

Perfluorinated compounds (PFCs) in Yodo River system, Japan

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ABSTRACT

There is increasing concern about occurrences of perfluorinated compounds (PFCs) in the environment due to their persistent, bioaccumulation, and potentially toxic effects. We investigated contamination of 11 PFCs (C4-C12) in the Yodo River system, which is a major source of drinking water for more than 11 million people of Kansai region in Japan. PFCs were detected in higher concentration even exceeding more than 1000 ng/L in some cases. Composition profile of total PFCs concentration showed that PFOS, PFHxA, PFOA, and PFNA were occurring dominantly in the river system. PFOS and PFOA concentration were nearly proportional to a previous study in the same river system, indicating continuous sink of the compounds into the river system. Although discharge of PFCs from wastewater effluents at upstream could be one of the major point sources, concentration did not exceed 29.4 ng/L at the downstream of main Yodo River, possibly, due to dilution effects. Total mass load of PFCs in mainstream of Yodo River was estimated 451.7 g/d based on observed river discharge and PFCs concentration. Results showed that Yodo River system could have a unique upstream-downstream linkage of PFCs contamination and the river could be a continuous pathway of PFCs exposure to the people of Kansai region.

Key words | downstream, PFHxA, PFNA, PFOA, PFOS, upstream, wastewater effluents

INTRODUCTION

Perfluorinated compounds (PFCs) are manmade fully fluorinated organic compounds that have been used for more than 50 years due to their unique physico-chemical properties such as high chemical and thermal stability, low surface free energy, and water and fat repellent properties. They have multitude of applications such as surface protectors in carpets, leather, paper, packaging, fabrics, and coatings of the non-sticky frying-pan, and as surfactants in aqueous film-forming foams (AFFF), acid mist suppressants, alkaline cleaners, floor polishes, cleaners, photographic films, pesticides, shampoos and cosmetics (Key *et al.* 1997; Kissa 2001; Schultz *et al.* 2003). There are several reports about their occurrences in oceans, lakes, rivers, and biota including humans (Giesy & Kannan 2002; Kannan

et al. 2004; Saito *et al.* 2004; Houde *et al.* 2006). Among PFCs, PFOS and PFOA have got major attention due to their widespread occurrences in the environment and biota. PFOS production has already been phased out by its main manufacturer 3M in 2001, and recent COP4 meeting to the Stockholm convention (2009) has listed PFOS in Annex B of persistent organic pollutants (POPs) list (see details in <http://chm.pops.int/>). PFOA is still under debate for its toxicity, although USEPA has recently started a stewardship program, with cooperation from various manufactures and user industries, for the abatement of PFOA problem by 2015 (USEPA 2006). However, there is still lacking of sufficient studies on range of PFCs which could have similar or more toxic effects than PFOS or PFOA.

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Large scale uses of PFCs will continue in future as well due to lack of appropriate alternatives to replace them. As a result, they will be constantly released into the water environment through different point and non-point sources. Similarly, due to lack of an efficient removal method of these compounds, wastewater treatment plants (WWTPs) and water purification plants (WPPs) could not treat these compounds effectively. Monitoring of PFCs levels in water environment and knowing their sources are quite important to make strategies to control further contamination and to assess the potential health risk. This paper will report about contamination of PFCs in Yodo River system in Kansai region of Japan. There are several reasons for selecting Yodo River system for this study. Firstly, Yodo River system is a major source of water supply to more than 11 million people of Kansai region (mainly downstream of Kyoto, Osaka, and Hyogo region). Secondly, the river system has a unique upstream-downstream link of PFCs contamination, which could be a good example of river basin management issue related with organic micro-pollutants. In the upstream, several WWTPs (treating both domestic and industrial wastewater) discharge treated effluents into the river, while in the downstream, several large scale WPPs utilize Yodo River as a single source of raw water, *i.e.*, the WWTP effluents are partially reused. Especially, the Yodo River basin is a major economic and industrial zone of Japan, which could be discharging PFCs into surface water. Thirdly, PFCs are reported in high concentration in river water (Lien *et al.* 2008; Saito *et al.* 2004), WWTPs effluents (Lien *et al.* 2008), water purification plants and tap water (Takagi *et al.* 2008), and human serum (Harada *et al.* 2007) in this river basin. This study is a continuation of our previous study (Lien *et al.* 2008), which had mainly observed occurrence of two PFCs (PFOS and PFOA) in Yodo River system. This study reported about occurrences of 11 PFCs, including PFOS and PFOA, across the Yodo River system.

MATERIALS AND METHODS

Study area and sampling campaign

Yodo River is the main river flowing in Kansai region of Japan. The river basin has an area of 8,240 km², which also includes Lake Biwa in the upstream (largest lake of Japan) and Ai River sub-basin (which includes Ina River and Kanazaki River) at the downstream. Sampling campaign was conducted on fine weather day of 2008/12/03 across Yodo River system. Totally, 40 samples (River: 30; WWTP effluents: 10) were collected simultaneously by four teams starting from

8:00 A.M. and completed by 16:00 P.M. Samples were collected from mainstream and tributaries of Uji River (U1-U8), Katsura River (K1-K6), Kizu River (R1), Yodo River (Y1-Y9) and Ai River (A1-A6), and also at WWTPs effluents discharge points (W1-W10). The map of Yodo River system and details about sampling points are shown in Figure 1. Upstream (headwaters) of Yodo River consists of three main rivers, namely, Uji River (which originates from Lake Biwa), Katsura River and Kizu River. Especially, Uji River and Katsura River receive effluents from seven major WWTPs (W1-W8) of Kyoto, which have capacity to treat industrial and domestic wastewater ranging from 14,963 to 5,869,50 m³/d and serving population in the range of 35,902–667,100 capita. Sampling points W6 & W7 were effluents of same WWTP but they represented separate units serving populations from different areas. After merging of Uji, Katsura, and Kizu River, the main Yodo River stream flows along populated areas such as Takasuki and Osaka before draining into Osaka Bay. Although Ai River does not drain into Yodo River (*i.e.*, drains into Osaka Bay), samples were collected from it due to its location in the lower reach of Yodo River basin, where number of industrial activities are occurring. Two points in Ai River were WWTP effluent samples, in which W9 represented discharge from industrial activities and W10 represented effluents from domestic and industrial activities.

Grab samples were collected in methanol washed 2L polyethylene terephthalate (PET) bottles for each sampling point. Field blanks were carried to confirm that no contamination occurred during sampling. Before collecting sample, bottle was also washed by sample (2 times). River flow rate (m³/s) was measured from each point whenever it was possible but daily discharges (m³/d) were also acquired from existing monitoring stations and respective WWTPs.

Sample pre-treatment and analysis of PFCs

All chemicals were of analytical reagent grade and used as supplied. Samples were brought back to laboratory and stored at 4°C and filtration was completed within 2 days of sampling. 1L sample was filtered through Whatman GF/B (1 µm pore size) filter and two sets of filtered samples (1L each) for each sampling point were prepared. GF/B filter was also kept for the analysis of PFCs in suspended solids (particulate phase, Pr.). Solid phase extraction (SPE) was used to extract PFCs in liquid samples (Liq.) by using two reverse phase cartridges in series, namely, Oasis HLB plus (from Waters) and PreSep-C (Agri-short) (from Wako Chemicals). At first, cartridges were pre-conditioned with 10 mL methanol followed by 20 mL ultra-pure water (Milli-Q Advantage A10 system) in 1 and 2 min for

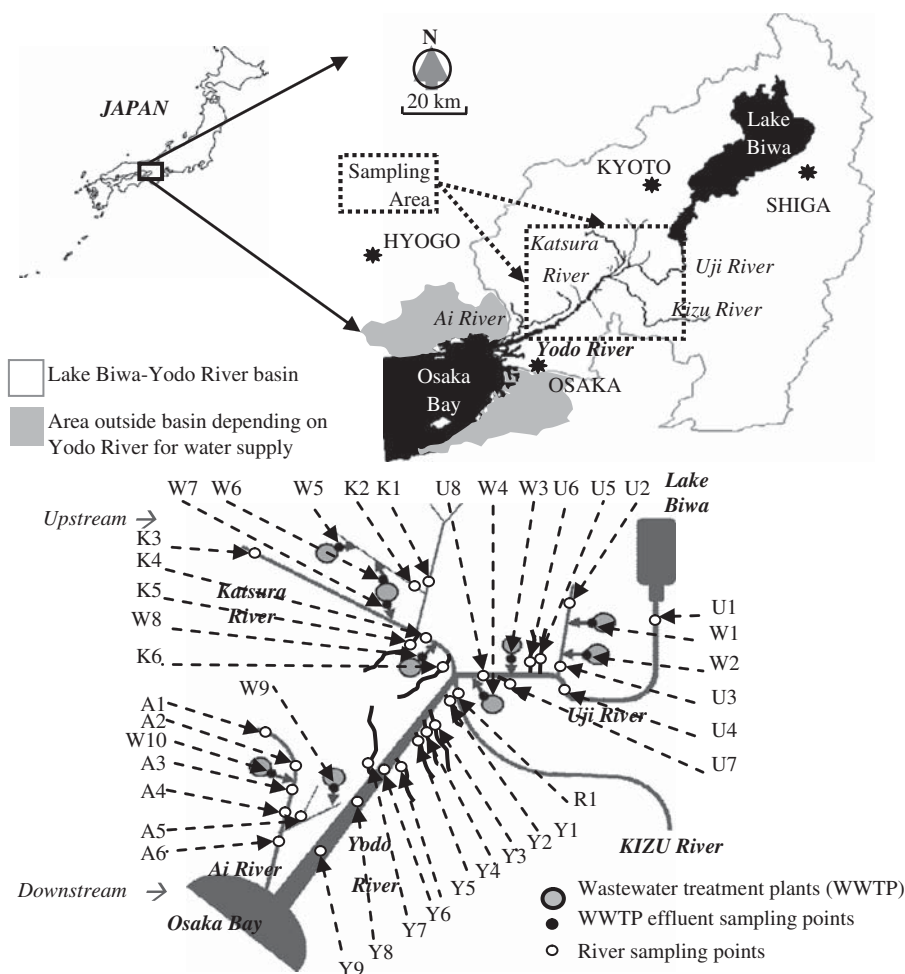


Figure 1 | Map of Yodo River basin and details of sampling points.

each, respectively. Then, "Liq." sample was passed through two reverse phase cartridges (Oasis HLB plus → PreSepC) at the rate of 5 mL/min. PFCs in solid sample in GF/B filter was extracted by using accelerated solvent extraction (ASE 200 from Dionex Co). The GF/B filter containing solid sample was inserted into an ASE cell (volume: 33 mL) and fitted with ASE 200 for extraction. Each sample was subjected to 3 static cycles using total 60 mL extraction solvent (methanol). Each static cycle maintained a sample in methanol at 100°C temperature and 2000 psi pressure for 10 min. The extracted solvent was dried to less than 10 mL in a water bath (60°C) and remaining methanol was mixed to 1 L by ultrapure water. Finally, each 1 L mixed sample was passed through two cartridges in series (Oasis HLB plus → PreSepC) as explained earlier. Loaded cartridges were dried in vacuum, then adsorbed PFCs in cartridges were eluted with 4 mL LCMS grade methanol, then extracted methanol was dried with pure nitrogen gas, and finally the dried sample was reconstituted by 1 mL 40% LCMS grade acetonitrile solvent for further analysis.

Sample analysis

The reconstituted samples were directly analyzed by using LC/MS/MS. In HPLC, Agilent 1200 module (Agilent) binary pump was used to control the flow and pressure. Then, 10 µL sample was injected into a 2.1 × 100 mm (5 µm) Agilent Eclipse XDB-C18 column at 40°C. Mobile phase (LCMS grade) consisted of 5 mM ammonium acetate in ultrapure water (A) and 100% acetonitrile (B). Linear gradient mode of A and B proportions was used during the separation of PFCs in HPLC at the flow rate of 0.25 mL/min. For quantitative determination, HPLC was interfaced with Agilent 6400 Triple Quadrupole MS/MS. The MS/MS was operated with the multimode ionization (MMI) in negative mode. In MMI, the vaporizer temperature was set at 150°C for efficient ionization of analyte ions in electrospray ionization (ESI) unit. Analyte ions *m/z* (parent and daughter) were monitored by multiple reaction monitoring (MRM).

Method validation, quantification, and measurement accuracy

Altogether 11 PFCs (C4-C12) were analyzed which included eight (C5-C12) perfluorocarboxylic acids (PFCAs) and three (C4-C8) perfluoroalkane sulfonates (PFASs). Details of PFCs, analytical parameters of LC/MS/MS, limit of detection (LOD), and limit of quantification (LOQ) are shown in Table 1. All samples were analyzed in duplicate, one of which was spiked with 10 ng/L of PFCs to calculate overall recovery of the whole process. For “Liq” samples, PFCs standards (from Wellington Laboratories, Canada) were spiked after filtration, while for “Pr.” phase samples they were added just before extraction by ASE. In order to confirm consistent signal of analyte by LC-MS/MS, 2 µg/L of four mass labeled internal standards (MPFOS, MPFHxA, MPFOA, and MPFDA) (from Wellington Laboratories, Canada) were added to each reconstituted sample just before injection into HPLC. For the quantification, eight known concentrations of standards (0.01, 0.05, 0.1, 0.5, 1, 2.5, 5, and 10 µg/L) were prepared which produced good linearity ($R^2 > 0.995$) for all PFCs. LOD for LC/MS/MS was defined as

concentration with “signal-to-noise ratio (S/N)” equal to 3 in 40% acetonitrile (LC/MS grade), but LOQ, defined as $S/N \geq 10$, was used for practical quantification. For LOD and LOQ, their coefficient of variation ($n = 5$) was also observed less than 20% of theoretical values. Samples below LOD were considered ‘not detected (ND)’.

Analysis of field blanks and procedure blanks (40% LCMS grade methanol) found that all PFCs were below LOD, which confirmed that there was no significant contamination during sampling, preprocessing and analysis. The recoveries were calculated on the basis of detected spiked concentration for both “Liq.” and “Pr.” phase samples. Mean recovery ($n = 40$) of PFBuS, PFHxS and PFOS were in the range of 88–107%, while min-max range was slightly larger (51–132%). While for PFCAs (C5-C11) the mean recovery were in the range of 64–101%, while min-max range was 45–132%. Especially, mean recovery of PFPeA was slightly lower (<76%), while recovery of PFDoDA was ignored due to all ND cases. In addition, it was observed that the coefficient of variation (CV%) of the response of internal standards of all samples were 22% for MPFHxA, 12% for MPFOA and MPFDA, and 9% for MPFOS. It indicated that there was

Table 1 | Analyzed PFCs and their parameters, LOD and LOQ

Compound	No. of carbon	Common name	Parent ion (m/z)	Daughter ion (m/z)	LOD ² (ng/L)	LOQ ² (ng/L)
PFBuS	C4-S ^{*1}	Perfluorobutane sulfonate	299	80	0.01	0.03
PFHxS	C6-S	Perfluorohexane sulfonate	399	80	0.01	0.03
PFOS	C8-S	Perfluorooctane sulfonate	499	80	0.01	0.04
PEPA	C5-A	Perfluoropentanoic acid	263	219	0.02	0.05
PFHxA	C6-A	Perfluorohexanoic acid	313	269	0.01	0.02
PFHpA	C7-A	Perfluoroheptanoic acid	363	319	0.01	0.03
PFOA	C8-A	Perfluorooctanoic acid	413	369	0.01	0.03
PFNA	C9-A	Perfluorononanoic acid	463	419	0.01	0.02
PFDA	C10-A	Perfluorodecanoic acid	513	469	0.01	0.04
PFUnDA	C11-A	Perfluoroundecanoic acid	563	519	0.07	0.22
PFDoDA	C12-A	Perfluorododecanoic acid	613	569	0.07	0.22
¹⁵ C ₄ -PFOS	C8-S	Mass label (M) PFOS	5.3	80	0.01	0.04
¹⁵ C ₂ -PFHxA	C6-A	Mass label (M) PFHxA	315	271	0.01	0.04
¹⁵ C ₄ -PFOA	C8-A	Mass label (M) PFOA	417	373	0.01	0.03
¹⁵ C ₂ -PFDA	C10-A	Mass label (M) PFDA	515	471	0.01	0.03

*1S = Perfluoroalkane sulfonates (PFASs); A = Perfluorocarboxylic acids (PFCAs).

*2LOD: Limit of detection (S/N = 3); LOQ: Limit of quantification (S/N ≥ 10).

no significant ion-suppression or ion-enhancement during analysis by LC/MS/MS.

RESULTS AND DISCUSSION

Occurrences of PFCs

Table 2 summarizes the concentration (ng/L) profile of PFCs in all sampling points for both “Liq.” and “Pr.” phase samples. PFCs were detected in all samples; however, PFDoDA was ND in all analyzed samples. Other PFCs with majority of ND or <LOQ were PFUnDA and PFDA. In addition, majority of “Pr.” phase samples, except PFHpA, PFOA and PFNA, were found ND or <LOQ. Among detected cases, concentrations of PFCs in “Liq.” phase samples were higher in majority of samples (except 8 cases), up to 253 times higher. It could mean that PFCs might remain dissolved in river water rather than adsorbed in suspended solids. The highest concentration of PFCs was detected mainly in effluents of WWTPs, including W3 in Uji River sub-basin, W5 in Katsura River sub-basin, and W10 in Ai River sub-basin. W10 showed the highest concentration of PFCs among all samples, while W9 was second highest among WWTPs. As effluent at W9 was mainly originated through industrial activities, their discharges could be crucial for PFCs contamination in environment. Comparing higher PFCs concentration of WWTP effluents in Katsura River sub basin and Ai River sub-basin, and lower concentration in Uji River sub-basin, it could be stated that additional point sources of PFCs could exist at higher PFCs concentration cases, in addition to domestic activities.

In Kizu River (R1), the detected concentration was nearly two times lesser than at Uji River outlet (U8). In Uji River, the concentrations of PFCs were similar at upstream (U1,4) and downstream (U8). That could be due to lesser contribution from WWTP effluents. Contribution from Lake Biwa (U1) could be one of the major sources of PFCs in Uji River. In Katsura River there was a big difference of concentration between upstream (K3) and downstream (K4), where the concentration at K4 increased by nearly 21 times. It was quite apparent that the contribution of WWTP effluents (W5,6,7) caused elevation of concentration at K4. In case of Yodo River, the contribution from tributaries (Y1-5,7) ranged from 21.8 to 194.9 ng/L for “Liq” phase, although final concentration in the main stream (Y6,8,9) was only in the range of 27.2–29.4 ng/L. Similar concentration of PFCs along main stream (Y6,8,9) could indicate that there could be either limited discharges of PFCs through point sources at

mid/lower reach or increased flux in main Yodo River could have dilution effect on PFCs concentration. Especially, after Y6 point, there are at least six large scale WPPs having capacity to treat in the range of 180,000–916,000 m³/d, which are solely extracted from Yodo River. Especially, dilution of PFCs in the mainstream could be considered crucial for relatively lower concentration of PFCs in raw water of WPP. However, considering reported detection cases of PFCs in tap water (Takagi *et al.* 2008) and human serum (Harada *et al.* 2007) in this area, the risk of PFCs exposure through Yodo River could not be ignored.

Figure 2 shows the composition profile (%) of PFCs in all sampling sites. Majority of analyzed PFCs (PFBuS, PFHxS, PFPeA, PFHpA, PFDA, PFUnDA, and PFDoDA) accounted for less than 23% of total PFCs concentration (Liq. + Pr.). While, other analyzed PFCs (PFOS, PFHxA, PFOA, and PFNA) were contributing more than 30% of total PFCs concentration across Yodo River system. PFOS was detected in higher proportion (>15%) in more than 9 cases, which have concentration range of 4.5–219.5 ng/L mainly from Katsura sub-basin and some other sites of Yodo River (Y2,3&6) and Uji sub-basin (W3). PFOA was the most dominant PFC in Yodo River system. Except few cases (W6, A4 & A6), the proportion of PFOA was in the range of 20.6–94%, while the concentration range was 4.2–1098.3 ng/L. Higher concentration of PFOA was also reported in previous study in the same river system (Lien *et al.* 2008). Figure 3 shows the comparison of concentration of PFOS and PFOA between previous surveys (2005/03/16 and 2005/11/01) and this study (2008/12/03) for river and WWTP effluent samples. It could be observed that both concentration profiles of PFOS and PFOA were within comparable ranges for both river water samples and WWTP effluents in all surveys dates. The consistency in the detection of similar levels PFOS and PFOA could indicate continuous discharge of these two PFCs into the Yodo River system. Detection of PFHxA and PFNA in higher concentration indicated that there could be possibility of wide use of different kinds of PFCs other than PFOS and PFOA. PFHxA was mainly detected in higher concentration in Ai River sub basin, where the major source of PFHxA seemed to be WWTP effluent (W10) (1610.4 ng/L) because the values were very small (<7 ng/L) at headwater sites (A1,2). PFNA was detected in higher proportion (>15%) in 26 cases, while in some its contribution was even more than 50% of total PFCs concentration. Important aspect is that, PFNA in surface water has been already reported in other parts of Japan, while they are not detected consistently at higher concentration in other parts of the world (Murakami *et al.* 2008).

Table 2 | Summary of concentration (ng/L) profile of analyzed PFCs in all sampling points

River	Type + ID	PFBS (C4-S)		PFHS (C6-S)		PFOS (C8-S)		PFPeA (C5-A)		PFHxA (C6-A)		PFHpA (C7-A)		PFOA (C8-A)		PFNA (C9-A)		PFDA (C10-A)		PFUnDA (C11-A)		PFDoDA Total (C12-A)		PFCs	
		Liq [†]	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr	Liq	Pr		
Kizu	Main R1	1.3	ND [§]	0.2	ND	1.1	ND	0.6	0.1	0.5	ND	1.5	<LOQ	10.9	0.7	6.8	0.2	0.1	<LOQ	0.4	<LOQ	0.4	ND	23.4	1.0
Uji	Main U1	0.4	ND	0.6	ND	1.0	ND	0.2	ND	0.4	ND	1.3	ND	4.8	0.3	35	0.1	ND	ND	ND	ND	ND	ND	12.2	0.3
Uji	Tributary U2	0.4	ND	1.2	ND	2.4	ND	0.2	ND	15	ND	2.3	ND	10.9	0.2	6.1	ND	0.1	ND	<LOQ	ND	ND	ND	25.2	0.2
Uji	Tributary U3	0.6	ND	1.4	ND	33	0.4	0.5	ND	0.8	ND	0.9	0.1	12.9	1.5	9.7	0.7	1.4	0.4	0.4	0.2	ND	ND	31.9	33
Uji	Main U4	0.4	ND	0.7	ND	1.0	ND	0.2	ND	0.4	ND	1.3	ND	6.3	0.3	4.8	2.2	ND	ND	ND	ND	ND	ND	15.1	0.4
Uji	Tributary U5	0.1	ND	0.4	ND	0.8	ND	ND	<LOQ [§]	0.4	ND	1.4	0.3	6.3	0.8	2.2	0.1	ND	ND	ND	ND	ND	ND	11.7	1.2
Uji	Tributary U6	0.1	ND	0.4	ND	0.7	ND	0.2	ND	0.4	ND	1.1	1.1	5.2	0.2	1.8	ND	ND	ND	ND	ND	ND	ND	9.9	1.3
Uji	Tributary U7	0.6	ND	0.6	ND	1.6	ND	<LOQ	ND	0.4	ND	0.6	ND	13.0	0.4	2.7	ND	0.4	<LOQ	1.0	ND	ND	ND	21.2	0.4
Uji	Main U8	0.3	ND	0.6	ND	0.7	ND	0.2	ND	0.4	ND	1.1	1.1	5.2	0.2	1.8	ND	ND	ND	ND	ND	ND	ND	12.8	0.1
Uji	WWTP W1	1.0	ND	1.3	ND	2.7	0.5	0.4	<LOQ	0.4	ND	1.1	<LOQ	10.7	0.9	7.3	0.3	1.1	0.1	<LOQ	ND	ND	ND	28.8	4.3
Uji	WWTP W2	0.4	ND	1.5	ND	1.9	ND	<LOQ	ND	0.3	ND	0.6	0.0	1.04	0.7	7.3	0.3	1.1	0.1	<LOQ	ND	ND	ND	23.7	1.0
Uji	WWTP W3	1.5	ND	7.0	ND	18.1	1.4	0.2	ND	3.0	ND	2.1	ND	18.8	0.6	10.5	0.5	2.6	0.1	1.6	<LOQ	ND	ND	65.3	2.7
Uji	WWTP W4	23	ND	0.5	ND	2.7	ND	0.1	ND	0.1	ND	0.9	ND	6.4	0.7	13.9	0.9	1.9	0.1	1.7	03	ND	ND	30.3	2.1
Katsura	Tributary K1	0.1	ND	0.8	ND	0.8	ND	<LOQ	ND	0.6	ND	1.1	0.1	4.9	1.4	3.5	0.2	ND	0.1	ND	ND	ND	ND	11.7	1.8
Katsura	Tributary K2	1.4	ND	6.1	ND	104.3	8.9	0.1	<LOQ	1.0	ND	2.3	0.1	58.5	0.8	44.6	1.5	7.1	1.3	17.5	3.0	ND	ND	242.8	15.7
Katsura	Main K3	ND	ND	ND	ND	0.3	ND	0.4	<LOQ	0.1	ND	0.3	ND	2.7	1.4	1.5	0.4	ND	ND	<LOQ	ND	ND	ND	5.3	1.8
katsura	Main K4	0.8	ND	2.4	ND	26.6	0.6	ND	0.1	1.1	ND	2.5	0.0	50.0	0.7	15.5	0.4	7.2	0.3	5.7	0.4	ND	ND	111.7	2.5
Katsura	Tributary K5	4.9	ND	1.8	ND	4.5	ND	<LOQ	ND	0.7	ND	0.9	0.2	4.5	0.7	3.6	0.1	<LOQ	ND	<LOQ	ND	ND	ND	20.9	1.0
Katsura	Tributary K6	0.6	ND	0.8	ND	1.7	ND	0.1	ND	0.5	ND	1.6	ND	9.3	0.5	30.2	1.3	<LOQ	ND	0.9	ND	ND	ND	45.5	1.8

Katsura	WWTP	W5	3.4	ND	5.8	ND	192.0	27.7	0.3	0.1	2.6	ND	7.7	0.3	237.7	10.5	149.8	9.4	16.9	4.6	55.7	14.3	ND	ND	669.9	66.8
Katsura	WWTP	W6	1.9	ND	4.6	ND	54.2	1.2	0.5	<LOQ	0.7	ND	1.2	0.0	11.0	0.7	21.2	0.2	3.9	0.2	4.5	1.5	ND	ND	103.5	3.8
Katsura	WWTP	W7	1.7	ND	4.6	ND	23.4	2.4	0.2	<LOQ	0.4	ND	2.5	ND	51.4	1.2	24.5	1.2	6.0	1.7	6.8	4.4	ND	ND	121.5	10.8
Katsura	WWTP	W8	3.8	ND	1.0	ND	3.5	0.3	<LOQ	ND	0.4	ND	0.8	0.1	42.7	2.6	71.2	1.6	0.5	0.1	1.6	0.6	ND	ND	125.5	5.3
Yodo	Tributary	Y1	0.1	ND	1.7	ND	2.3	ND	0.8	0.1	1.5	ND	1.5	0.2	45.0	0.6	5.6	0.2	0.2	0.1	0.2	ND	ND	ND	58.9	1.2
Yodo	Tributary	Y2	0.9	ND	18.4	ND	46.8	11.1	0.5	0.1	2.8	ND	2.6	0.6	60.1	1.1	11.4	1.2	0.3	0.3	0.3	<LOQ	ND	ND	144.1	14.5
Yodo	Tributary	Y3	3.1	ND	13.8	ND	55.1	17.2	0.3	0.1	2.4	ND	4.1	0.8	106.1	2.4	90.2	1.1	0.5	0.3	<LOQ	0.4	ND	ND	194.9	22.2
Yodo	Tributary	Y4	0.1	ND	2.9	ND	3.7	1.0	0.4	0.1	1.4	ND	2.0	0.5	113.7	1.7	5.3	0.4	0.5	0.3	<LOQ	ND	ND	ND	130.0	4.0
Yodo	Tributary	Y5	1.6	ND	2.4	ND	2.1	0.8	0.6	ND	2.2	ND	5.0	0.1	106.9	2.2	7.3	0.7	0.6	0.2	0.3	ND	ND	ND	128.8	3.9
Yodo	Tributary	Y6	0.5	ND	2.2	ND	3.8	5.9	0.3	<LOQ	0.8	ND	2.1	0.2	12.3	0.7	6.0	0.5	0.9	0.3	0.2	<LOQ	ND	ND	29.2	7.6
Yodo	Tributary	Y7	0.1	ND	0.1	ND	0.6	0.1	0.1	ND	0.5	ND	0.8	0.2	7.5	0.8	11.8	0.4	ND	ND	<LOQ	ND	ND	ND	21.8	1.4
Yodo	Main	Y8	1.3	ND	2.1	ND	3.3	1.2	0.1	0.2	0.4	<LOQ	2.2	0.8	10.4	1.1	6.5	6.1	0.6	0.5	<LOQ	0.3	ND	ND	27.2	10.2
Yodo	Main	Y9	0.5	ND	1.2	ND	4.3	0.1	0.1	ND	0.7	ND	1.4	0.1	11.3	0.4	8.3	0.2	1.0	<LOQ	0.5	ND	ND	ND	29.4	0.8
Ai	Main	A1	0.3	ND	1.2	ND	1.3	ND	0.1	0.5	0.2	0.5	0.7	1.0	10.3	0.8	2.6	0.4	ND	0.1	ND	ND	ND	ND	16.7	3.3
Ai	Main	A2	0.1	ND	0.6	ND	1.6	ND	0.1	<LOQ	0.1	ND	0.6	0.4	5.6	0.47	1.5	0.2	ND	ND	ND	ND	ND	ND	10.1	1.2
Ai	Main	A3	0.8	ND	1.6	ND	5.4	ND	0.3	0.1	1507.6	8.7	3.3	0.3	499.6	5.4	42.5	1.6	5.6	0.4	1.7	ND	ND	ND	2068.6	16.4
Ai	Main	A4	1.4	ND	1.3	ND	3.8	2.0	0.1	0.2	1411.5	8.7	2.4	5.7	136.6	1.6	11.6	0.9	1.4	0.3	0.6	ND	ND	ND	1570.8	19.3
Ai	Tributary	A5	1.0	ND	1.1	ND	5.3	ND	0.4	<LOQ	6.3	ND	1.8	ND	25.2	0.6	8.7	0.3	1.6	0.1	1.2	ND	ND	ND	52.5	0.9
Ai	Main	A6	0.7	ND	1.2	ND	3.6	0.5	0.1	ND	1625.4	11.5	2.1	0.2	135.5	2.5	10.1	1.5	1.7	0.4	0.8	ND	ND	ND	1781.2	16.7
Ai	WWTP	W9	0.8	ND	1.6	ND	21.3	4.9	0.6	<LOQ	5.8	ND	5.3	0.5	1081.3	17.0	16.9	0.8	4.8	1.4	3.3	1.0	ND	ND	1141.6	25.7
Ai	WWTP	W10	0.8	ND	1.2	ND	4.2	1.0	0.4	0.1	1602.2	8.2	3.0	0.3	561.2	2.2	51.8	0.4	5.3	<LOQ	1.3	ND	ND	ND	2231.4	12.1

† Type of sample: Main: Samples from mainstream; Tributary: Samples from tributary; WWTP: Waste water effluent samples.

‡ Liq: PFCs in liquid phase; Pr: PFCs in particulate phase.

§ ND: Not Detected (<Limit of detection, LOD); <LOQ: less than limit of quantification but greater than LOD.

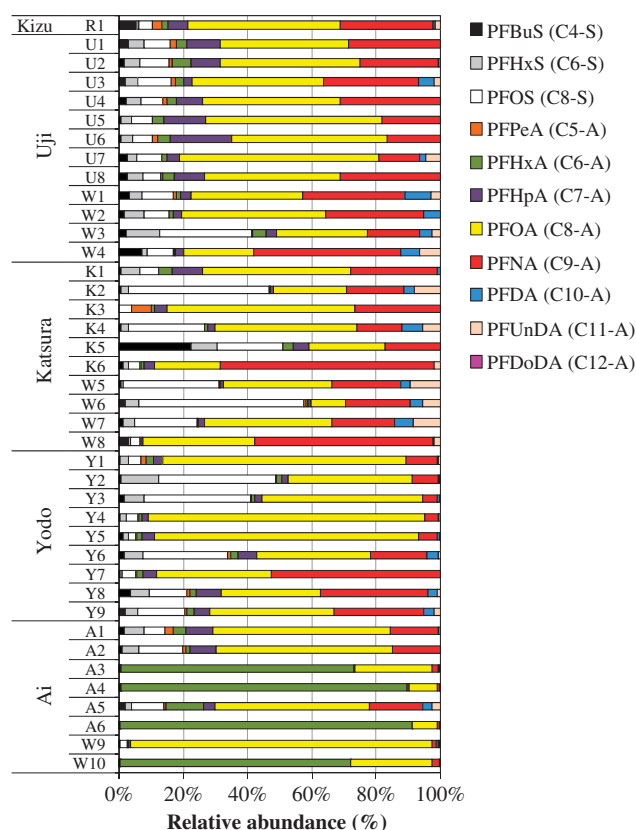


Figure 2 | Composition profile (%) of analyzed PFCs across Yodo River system. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

Daily mass load (g/d)

Figure 4 shows the daily mass load of PFCs in main Yodo River and headwaters tributaries. Mass load (g/d) was calculated by the product of PFCs concentrations (ng/L) and daily river discharge (m^3/d) recorded on the sampling day. Ai river mass load was not shown due to unavailability of discharge

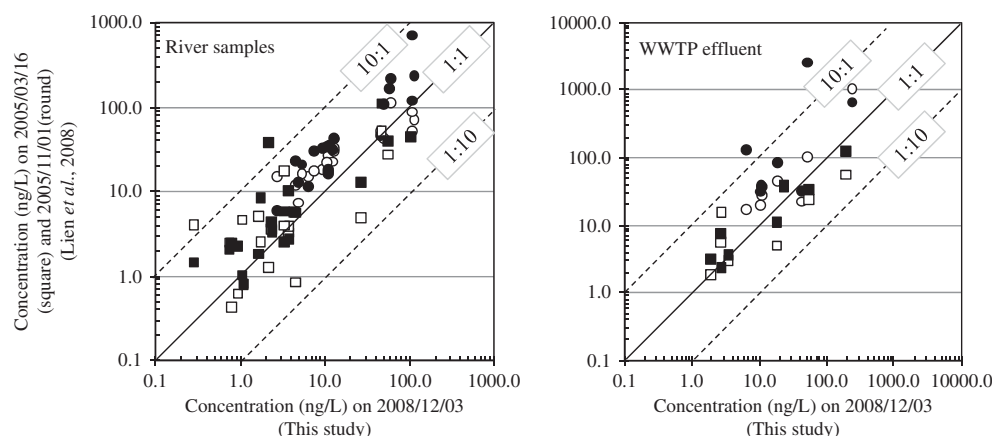


Figure 3 | Concentrations of PFOS (black) and PFOA (white) in the previous study (Lien *et al.* 2008) vs. in this study (Ai River data are not included in the figure).

data. Among the main rivers in the headwaters, the highest daily PFCs mass load was discharged by Katsura River (200 g/d), followed by Uji River (139 g/d) and Kizu River (51.1 g/d). However, there were huge differences in the relationship between daily discharge and calculated mass load in each river case. In Katsura River, WWTPs effluents contributed nearly 64% of total PFCs load into the river while discharge quantity (m^3/d) of effluent was only 39%. In Uji River, contribution of WWTPs effluents for both mass load and discharge quantity was 6% and 2% respectively. As most of the flows in Uji River come from Lake Biwa, so the source of majority of PFCs could be the lake water. In case of Kizu River, its daily discharge was slightly higher (by 5%) than Katsura River, but its mass load was nearly four times lower than Katsura River. It could indicate that Kizu River sub-basin may not have significant sources of PFCs. In case of main Yodo River, the total PFCs mass load at Y6 site was estimated 451.7 g/d. Analyzing mass loads from upstream tributaries revealed that Katsura River contributed the highest by 44.4% (flow contribution: 15.5%) to the total mass load at Y6, followed by Uji River by 30.8 (flow contribution: 60.8%), Yodo tributaries (Y1-5) by 13.5% (flow contribution: 0.5%) and Kizu River by 11.3% (flow contribution: 16.2%). Especially, WWTP effluents contributed nearly 30% of PFCs load, while their total discharge was less than 8% of main Yodo River discharge. The results indicated that control of PFCs released from WWTP effluents could substantially reduce the contamination level of PFCs in Yodo River system, although there could be other point and non-point sources yet to be investigated.

CONCLUSIONS

Occurrences of 11 perfluorinated compounds (PFCs) in the Yodo River system was investigated through a sampling

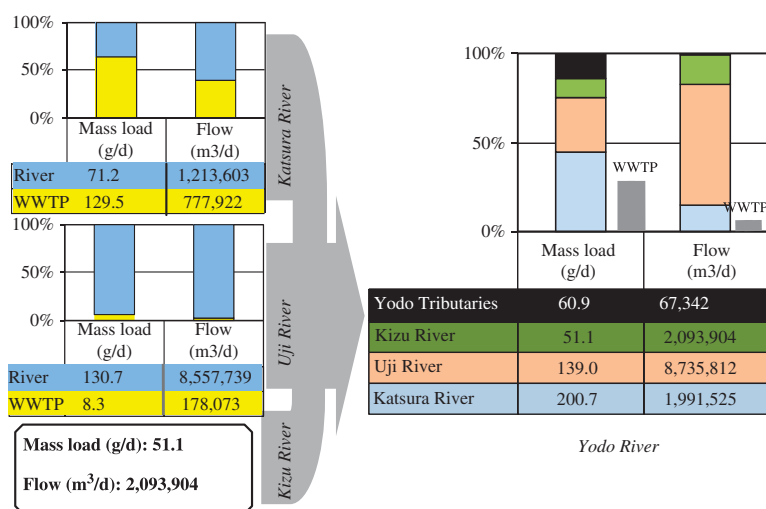


Figure 4 | Daily mass load (g/d) of PFCs across Yodo River system. (Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>).

campaign covering 40 sampling sites that included main river, tributaries and WWTP effluents. PFCs were detected in all sites and it even exceeded more than 1000 ng/L in some cases. PFDoDA was ND in all samples, while majority ND samples were for PFUnDA, PFDA and suspended solid (Pr.) samples. PFOS, PFHxS, PFOA and PFNA were the most dominant PFCs occurring at higher concentration in the river system. PFOS and PFOA levels were comparable to a previous study. It was found that WWTP effluents in Katsura River sub-basin mainly discharged PFCs into river, while Lake Biwa was thought to be the main source of PFCs into Uji River. However, PFCs concentrations observed at three different points of main Yodo River stream did not exceed more than 29.4 ng/L in spite of higher discharge of PFCs from headwater tributaries. Possibly, higher dilution effects by main Yodo River flow caused nearly similar concentration. Daily mass load of PFCs at the downstream of main Yodo River was estimated 451.7 g/d, of which nearly 30% was contributed by WWTP effluents. Results showed that Yodo River system could have a unique upstream-downstream linkage of PFCs contamination and the river could be a continuous pathway of PFCs exposure to the people of Kansai region.

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