arctic region (Bossi et al., 2005) (Fig. 4). In Ganges dolphins, only PFOS, PFUnDA, PFDA were found, while other PFCs such as PFOSA, PFDoDA, PFNA, and PFOA were found in cetaceans such as finless porpoises (*Neophocaena phocoenoides*) and Indo-Pacific humpback dolphins (*Sousa chinensis*) (Yeung et al., 2009) and harbor porpoises from China (Van de Vijver et al., 2007).

No significant correlations were observed between PFOS/PFDA, PFOS/PFUnDA, and PFDA/PFUnDA ($p > 0.05$, n = 7) in fishes; however, significant correlations were found between PFUnDA/PFOS (Pearson correlation coefficient = 0.718, $p < 0.001$, $n = 12$), PFDA/PFOS (Pearson correlation coefficient = 0.937, $p < 0.001$, $n = 12$), and PFDA/PFUnDA (Pearson correlation coefficient = 0.885, $p < 0.001$, $n = 12$) in dolphins. The contrasting correlations between fish and dolphin suggested that the sources of these PFCs to fish and dolphin might be different. However, species differences might also account for this variation. Further investigation should clarify this point.

Biomagnification factors (BMF) and bioconcentration factors (BCF) of PFCs were estimated for the Ganges River Dolphins, based on the concentrations in water from the Ganges River (Patna), shrimp, fish livers and Ganges River Dolphins (Martin et al., 2004; Tomy et al., 2004; Kannan et al., 2005) (Fig. 5). The estimated BCF of PFOS in shrimp was similar to those reported for invertebrates (i.e. benthic algae and zebra mussels), in a previous study (Kannan et al., 2005). The BCF of PFOA could not be determined for shrimp (Martin et al., 2003) because this compound was not detected (<0.25 ng g^{-1} ww); The estimated BCF of PFOS in fish livers was similar to those reported for rainbow trout (5400 ± 860) exposed under laboratory conditions (Martin et al., 2003). The estimated BMFs of PFOS from fishes to Ganges River Dolphin were similar to the BMFs reported for narwhals (*Monodon monoceros*) and beluga whales (*Delphinapterus leucas*) in an eastern Arctic food web (4.0–8.4) (Tomy et al., 2004), and in bottlenose dolphin food web from coastal Florida (1.5–35), USA (Houde et al., 2006). The estimated BMFs of PFUnDA and PFDA were similar to those reported for bottlenose dolphins from the US coast (PFUnDA: 0.9–3.9; PFDA: 0.9–3.9) (Houde et al., 2006).

Overall, the PFC pollution in India is relatively low when compared with other countries such as China and the USA. The residue levels of several PFCs in Indian waters and biota are similar to or even lower than those reported for water and biota from remote marine locations. The patterns of PFCs are unique in Indian waters



Data *: present study; a: ref Kannan et al., 2001; b: ref Bossi et al., 2005; c: ref Van de Vijver et al., 2007; d: ref Law et al., 2008; e: ref Kannan et al., 2002; f: ref Yeung et al., in press; g: ref Nakata et al., 2006; h: ref Hart et al., 2008; i: Houde et al., 2006; j: ref Leonel et al., 2008; k: ref Tao et al., 2006; SSD: Short-snouted spinner dolphin, SD, Striped dolphin, BD: Bottlenose dolphin PB: Polar bear, RS: Ringed seal; HP: Harbour porpoise; IPHD: Indo-Pacific humpback dolphin; FP: Finless porpoise; MHW: Melon-headed whale; FD: Franciscana dolphin, ES: Elephant seal; AP: Adelie penguin; SA: Several species of Albatross; BA: Black-browed albatross; Polar skua. Details of the references are given in the Supporting Information.

Fig. 4. Global comparison of PFOS concentrations in liver samples from different species (marine mammals and seabirds).

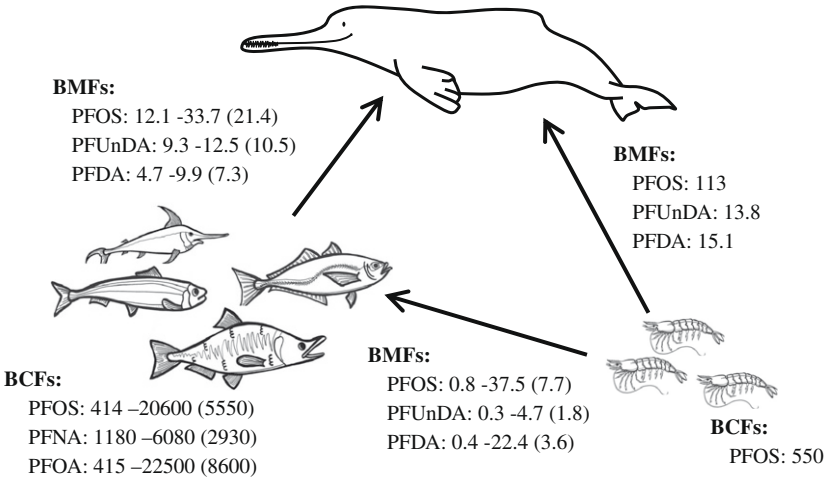


Fig. 5. Schematic diagram of bioconcentration/biomagnification factors of perfluorochemicals in the Ganges River dolphin foodweb (arithmetic mean values are given in parentheses).

with a predominant contribution from PFOS rather than PFOA. PFOS concentrations are higher than those of PFOA in most of the sampling stations. To our knowledge, information regarding fluoropolymer manufacturing in India is not available. The findings presented here could serve as baseline information for future trend monitoring studies in India. Long-term monitoring of PFCs in the Ganges River would enable understanding of fluxes of PFCs into the Bay of Bengal.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.02.055.

References

Bossi, R., Riget, F.F., Dietz, R., Sonne, C., Fauser, P., Dam, M., Vorkamp, K., 2005. Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands. Environ. Pollut. 136, 323–329.

Chen, Z.Y., Li, J.F., Shen, H.T., Wang, Z.H., 2001. Yangtze River of China: historical analysis of discharge variability and sediment flux. Geomorphology 41, 77–91.

Dalai, T.K., Krishnaswami, S., Sarin, M.M., 2002. Major ion chemistry in the headwaters of the Yamuna river system: chemical weathering, its temperature dependence and CO_2 consumption in the Himalaya. Geochim. Cosmochim. Acta 66, 3397–3416.

De Vijver, K.I.V., Hoff, P.T., Van Dongen, W., Esmans, E.L., Blust, R., De Coen, W.M., 2003. Exposure patterns of perfluorooctane sulfonate in aquatic invertebrates from the Western Scheldt estuary and the southern North Sea. Environ. Toxicol. Chem. 22, 2037–2041.

Dorneles, P.R., Lailson-Brito, J., Azevedo, A.F., Meyer, J., Vidal, L.G., Fragoso, A.B., Torres, J.P., Malm, O., Blust, R., Das, K., 2008. High accumulation of perfluorooctane sulfonate (PFOS) in marine tucuxi dolphins (*Sotalia guianensis*) from the Brazilian coast. Environ. Sci. Technol. 42, 5368–5373.

Falandysz, J., Taniyasu, S., Gulkowska, A., Yamashita, N., Schulte-Oehlmann, U., 2006. Is fish a major source of fluorinated surfactants and repellents in humans living on the Baltic coast? Environ. Sci. Technol. 40, 748–751.

Gulkowska, A., Jiang, Q.T., So, M.K., Taniyasu, S., Lam, P.K.S., Yamashita, N., 2006. Persistent perfluorinated acids in seafood collected from two cities of China. Environ. Sci. Technol. 40, 3736–3741.

Guruge, K.S., Taniyasu, S., Yamashita, N., Manage, P.M., 2007. Occurrence of perfluorinated acids and fluorotelomers in waters from Sri Lanka. Mar. Pollut. Bull. 54, 1667–1672.

Hamner, S., Tripathi, A., Mishra, R.K., Bouskill, N., Broadaway, S.C., Pyle, B.H., Ford, T.E., 2006. The role of water use patterns and sewage pollution in incidence of water-borne/enteric diseases along the Ganges River in Varanasi, India. Int. J. Environ. Heal. Res. 16, 113–132.

Hansen, K.J., Clemen, L.A., Ellefson, M.E., Johnson, H.O., 2001. Compound-specific, quantitative characterization of organic: fluorochemicals in biological matrices. Environ. Sci. Technol. 35, 766–770.

Hart, K., Kannan, K., Isobe, T., Takahashi, S., Yamada, T.K., Miyazaki, N., Tanabe, S., 2008. Time trends and transplacental transfer of perfluorinated compounds in melon-headed whales stranded along the Japanese coast in 1982, 2001/2002, and 2006. Environ. Sci. Technol. 42, 7132–7137.

Hoff, P.T., Van Campenhout, K., de Vijver, K., Covaci, A., Bervoets, L., Moens, L., Huyskens, G., Goemans, G., Belpaire, C., Blust, R., De Coen, W., 2005. Perfluorooctane sulfonic acid and organohalogen pollutants in liver of three freshwater fish species in Flanders (Belgium): relationships with biochemical and organismal effects. Environ. Pollut. 137, 324–333.

Houde, M., Bujas, T.A.D., Small, J., Wells, R.S., Fair, P.A., Bossart, G.D., Solomon, K.R., Muir, D.C.G., 2006. Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (*Tursiops truncatus*) food web. Environ. Sci. Technol. 40, 4138–4144.

ISO25101, 2009. Water quality – determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) - method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry. In: The International Organization for Standardization, Geneva, Switzerland, p. 24.

IUCN, 2006. IUCN Red List (species search page).

Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K.S., Loganathan, B.G., Mohd, M.A., Olivero, J., Van Wouwe, N., Yang, J.H., Aldous, K.M., 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ. Sci Technol. 38, 4489–4495.

Kannan, K., Senthilkumar, K., Sinha, R.K., 1997. Sources and accumulationof butyltin compounds un Ganges River dolphin, *Platanista gangetica*. Appl. Organomet. Chem. 11, 223–230.

Kannan, K., Sinha, R.K., Tanabe, S., Ichihashi, H., Tatsukawa, R., 1993. Heavy metals and organochlorine residues in Ganges River dolphins from India. Mar. Pollut. Bull. 26, 159–162.

Kannan, K., Tao, L., Sinclair, E., Pastva, S.D., Jude, D.J., Giesy, J.P., 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch. Environ. Contam. Toxicol. 48, 559–566.

Karn, S.K., Harada, H., 2001. Surface water pollution in three urban territories of Nepal, India, and Bangladesh. Environ. Manage. 28, 483–496.

Leonel, J., Kannan, K., Tao, L., Fillmann, G., Montone, R.C., 2008. A baseline study of perfluorochemicals in Franciscana dolphin and subantarctic fur seal from coastal waters of Southern Brazil. Mar. Pollut. Bull. 56, 778–781.

Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. Environ. Pollut. 157, 561–568.

Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). Environ. Toxicol. Chem. 22, 196–204.

Martin, J.W., Whittle, D.M., Muir, D.C.G., Mabury, S.A., 2004. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environ. Sci. Technol. 38, 5379–5385.

Mclachlan, M.S., Holmstrom, K.E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European continent. Environ. Sci. Technol. 41, 7260–7265.

Murakami, M., Imamura, E., Shinohara, H., Kiri, K., Muramatsu, Y., Harada, A., Takada, H., 2008. Occurrence and sources of perfluorinated surfactants in rivers in Japan. Environ. Sci. Technol. 42, 6566–6572.

Nakayama, S., Strynar, M.J., Helfant, L., Egeghy, P., Ye, X.B., Lindstrom, A.B., 2007. Perfluorinated compounds in the Cape Fear Drainage Basin in North Carolina. Environ. Sci. Technol. 41, 5271–5276.

Öry, F., Rahman, F., Shukla, A., Zwaag, R., Burdorf, A., 1996. Industrial counseling: linking occupational and environmental health in tanneries of Kanpur, India. Int. J. Occup. Environ. Heal. 2, 311–318.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32–44.

Rao, K., 1975. India's Water Wealth. Orient Lonman Ltd., New Delhi.

Rostkowski, P., Yamashita, N., So, I.M.K., Taniyasu, S., Lam, P.K.S., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K., Giesy, J.P., 2006. Perfluorinated compounds in streams of the Shihwa industrial zone and Lake Shihwa, South Korea. Environ. Toxicol. Chem. 25, 2374–2380.

Sankararamakrishnan, N., Kumar Sharma, A., Sanghi, R., 2005. Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India. Environ. Int. 31, 113–120.

Sarin, M.M., Krishnaswami, S., Dilli, K., Somayajulu, B.L.K., Moore, W.S., 1989. Major ion chemistry of the Ganga-Brahmaputra river system - weathering processes and fluxes to the Bay of Bengal. Geochimica Et Cosmochimica Acta 53, 997–1009.

Sinclair, E., Kannan, K., 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 40, 1408–1414.

So, M.K., Miyake, Y., Yeung, W.Y., Ho, Y.M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam, P.K.S., 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China. Chemosphere 68, 2085–2095.

Taniyasu, S., Kannan, K., So, M.K., Gulkowska, A., Sinclair, E., Okazawa, T., Yamashita, N., 2005. Analysis of fluorotelomer alcohols, fluorotelorner acids, and short- and long-chain perfluorinated acids in water and biota. J. Chromatogr. A 1093, 89–97.

Taniyasu, S., Kannan, K., Yeung, L.W.Y., Kwok, K.Y., Lam, P.K.S., Yamashita, N., 2008. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5–C18). Anal. Chim. Acta 619, 221–230.

Tomy, G.T., Budakowski, W., Halldorson, T., Helm, P.A., Stern, G.A., Friesen, K., Pepper, K., Tittlemier, S.A., Fisk, A.T., 2004. Fluorinated organic compounds in an eastern Arctic marine food web. Environ. Sci. Technol. 38, 6475–6481.

UNESCO, 1971. Discharge of selected rivers of the world. Monthly and Annual Discharges Recorded at Various Selected Stations, vol II, p. 194.

Van de Vijver, K.I., Holsbeek, L., Das, K., Blust, R., Joiris, C., De Coen, W., 2007. Occurrence of perfluorooctane sulfonate and other perfluorinated alkylated substances in harbor porpoises from the Black Sea. Environ. Sci. Technol. 41, 315–320.

Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.K.S., Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70, 1247–1255.

Yeung, L.W.Y., Miyake, Y., Wang, Y., Taniyasu, S., Yamashita, N., Lam, P.K.S., 2009. Total fluorine, extractable organic fluorine, perfluorooctane sulfonate and other related fluorochemicals in liver samples of Indo-Pacific humpback dolphins (*Sousa chinensis*) and finless porpoises (Neophocaena phocaenoides) from South China. Environ. Pollut. 157, 17–23.

Yeung, L.W.Y., So, M.K., Jiang, G.B., Taniyasu, S., Yamashita, N., Song, M.Y., Wu, Y.N., Li, J.G., Giesy, J.P., Guruge, K.S., Lam, P.K.S., 2006. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. Environ. Sci. Technol. 40, 715–720.