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Perfluorooctane Sulfonate Concentrations in Surface Water in Japan

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Abstract. Perfluorooctane sulfonate (PFOS) is a class of specialty chemicals used in a variety of applications, and has been found to be globally distributed in many living organisms including humans. Several analytical methods have been developed for determination of PFOS in environmental samples and biological matrices. However, these methods employ liquid chromatography/tandem mass spectrometry (LC/MS/MS), an instrumentation which has limited accessibility because it is expensive to use and maintain. In the present study we present the development of a robust analytical method using liquid chromatography/mass spectrometry (LC/MS) in combination with solid phase extraction. The high yield and concentration of the present method enabled us to quantify PFOS as low as 0.1 ng/L. This method was applied to the determination of PFOS in 142 surface water samples collected from various geographic locations around Japan. The geometric mean (geometric standard deviation) (ng/L) for river samples ($n = 126$) was 2.37 (4.13), with a median of 1.68 and a range of 0.3–157 ng/L, and for coastal sea water samples ($n = 16$) was 1.52 (4.14), with a median of 1.21 and a range of 0.2–25.2 ng/L. However, the concentrations in most of the samples were much lower than the values reported in the US, except for those from the Jinzu (135.0 ng/L) and Tama (157 ng/L) Rivers. Because surface waters in the Ara (13.0–38.5 ng/L), Tama (0.7–157.0ng/L), and Yodo (0.9–27.3 ng/L) Rivers, sources of drinking water for more than eight million people, were moderately contaminated with PFOS, more work is needed to assess exposure to PFOS.

Perfluorinated alkyl sulfonates are a class of specialty chemicals used in a variety of applications, such as in lubricants, paints, cosmetics, and fire-fighting foams (Key *et al.* 1997; US EPA 2000; Kissa 2001). PFOS has been an important perfluorinated surfactant, but recently, in 2002, after 50 years of production its manufacture has been phased out worldwide (Renner 2001).

Compelling and disturbing evidence regarding PFOS has been reported: it has been found to be globally distributed in versatile living organisms including humans (Hansen *et al.* 2001), polar bears (Giesy and Kannan 2001), water birds (Kannan *et al.* 2001a), marine mammals (Kannan *et al.* 2001b), and oysters (Kannan *et al.* 2002). Enigmatic worldwide distribution of PFOS has been attributed to its resistance to degradation in ecological systems (US EPA 2000). The fluoride atoms around carbon atoms of PFOS make it resistant to enzymatic degradation (Kissa 2001).

Several analytical methods have been developed for determination of PFOS in environmental samples (Olsen *et al.* 1999; Moody *et al.* 2001; Hansen *et al.* 2002; Hebert *et al.* 2002; Moody *et al.* 2002) and biological matrices (Olsen *et al.* 1999; Hansen *et al.* 2001; Moody *et al.* 2002). Recently, a very sensitive analytical method was developed which uses a solid-phase extraction method coupled with high performance liquid chromatography (HPLC)-negative-ion electrospray tandem mass spectrometry (LC/MS/MS) (Moody and Field 1999; Moody *et al.* 2001; Hansen *et al.* 2002; Moody *et al.* 2002). However, mainly due to its high purchase and maintenance costs, LC/MS/MS is of limited availability for routine use.

In the present study we developed a robust analytical method using liquid chromatography/mass spectrometry (LC/MS) in combination with solid phase extraction. The high yield and concentration of the present method enabled us to quantify PFOS as low as 0.1 ng/L. The present method was employed for the determination of PFOS concentrations in surface waters collected from various geographic locations in Japan. The results indicated that PFOS contamination has spread throughout Japan.

Methods and Materials

Standard

Haptadecafluorooctane sulfonic acid potassium salt (FW.538.22), used as a standard for PFOS and as matrix spikes, was purchased from Fluka (Milwaukee, WI). The purity of PFOS used as the standard was 98%, and the reported concentrations were not corrected for purity.

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Surface Water Sampling

Surface water samples were collected from rivers and coastal waters from all over Japan. Two sets of 1-L surface water samples were collected in polyethylene terephthalate disposable containers with narrow-mouth bottle tops and screw caps. To minimize the possibility of any sample contaminations, containers were thoroughly rinsed with methanol and deionized water prior to use. Teflon bottles and Teflon-lined caps were avoided throughout the experiment to prevent sample contamination. In our preliminary study, waters including deionized water were found contaminated with PFOS (n = 5, 0.1–0.2 ng/L). Therefore, deionized water was only used after passing through a Presep-C Agri cartridge (Solid phase: Styrenedivinylbenzene polymethacylate on a polyethyelene housing) (Presep-C, 220 mg cartridge: Wako Pure Chemicals, Osaka Japan) to remove residual PFOS throughout this experiment. We confirmed that the concentration of PFOS in the methanol used was less than the detection limit (<0.1 ng/L). Samples were collected using a subsurface grab-sampling device with the amount of sediment kept to a minimum. The samples were stored at room temperature (22°C) prior to analysis. In the preliminary study, we prepared trip blanks in polyethylene terephthalate disposable containers (n = 3), which contained PFOS at 10 ng/L. These blanks were stocked in a similar manner to those with samples. The concentrations (10.1 ± 0.3 ng/L) had not changed when concentrations were determined again after six months.

Surface Water Preconcentration

One liter from each of the surface water samples was first filtered through glass fiber filters (1.0 μm ϕ) (ADVANTEC GA 100, 55 mm ϕ, ADVANTEC, Tokyo Japan) to remove sediments and biota. Subsequently it was passed through a membrane filter (Millipore JAWPO4700, 47 mm ϕ, pore size 1.0 μm) (Millipore, Tokyo, Japan). The samples were passed through the Presep-C Agri column at a flow rate of 10 mL/min using a Water Concentrator System (Concentrator Plus, Waters, Tokyo, Japan). Presep-C cartridges were then eluted with 1.5 mL of methanol and concentrated at room temperature under nitrogen gas flow to 1 mL/min to be analyzed by LC/MS.

LC/MS and Quantification

Standard compounds were infused through a flow injection at a flow rate of 0.2 mL/min for adjusting of the ion sprayer and tuning of the mass spectrometer. The methanol extracts (10 μl injection volume) were chromatographed using HPLC with a flow rate of 0.2 mL/min as shown in Table 1. Total runtime was 20 min, without any equilibration time between samples.

Mass spectra were taken on an LC/MS system equipped with an orthogonal spray interface, and employing electron spray ionization in negative mode. The fragmentor and Vcap voltages were 200 V and 4000 V, respectively (Table 1). The nebulizer pressure was 50 psig and the drying N_2 gas flow rate was 10.0 L/min. Selected ion monitoring mode was employed for quantification of PFOS (Table 1). Calibration curves constructed for PFOS ranged from 0.1 to 100 μg/L. Means of two separate determinations of the two sets of bottles were calculated for individual locations.

Spike and Recovery of Surface Water Samples by LC/MS

Spike and recovery experiments were performed to determine the precision and accuracy of the method. One set of spike and recovery experiments was performed using deionized water that contained known amounts of PFOS. Standard addition analyses were also performed using surface water samples. Known amounts of PFOS were added to the surface water samples to obtain the target concentrations. The spike and recovery experiments included preconcentration steps covering filtration with the glass fiber and membrane filters.

Table 1. An optimized analytical method for PFOS using LC/MS

HPLC	
Instrument	Agilent 1100
Column	Zorbax XDB C-18 (Agilent Narrow-Bore 2.1 × 150 mm, 5 μm)
Mobile phase	A: CH_3CN B: 10mM CH_3COONH_4/H_2O A:B = 45:55
Flow rate	0.2 mL/min
Oven temperature	40°C
Injection volume	10 μL
MS	
Instrument	Agilent MSD SL
Ionization	Electrospray ionization
Nebulizer pressure	N_2 (50 psig)
Drying gas flow	N_2 (10.0 L/min, 350°C)
Polarity mode	Negative
Fragmentor voltage	200 V
Vcap voltage	4000 V
SIM (m/z)	499 $(M\text{-}K)^-$
Instrumental detection limit[a]	0.3 pg
The limit of quantification[b]	0.1 ng/L when starting from 1 L of surface water

[a] Defined by a signal-to-noise (S:N) ratio of 3:1.
[b] Defined by CV limit less than 20%.

Results

Optimization of the Separation of PFOS

We applied 1 L of a deionized water sample containing PFOS at 20 ng/L in various pHs ranging from 2 to 12 to the cartridge, and eluted with 1.5 mL of methanol. The recoveries were greater than 98.8% at pHs between 6 and 11, while an acidic pH of less than or equal to 5 decreased the recovery to 80% (data not shown). Thus we adjusted the pH of the solution to a pH >6.

We next investigated conditions for separation of PFOS using HPLC (Table 1) and eluted with a mixture of various proportions of acetonitrile solution and 10 mM ammonium acetate. The retention time was variable depending on the proportion of the two solutions. We employed a mixture containing acetonitrile and 10 mM ammonium acetate at 45:55 to obtain a retention time of approximately 11 min (Figure 1). We did not employ a gradient operation because it changed chromatographic patterns and resulted with retention time instability (data not shown).

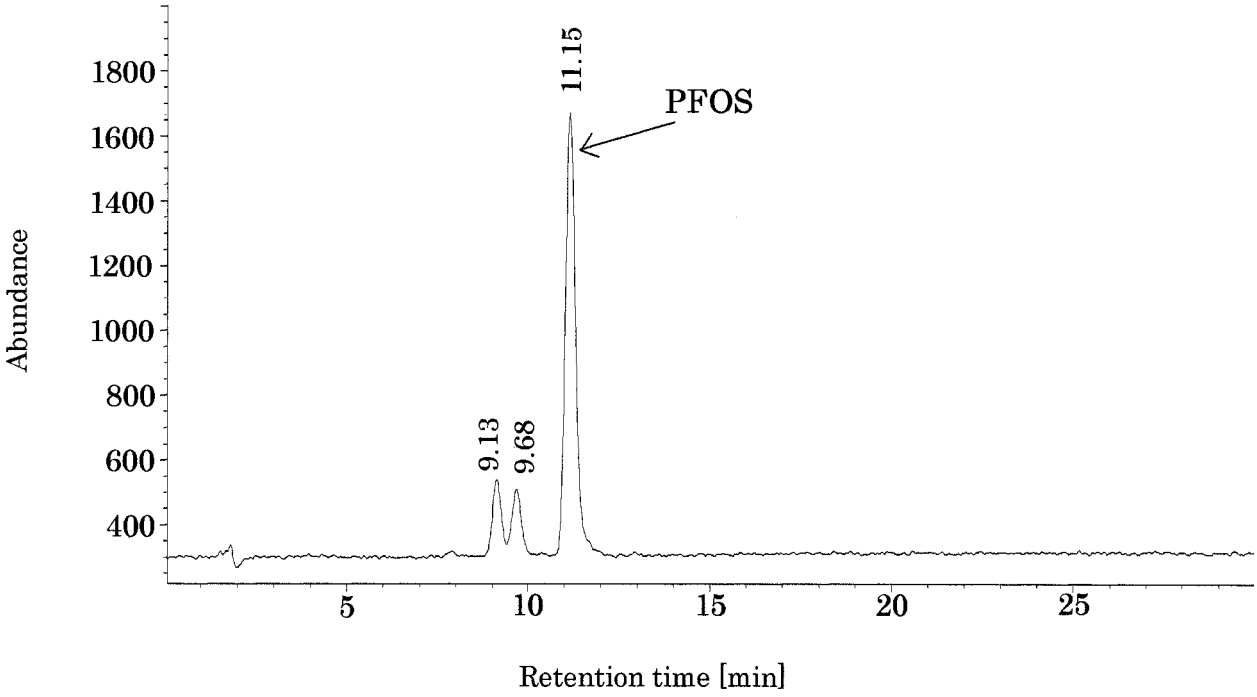

Figure 1. Typical LC-MS chromatogram of PFOS (μg/L) in a deionized water sample

Table 2. Recoveries and spiked tests of PFOS in deionized water and surface water samples

	Deionized water[a]				A surface water sample from a river[a]			A surface water sample from a coastal sea[a]		
	Spiked concentration (ng/L)				Spiked concentration (ng/L)			Spiked concentration (ng/L)		
		0.1	0.3	0.5		1	10		1	5
	0[b] ng/L	Recovery (%)			0 ng/L	Recovery (%)		0 ng/L	Recovery (%)	
1	<0.1	68	82	108	1.42	100	97	0.29	87	99
2	<0.1	81	83	105	1.40	102	98	0.26	96	97
3	<0.1	79	87	108	1.32	107	98	0.26	90	103
4	<0.1	63	91	100	1.36	108	100	0.30	87	100
5	<0.1	68	89	99	1.58	106	100	0.22	91	95
6	<0.1	82	87	107	1.46	108	95	0.20	86	96
7	<0.1	81	90	105	1.44	110	98	0.22	85	100
Mean	-	74.7	87.0	104.6	1.43	105.9	98.0	0.25	88.9	98.7
S.D. ($n-1$)	-	7.94	3.42	3.74	0.08	3.58	1.88	0.04	3.80	2.76
CV(%)	-	10.6	3.9	3.6	5.8	3.4	1.9	15.1	4.3	2.8

[a] PFOS was added to the 1 L of water samples.
[b] Assumed to be zero ng/L.

Chromatographic Identification of PFOS

Figure 1 shows a typical chromatographic pattern of PFOS in a deionized water sample at 1.0 μg/L. In selected negative-ion mode monitoring of ions, the parent ion $(M-K)^-$ for PFOS m/z 499 ($C_8F_{17}SO_3^-$) was monitored for quantification. The monitoring revealed a major peak at a retention time of 11.15 min, and two minor peaks at retention times of 9.13 and 9.68 min. To avoid interference and to ensure complete selectivity, the transitions of PFOS, m/z 499 ($C_8F_{17}SO_3^-$) to m/z 99 (daughter fragment, FSO_3^-) and to m/z 80 (daughter ion, SO_3^-), with optimal parameters, were monitored. The 11.15-min peak had two daughter ions, suggesting that these peaks correspond to PFOS while the 9.13-min and 9.68-min peaks did not have the two daughter fragments of PFOS (Kannan *et al.* 2001). We thus considered that the 11.15 min-peak was PFOS and other two peaks were not.

Portions of the surface water samples (River samples, $n = 3$) were also analyzed by LC/MS/MS (Applied Biosystems ABI3000TM, Tokyo, Japan) for confirmation of PFOS. The

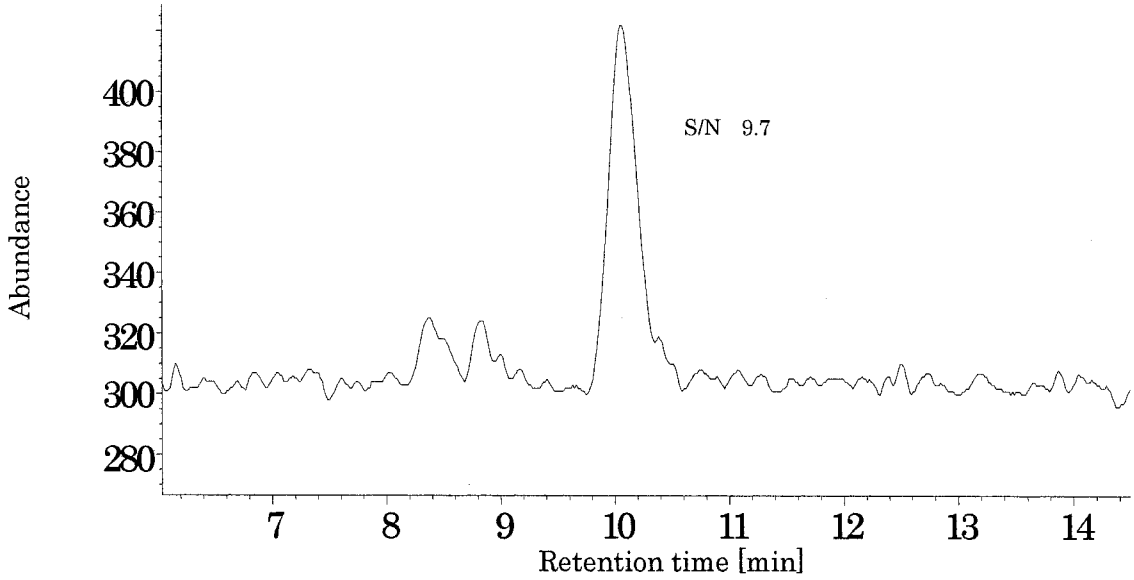

Figure 2. LC/MS chromatogram of PFOS in a surface water sample (0.1 ng/L) from a river. A surface water sample collected from a river analyzed with LC/MS with an S/N ratio of 9.7. The sample was concentrated as described in the text from 1 L of the sample

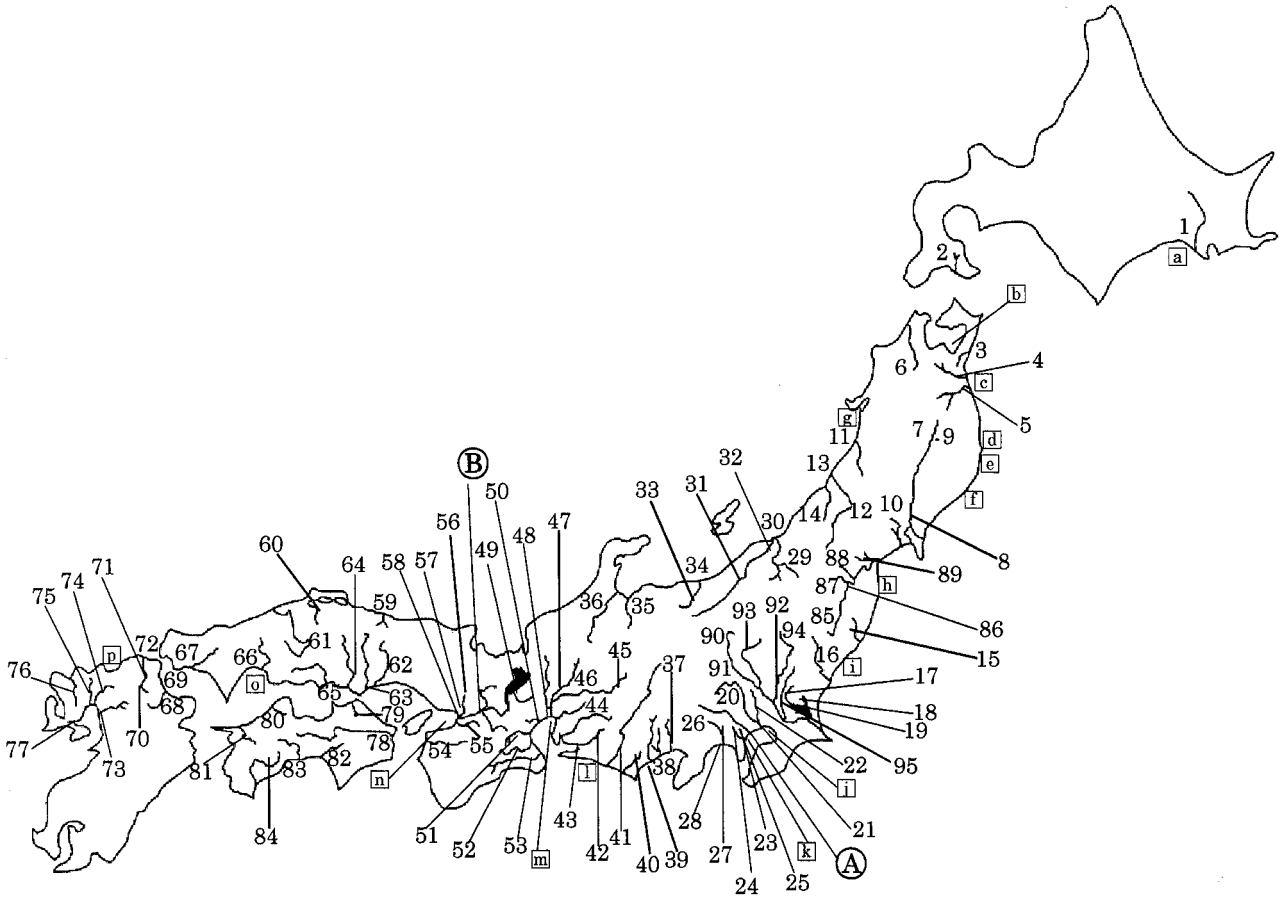

Figure 3. Map of Japan and sampling sites

Table 3. PFOS concentrations in the surface water samples from the rivers

Site[a]	System	Name of the river	Collection date	PFOS concentration (ng/L)	Prefecture
1	Lake Kusharo	Kusiro River	3/1/2002	1.3	Hokkaido
2		Kameda River	3/5/2002	1.1	Hokkaido
3		Takase Rver	3/2/2002	2.6	Aomori
4		Oirase River	3/4/2002	0.6	Aomori
5		Mabuchi River	3/5/2002	1.0	Aomori
6		Iwaki River	3/6/2002	0.5	Aomori
7	Kitakami River	Upstream	2/25/2002	1.4	Iwate
8	Kitakami River	Downstream	2/25/2002	4.8	Miyagi
9	Kitakami River	Takamatsu Pond	2/25/2002	1.4	Iwate
10		Naruse River	2/18/2002	1.4	Miyagi
11		Koyoshi River	2/19/2002	1.9	Akita
12	Mogami River	Mogami River	2/15/2002	1.2	Yamagata
13	Mogami River	Mogami River	2/15/2002	1.0	Yamagata
14		Aka River	3/1/2002	2.1	Yamagata
15		Natsui River	3/12/2002	0.4	Fukushima
16		Naka River	3/12/2002	0.4	Tochigi
17	Lake Kasumigaura	Sakura River	3/7/2002	4.1	Ibaragi
18		Lake Kasumigaura (Northern coast)	3/7/2002	4.8	Ibaragi
19		Lake Kasumigaura (Western coast)	3/7/2002	5.3	Ibaragi
20	Ara River	Middle stream	3/15/2002	15.1	Saitama
21	Ara River	Down stream	3/15/2002	38.5	Saitama
22	Ara River	Middle stream	3/15/2002	13.0	Saitama
23	Tsurumi River	Tanimoto River	3/15/2002	4.2	Kanagawa
24	Tsurumi River	Onda River	3/15/2002	2.9	Tokyo
25	Tsurumi River	Tsurumi River	3/15/2002	72.6	Kanagawa
26	Sagami River		3/17/2002	3.3	Kanagawa
27			3/17/2002	5.9	Kanagawa
28			3/17/2002	31.2	Kanagawa
29	Agano River		3/20/2002	0.7	Niigata
30			3/20/2002	0.7	Niigata
31	Shinano River		3/21/2002	4.3	Niigata
32			3/21/2002	1.2	Niigata
33	Seki River		3/18/2002	1.6	Niigata
34			3/18/2002	2.6	Niigata
35		Jinzu River	3/19/2002	135.0	Toyama
36		Shou River	3/19/2002	1.0	Toyama
37		Fuji River	3/10/2002	1.4	Shizuoka
38		Abe River	3/10/2002	0.7	Shizuoka
39		Ooi River	3/10/2002	1.2	Shizuoka
40		Kiku River	3/10/2002	0.5	Shizuoka
41		Tenryuu River	3/10/2002	0.5	Shizuoka
42	Toyo River		3/23/2002	0.6	Aichi
43			3/23/2002	1.7	Aichi
44		Yahagi River	3/18/2002	0.8	Aichi
45		Shounai River	3/18/2002	0.4	Aichi
46		Kiso River	3/21/2002	0.7	Gifu
47		Nagara River	3/19/2002	6.6	Gifu
48		Ibi River	3/17/2002	2.4	Gifu
49		Yasu River	4/1/2002	7.6	Shiga
50		Suzuka River	3/27/2002	10.3	Mie
51		Kumozu River	3/27/2002	1.7	Mie
52		Kusida River	3/27/2002	0.3	Mie
53		Miya River	3/27/2002	0.3	Mie
54		Kino River	3/25/2002	1.0	Wakayama
55		Yamato River	3/25/2002	13.1	Osaka
56	Ina River		3/25/2002	1.3	Hyogo
57			3/25/2002	4.1	Hyogo
58			3/25/2002	32.3	Hyogo
59		Tenjinn River	3/19/2002	0.9	Totttori

Table 3. Continued

Site[a]	System	Name of the river	Collection date	PFOS concentration (ng/L)	Prefecture
60		Kii River	3/19/2002	19.6	Shimane
61		Gouno River	2/12/2002	0.5	Hiroshima
62		Yoshii River	2/13/2002	0.8	Okayama
63		Asahi River	2/14/2002	0.7	Okayama
64		Takanasi River	2/15/2002	1.0	Okayama
65		Ashida River	2/15/2002	0.6	Hiroshima
66		Oota River	2/15/2002	1.1	Hiroshima
67		Sanami River	2/18/200	1.3	Yamguchi
68	Yamakuni River	Upstream	3/1/2002	0.3	Ooita
69	Yamakuni River	Downstream	3/1/2002	0.9	
70	Onnga River		3/14/2002	1.5	Fukuoka
71			3/12/2002	0.8	Fukuoka
72			3/12/2002	1.3	Fukuoka
73		Yabe River	3/12/2002	0.4	Fukuoka
74		Chikugo River	3/13/2002	1.7	Fukuoka
75		Kase River	3/13/2002	0.4	Saga
76		Matsuura River	3/13/2002	1.2	Saga
77		Motoake River	4/2/2002	0.6	Nagasaki
78		Yoshino River	4/10/2002	0.6	Tokushima
79		Doki River	4/2/2002	15.8	Kagawa
80		Sigenobu River	4/7/2002	0.6	Ehime
81		Hiji River	4/7/2002	2.6	Ehime
82		Mononobe River	4/8/2002	0.4	Kouchi
83		Niyodo River	4/8/2002	3.5	Kouchi
84		Shimanto River	4/8/2002	0.7	Kouchi
85	Abukuma River		3/15/2002	5.5	Fukushima
86			3/15/2002	0.4	Fukushima
87		Matu River	3/15/2002	0.4	Fukushima
88		Suriage River	3/15/2002	0.3	Fukushima
89		Siroishi River	3/15/2002	0.6	Miyagi
90	Tone River		2/11/2002	3.0	Gummna
91			2/11/2002	2.6	Gummna
92			2/11/2002	10.2	Ibaragi
93		Watarase River	2/11/2002	2.4	Gunma
94		Kido River	2/11/2002	4.3	Tochigi
95		Kogai River	2/11/2002	6.2	Ibaragi

[a] For locations, see Figure 3.

Table 4. PFOS concentrations in the major river systems and coastal sea waters

Site[a]	Name	Date of sample collection	Location	Concentration of PFOS (ng/L)
a	Sea of Kushiro	4/1/2002	Hokkaido	1.6
b	Mutsu bay	4/3/2002	Aomori	0.6
c	Hachinohe Bay	4/3/2002	Aomori	0.4
d	Jyodoga Coast	4/5/2002	Iwate	0.5
e	Miyako Bay	3/31/2002	Iwate	0.2
f	Kamaishi Bay	3/31/2002	Iwate	1.0
g	Honjyo Marina	3/25/2002	Akita	1.5
h	Souma Bay	3/25/2002	Fukushima	0.7
i	Nagasaki Bay	3/25/2002	Fukushima	0.4
j	Chiba-Funahashi Bay	3/11/2002	Chiba	3.4
k	Yamashita Bay	3/12/2002	Kanagawa	7.4
l	Pacific Ocean	4/2/2002	Aichi	0.5
m	Nagoya Bay	4/2/2002	Aichi	20.6
n	Koshien Bay	4/5/2002	Hyogo	25.2
o	Motoujina Shima coast	4/2/2002	Hiroshima	1.5
p	Hakata Bay	4/3/2002	Fukuoka	4.6

[a] Refer to the site in Figure 3.

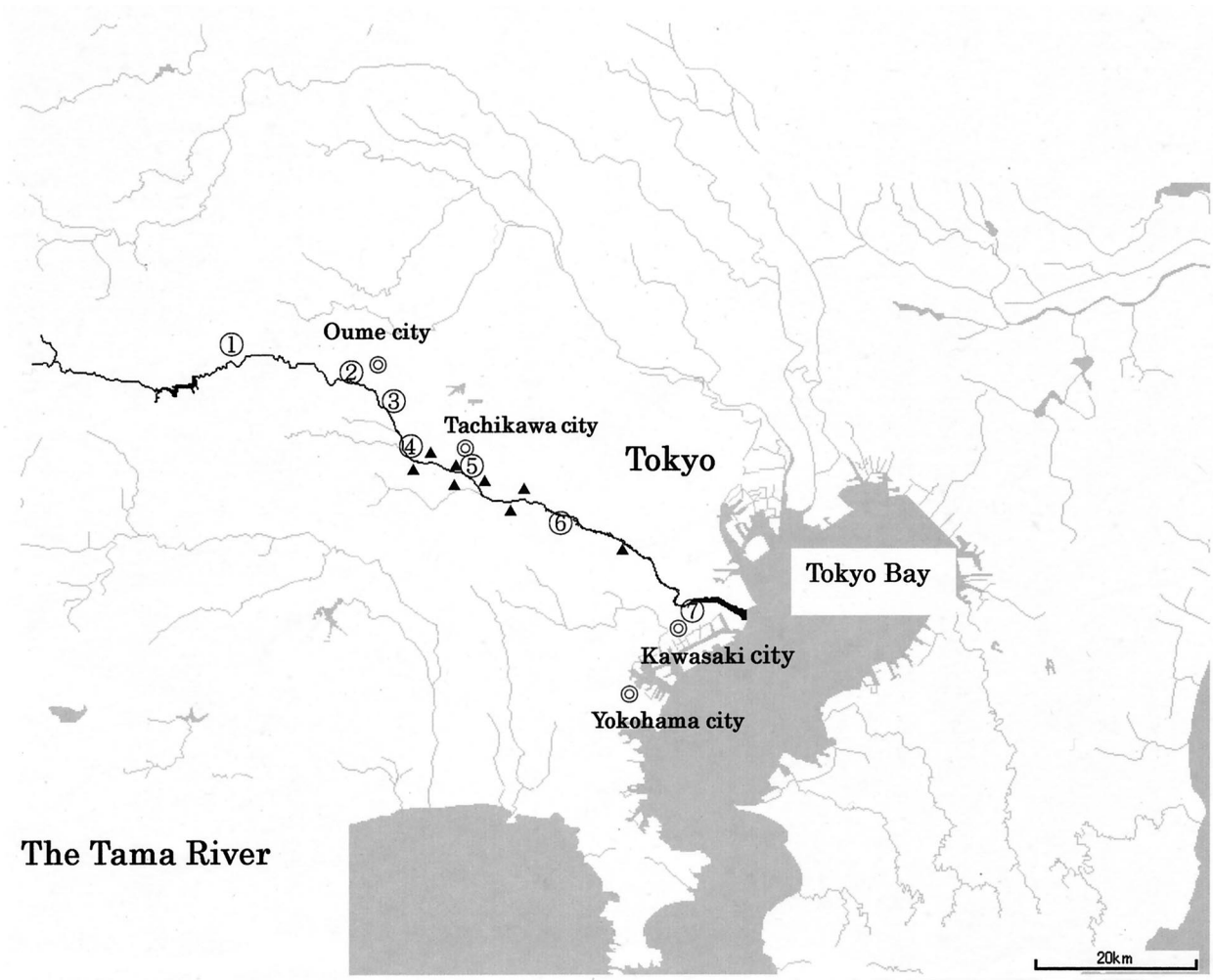

Figure 4. Systemic sampling from the Tama River. Solid triangles indicate sewer discharge sites. For the location of Tama River, refer to site A in Figure 3

11.15-min peak had the parent ion $(M\text{-}K)^-$ (m/z 499) and had two daughter ions (m/z 99 and 80), suggesting that the peak corresponded to PFOS (data not shown). Thus, in the present study, we assigned the 11.15-min peak as PFOS. Although multiple daughter ions were monitored, quantification was based on a single product ion, m/z 499.

Accuracy, Precision, and Detection Limits for LC/MS

Calibration curves for low and high concentrations of PFOS went from 0.1 μg/L to 100 μg/L and were linear with correlations $r > 0.998$ (data not shown).

The spike and recovery experiments are shown in Table 2. Percent recoveries for PFOS (at three different concentration levels) ranged from 74.7 to 104.6 % (Table 2) with the maximum coefficient of variation (CV) being 10.6% at 0.1 ng/L for deionized water samples. Standard addition experiments revealed the mean recoveries for surface water samples from rivers or coastal seas, and are shown in Table 2. The CVs for surface water samples from rivers and coastal seas after seven repeated determinations are also shown (Table 2). The CVs for coastal sea samples were as large as 15.1%. Taken together, we considered the actual limit of quantification for the 1 L surface water samples to be 0.1 ng/L, which gave a signal-to-noise (S:N) ratio ≥3 and CVs <20% (Figure 2). It corresponded to a lowest limit of quantification as being 0.1 ng/L when field samples were concentrated by a factor of 1000 in the preconcentration step.

Determination of PFOS in Surface Waters in Japan

Surface water samples from rivers and the sea were analyzed to determine the concentrations of PFOS (Figure 3). Concentrations of PFOS in surface water samples collected from rivers are summarized in Table 3.

PFOS was also detectable in surface water samples from coastal seas and ranged from 0.2 ng/L to 25.2 ng/L as shown in Table 4. Concentrations were greater in the bay regions of Nagoya and Koshien than in open seas.

It was clearly demonstrated that detectable levels of PFOS

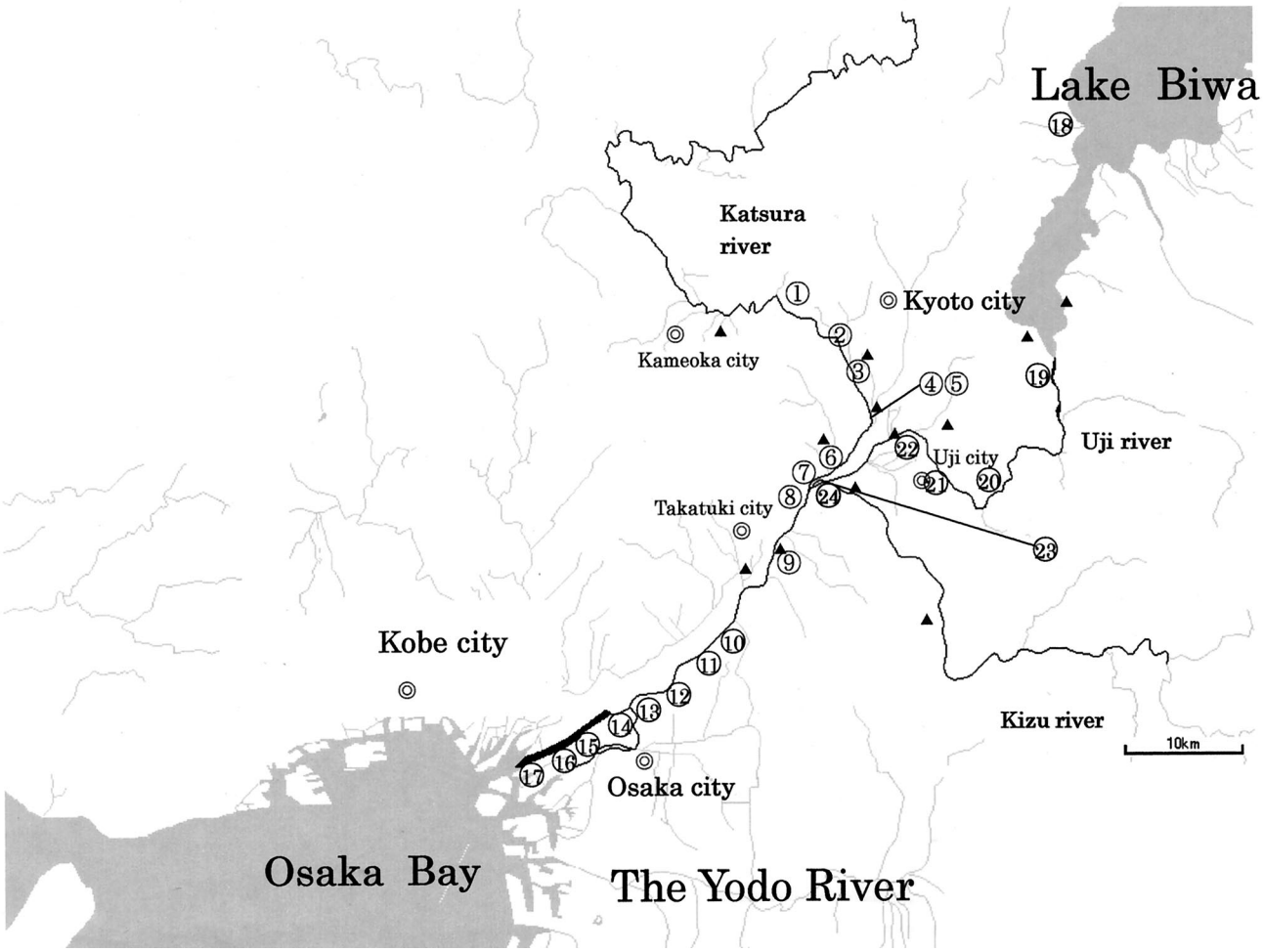

Figure 5. Systemic sampling from the Yodo River. Solid triangles indicate sewer discharge sites. Circled numbers indicate drinking water intakes. For the location of Yodo River, refer to site B in Figure 3

were found in all samples collected in Japan (Tables 3 and 4), with more than 100-fold differences being found among the surface water samples collected.

Geographic Differences in Concentrations of PFOS in the Tama and Yodo Rivers

We systemically collected surface water samples to determine the source of PFOS in the Tama and Yodo Rivers (Figures 4 and 5). The Tama River originates from Lake Okutama and flows through suburban and metropolitan areas of Tokyo and into Tokyo Bay (Figure 4). It has two drinking water intakes for residents in the Tokyo area: one upstream of sampling site 4, and another between sampling sites 6 and 7. The concentrations of PFOS were trace (0.7–1.7 ng/L) in samples collected at sampling sites 1–4, but abruptly increased at site 5 (157 ng/L) and then gradually decreased from sites 6 to 7 (Table 5). One or more of the four sewer or industrial waste water discharge sites, which are located between sites 4 and 5, are the most probable source of PFOS.

The Yodo River runs from Lake Biwa to the Osaka Bay and has 19 intakes for drinking water for various cities along with 12 sewer discharge sites (Figure 5). Samples were collected from various sites as shown in Figure 5. The concentrations of PFOS in waters released directly from sewer waste sites 5 or 9 were higher than others (Table 5). At sampling site 4, discharges from site 5 flowed into the Katsura River. The PFOS concentrations decreased from sites 14 to 17 by dilution with coastal sea water as shown by the excess chloride ion concentrations. Although there are a couple of discharge sites for sewer wastes, concentrations were low in samples collected from sites 18–22 and 24.

The Overall Estimation of Levels of Contamination in Japan

The geometric mean (geometric standard deviation) was 2.37 (4.13) with a median of 1.68 and a range of 0.3–157 ng/L for river samples (n = 126: Table 3 and 5) and was 1.52 (4.14)

Table 5. Systematic collection of surface water samples from Tama and Yodo Rivers

Reference	River	Site[a]	Location	Collection date	PFOS concentration (ng/L)	Prefecture
Figure 4	Tama River	1		4/15/2002	1.7	Tokyo
		2		4/15/2002	0.7	
		3		4/15/2002	1.6	
		4		4/15/2002	1.3	
		5		4/15/2002	157.0	
		6		4/15/2002	65.3	Kanagawa
		7		4/15/2002	50.3	
Figure 5	Yodo River	1	Katsura River	4/17/2002	1.1	Kyoto
		2	Katsura River	4/17/2002	1.8	
		3	Katsura River	4/17/2002	1.7	
		4	Katsura River	4/17/2002	23.2	
		5	Katsura River	4/17/2002	25.6	
		6	Katsura River	4/17/2002	7.3	
		7		4/17/2002	27.3	Osaka
		8		4/17/2002	8.0	
		9		4/17/2002	24.7	
		10		4/17/2002	9.5	
		11		4/17/2002	11.5	
		12		4/17/2002	13.4	
		13		4/17/2002	12.3	
		14		4/17/2002	5.9	
		15		4/17/2002	5.4	
		16		4/17/2002	5.9	
		17		4/17/2002	6.9	
		18	Lake Biwa	4/17/2002	1.6	Shiga
		19	Seta River	4/17/2002	3.6	
		20	Amagase Dam	4/17/2002	0.9	Kyoto
		21	Uji River	4/17/2002	2.6	
		22	Uji River	4/17/2002	1.7	
		23	Uji River	4/17/2002	3.5	Osaka
		24	Kizu River	4/17/2002	2.6	Kyoto

[a] Refer to the site and numbers in Figures 4 and 5.

with a median of 1.21 and a range of 0.2–25.2 ng/L for coastal sea water samples ($n = 16$: Table 4).

Discussion

Several methods have been developed for PFOS determinations in surface water samples (Moody *et al.* 1999; Moody *et al.* 2001; Hansen *et al.* 2002; Moody *et al.* 2002). Three procedures have generally been required: sample concentrations, separation using HPLC and analysis by LC/MS. In the present study, we have improved the purification procedures by using a Presep-C Agri cartridge with a mechanical concentrator at a very low flow rate, 10 mL/min. These improvements significantly economized the pretreatment efforts, increased sensitivity and enabled us to quantify on a routine basis trace amounts of PFOS in surface water samples.

The quantification of 1 L of surface water samples collected from all over Japan showed a definitive PFOS contamination of surface waters, in a range of 0.2–157.0 ng/L. The concentrations in most of the samples, however, are much lower than those collected in the Tennessee River (Hansen *et al.* 2002). Although the highest concentrations in Jinzu (135.0 ng/L, Table 4) and Tama (157 ng/L in Table 5) Rivers were comparable to those highest levels reported in the Tennessee River, the majority of values in Japan were much smaller than the background levels in the Tennessee River (Hansen *et al.* 2002).

Systemic collection of samples was undertaken in the Tama and Yodo Rivers. As expected, PFOS concentrations increased at some sewer discharge sites, suggesting that they were the major sources of PFOS. In terms of the origin of PFOS, there are several possible sources including industrial or domestic waste waters.

PFOS concentrations in urbanized areas have two ecological implications. First, it may imply that organisms living in urbanized areas are more heavily contaminated with PFOS. Indeed, it is known that the PFOS concentrations in biota are higher in urbanized than in remote areas (Giesy and Kannan 2001), suggesting that PFOS contamination from surface waters can bioaccumulate to the higher trophic levels of food chains in wildlife as has been reported (Kannan *et al.* 2001a). Another ecological implication arises from the Ara, Tama, and Yodo Rivers, which are mildly contaminated with PFOS, being the sources of drinking water for more than eight million people. We have recently shown that contamination levels in drinking water are comparable to those in those rivers (Harada *et al.* 2003). Further study is needed for assessment of exposure through drinking water.

PFOS is reported to be toxic in rodents and primates, and at relatively low doses caused wasting syndrome in a subchronic study (Goldenthal *et al.* 1978a; Goldenthal *et al.* 1978b; Thomford 1998). On the other hand, observations of workers working in PFOS producing plants have not suggested toxicity at mg/L levels of PFOS in plasma (Olsen *et al.* 1999). A rabbit and rat study failed to reveal developmental toxicity (Case *et al.* 2001). It is also known that PFOS has a strong peroxisome proliferating action (Haughom and Spydevold 1992; Sohlenius *et al.* 1993; Derbel *et al.* 1996). These fragmentary pieces of evidence suggest that although not an imminent danger, more toxicological information is needed for risk assessment of long-term toxicity in humans. We believe that identification of the hazards of PFOS in humans is urgently needed for a rational risk assessment, in part because of the large exposure population in the Tokyo and Osaka areas, albeit at low levels of PFOS in surface waters (0.7–157 ng/L).

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