

A NATIONWIDE SURVEY OF PERFLUORINATED COMPOUNDS IN JAPANESE RIVERS

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Introduction

Fluorochemicals such as poly- and per-fluorinated compounds (PFCs) have been widely used because of their special properties. Their partly lipophilic and partly hydrophilic chemical structures make them useful as surfactants in industrial, commercial and consumer products. The characteristics of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including the highly oxidized state of their carbon-fluorine bonds, their ionic nature and fairly low vapor pressure, allow these compounds to be highly mobile and stable in different environmental compartments, including in aquatic systems such as river water¹, lake water², coastal water³ and open-ocean water⁴. However, the environmental fate and sources of these chemicals is unclear, and their global occurrence, persistence and bioaccumulation have prompted widespread interest in the last decade.

Previous studies have examined potential PFC sources in the aquatic environment. Point sources such as effluents from sewage treatment plants receiving industrial discharge in Japan and the United States⁵⁻⁷ or factories⁸, have been investigated. Discharges from non-point sources, like wet or dry deposition and surface run-off, have also been proposed⁹⁻¹¹. In Japan, most of the monitoring data from aquatic environments mainly focused on PFOS and PFOA determinations^{5,12}. Extensive information on PFC composition profiles in Japanese river waters is scarce, and therefore data on levels of PFCs due to different human activities and geographical distribution of PFCs in the Japanese environments are not available. In order to have a better understanding of the extent of PFC contamination in Japan, river water samples from 47 prefectures receiving different sources were collected and analyzed. This study presents an initial report on PFC concentrations. In addition, the use of PFC chemical fingerprinting is discussed for source identification of PFCs in Japanese aquatic ecosystems.

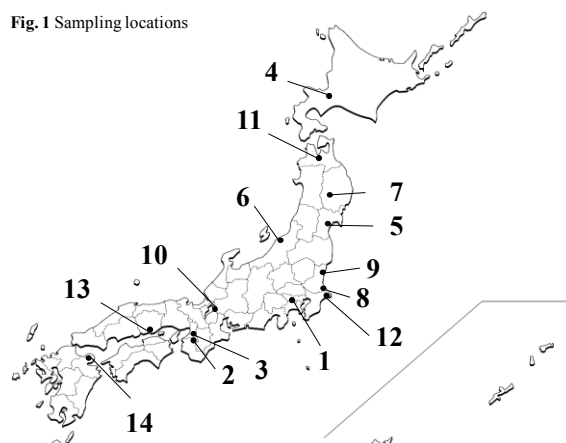
Materials and Methods

River water samples were collected nationally in 2004-2007 from 47 prefectures in Japan; three locations per prefecture were sampled. Five hundred-1000 mL samples of river water were collected and stored in 500 mL or 1000 mL polypropylene (PP) bottles with narrow mouths and screw caps. All samples were stored at -20 °C before extraction. In this initial report, fourteen samples were analyzed selectively from different locations (Fig. 1) and site categorization was proposed (Table 1).

No.	Prefecture	Location	Site description
1	Tokyo	Hachioji-shi	Shopping mall & residential
2	Wakayama	Katsuragi-cho	Clean site
3	Osaka	Izumi-shi	
4	Hokkaido	Sapporo-shi	Wastewater treatment
5	Miyagi	Sendai-shi	
6	Niigata	Niigata-shi	
7	Iwate	Kitakami-shi	Industrial area
8	Ibaraki-1	Kashima-shi	
9	Ibaraki-2	Hitachi-shi	
10	Shiga	Nagahama-shi	
11	Aomori	Aomori-shi	Fish port
12	Chiba	Choshi-shi	
13	Okayama	Kurashiki-shi	Agricultural site
14	Oita	Usa-shi	

All water samples (200 mL) were extracted using Oasis®WAX (6 cc) solid phase extraction (SPE) cartridges (Waters Corp., Milford, USA). The extraction procedure was described in detail elsewhere¹³. PFCs, including perfluorodecanesulfonate (PFDS), PFOS, 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), perfluorononanoic acid (PFNA), PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluorooctane sulfonamide (PFOSA), *N*-ethyl perfluorooctane

Fig. 1 Sampling locations



PFCs		Blank n=3 (ng/L)	Recovery (%) n=3	S.D.
PFDS	C10	<0.25	101	6
PFOS	C8	<0.25	94	9
PFHS	C6	<0.25	97	6
PFBS	C4	<0.25	95	7
PFOSA		<0.01	83	11
<i>N</i> -EtFOSAA		<0.05	98	5
PFOCDA	C18	<0.25	96	5
PFHxDA	C16	<0.25	90	6
PFTeDA	C14	<0.25	95	5
PFDoDA	C12	<0.25	112	8
PFUnDA	C11	<0.25	105	10
PFDA	C10	<0.25	107	7
PFNA	C9	<0.25	112	17
PFOA	C8	<0.25	97	7
PFHpA	C7	<0.25	104	6
PFHxA	C6	<0.25	112	3

sulfonamide (*N*-EtFOSA), and *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 electro-spray negative mode. A 10 µL aliquot of extract was injected onto a Keystone Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 µm, 100 Å pore size, endcapped) with 2 mM ammonium acetate and methanol as the mobile phases for the quantification^{13, 14}.

Procedural blank and recovery tests were carried out with every sample extraction batch. PFCs in all procedural blanks were below their corresponding limits of quantifications (LOQs), and the recovery rates of target PFCs ranged from 83% to 112% (Table 2). Duplicate water samples were analyzed if applicable. Concentrations were not corrected for recoveries.

Results and Discussion

Individual PFCs in water samples. A total of sixteen PFCs were analyzed in the fourteen river water samples. Twelve PFCs, PFBS, PFHxS, PFOS, PFDS, PFOSA, *N*-EtFOSAA, PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUnDA, could be quantified. The concentrations of long-chained perfluorinated carboxylate acid (PFCAs), including PFDoDA, PFTeDA, PFHxDA and PFOcDA, were below their corresponding LOQs (<0.25 ng/L) in all water samples. Among perfluorinated alkyl sulfonates (PFASs), PFOS occurred at the highest concentrations at all locations (0.36-7.09 ng/L) except in Wakayama (<0.25 ng/L) and Chiba where PFBS (113 ng/L) was the dominant PFAS. Among the six PFCAs, PFOA was consistently detected at all locations and occurred at the greatest concentrations [up to 15.2 ng/L in Ibaraki-2 (Hitachi)], but it was not detected in water from Aomori

(<0.25 ng/L). PFNA was the second most prevalent PFCA, reaching levels of up to 7.87 ng/L in water from Ibaraki-2 and 7.81 ng/L in water from Tokyo. In contrast, PFHpA (46.2 ng/L) was predominant in water from Niigata, where it also occurred at the greatest concentration among locations; however, PFHpA was not detected in most of the other samples. In general, PFCAs (sum of PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUnDA) occurred at higher concentrations than PFASs (PFBS, PFHxS, PFOS, PFDS, PFOSA and *N*-EtFOSAA) at all locations, except in Chiba. The greatest PFCA concentration was found in the water samples from Niigata, whereas samples from Chiba contained the greatest levels of PFAS. The greatest total PFC concentration was found in the water samples from Chiba, followed by those from Niigata and Ibaraki-2, and then Tokyo. Water samples from Wakayama contained neither PFASs (<0.25 ng/L) nor PFCAs (<0.25 ng/L), with the exception of a trace level of PFOA (0.333 ng/L).

Comparison of PFOS & PFOA in Japanese rivers with other studies.

A comparison of PFOS and PFOA concentrations in samples from Japan with those from other countries is shown in Figs. 2 & 3 respectively. Generally, the degree of contamination of PFOS and PFOA in the present study is either comparable to or lower than that in China¹ and U.S.⁷, but higher than in India¹⁵, with the exception of the Coom River. PFOS concentrations in the samples from the present study (<0.25-7.09 ng/L) were relatively lower than the peak

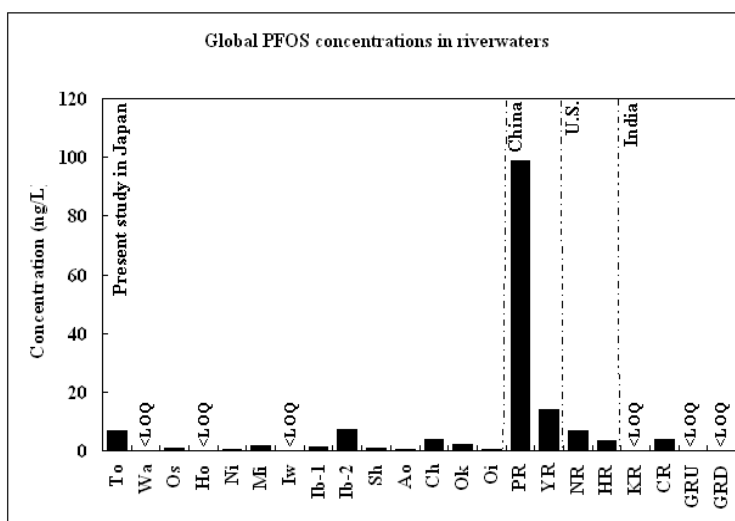


Fig. 2. Global PFOS concentrations in riverwaters. Data from China¹ – PR: Pearl River, YR: Yangtze River; U.S.⁷ – NR: Niagara River, HR: Hudson River; India¹⁵ – KR: Kallar River, CR: Coom River, GRU/D: Goa Zuari River, Upstream/Downstream

concentrations measured in samples from China¹ (Pearl River: 0.90-99 ng/L; Yangtze River: <0.01-14 ng/L), but they were comparable within the range measured for samples from U.S.⁷ (Niagara River: 3.3-6.7 ng/L; Hudson River: 1.5-3.4 ng/L) (Fig. 2), and higher than levels measured in water in India¹⁵ (Goa Zuari River: <0.0833 ng/L; Kallar River: <0.0833 ng/L; Coom River: 3.91 ng/L). The level of PFOA in Japanese waters (<0.25-15.2 ng/L) was much less than levels reported in other countries, such as the Yangtze River (2.0-260 ng/L) in China¹, the Niagara River (18-22 ng/L) and Hudson River (22-173 ng/L) in U.S.⁷, the Coom River (23.1 ng/L) in India¹⁵ and the Po River (200 ng/L) in Italy and Thames River (23 ng/L) in England¹⁶ (Fig. 3). However, the peak concentration of PFOA measured in the present study is comparable to the level in the Danube River (16.4 ng/L) in Bulgaria¹⁶, and is slightly higher than that of water from the Pearl River (0.83-13 ng/L) in China¹ and the Rhine River (11.6 ng/L) in Germany¹⁶.

To conclude, this study is part of a nationwide PFC survey in Japan focused on river water. Our group has also determined PFC concentrations in wild rat blood from Japan¹⁷. These river water samples were collected near the nesting places of the wild rats, and it is hoped that by analyzing PFC concentrations/patterns from the wild rat blood and river water samples, correlation analyses can be performed between these two datasets to assess

whether drinking PFC-contaminated water might be a major source of PFCs in wild rats. The information provided by these studies will provide a greater understanding of potential sources and distribution of PFCs in the Japanese environment.

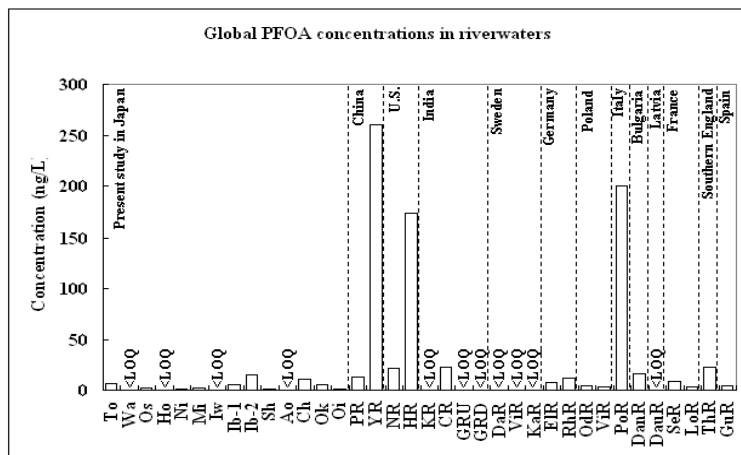


Fig. 3. Global PFOA concentrations in riverwaters. Data from China¹ – PR: Pearl River, YR: Yangtze River; U.S.⁷ – NR: Niagara River, HR: Hudson River; India¹⁵ – KR: Kallar River, CR: Cooun River, GRU/D: Goa Zuari River, Upstream/Downstream; European continent¹⁶ – DaR: Dalälven River, ViR: Vindelälven River, KaR: Kalix Älv River, ElR: Elbe River, OdR: Oder River, ViR: Vistula River, PoR: Po River, DanR: Danube River, DauR: Daugava River, SeR: Seine River, LoR: Loire River, ThR: Thames River, RhR: Rhine River, GuR: Guadalquivir River.

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