

## (74) PERFLUORINATED SUBSTANCES IN TAP WATER OF JAPAN AND SEVERAL COUNTRIES AND THEIR RELATIONSHIP TO SURFACE WATER CONTAMINATION

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Recently, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are concerned as a new class of persistent organic pollutants, have been found to be widely distributed in many living organisms including human. We measured concentrations of PFOS and PFOA in 38 tap water samples collected from several areas in Japan, Thailand, Malaysia, Sweden, Vietnam, China and Canada; and conducted systematic surveys of PFOS and PFOA at surrounding surface water sites. A solid phase extraction coupled with liquid chromatography/mass spectrometry (LC-MS) was used for analysis. Main conclusions were as follows: (1) Most of collected tap water samples were contaminated with PFOS and PFOA with the concentrations ranged from the limit of quantification levels to 13 ng/L for PFOS and 109 ng/L for PFOA. (2) The level of tap water concentrations was generally related to the level of surrounding surface water concentrations whether the source of tap water was the surface water or not. (3) In Japan, tap water PFOA concentrations were relatively high in Biwako-Yodo River area (Otsu, Kyoto, Osaka), mostly due to its contamination of Lake Biwa and Yodo River.

**Key Words:** *perfluorinated substances, PFOS, PFOA, tap water, surface water*

### 1. INTRODUCTION

From half a century ago, perfluorinated substances have been being used widely in industrial goods and processes as well as in consumer products<sup>1)</sup>. Recently, PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid), which are the end metabolic degradation products of major perfluorinated surfactant classes, receive emerging environmental concerns. PFOS and PFOA are persistent pollutants and PFOS is considered to be bioaccumulative<sup>2,3,4)</sup>.

Exposure to PFOS could affect the neuroendocrine system in rats<sup>5)</sup>. PFOA was reported as a potent hepatocarcinogen in rodents and exerts genotoxic effects on human cells<sup>6)</sup>. Half lives in the human body were estimated 8.67 and 1-3.5 years for PFOS and PFOA respectively<sup>7)</sup>. PFOS and PFOA accumulate in human blood not only in occupationally exposed workers but also in general population of various countries. The concentration level was several to several tens ng/mL for PFOS and generally lower for PFOA<sup>8)</sup>.

Contamination of PFOS and PFOA in non-biota has not been world-wide reported. **Table 1** shows

**Table 1** Global-viewed background of PFOS and PFOA concentrations in tap water and surface water

	Location	PFOS (ng/L)		PFOA (ng/L)		Note for R. value	Reference
		R. value	Max	R. value	Max		
Tap water	Japan	Morioka, Miyako, Kyoto, Setagaya, Hyogo, Osaka, Iwaté, Miyagi, Akita	NA	51	NA	40	9), 10)
	Canada	Toronto <sup>a)</sup>	265	995,000	13	113	Mean 11)
	European Nordic Countries	Finland, Sweden, Norway, Denmark, Iceland, Faeroe Islands	<1	NA	7.8	NA	Median 12)
Surface water	Japan	Contry-wide: Hokkaido-Tohoku, Kanto, Chubu, Kinki, Chugoku, Kyushu-Shikoku	0.9-14.9	157	1.0-11,000	87,000	Mean 9), 10), 13)
		Tomakomai (Hokkaido) <sup>b)</sup>	42.3	3690	4.1	162	Mean 14)
	United State	Alabama State	32-114	NA	<25-394	NA	Uptream-Downstream 15)
		Great Lake	40	70	43	50	Mean 16)
		Michigan State	1.8-17	29	4.4-22	36	Mean 17), 18)
		Minnesota State	NA	47	NA	19	19)
		NewYork State	1.6-64	1090	14-49	173	Mean 20)

\*: monitoring data after application of fire fighting foam <sup>a)</sup>151 days after, <sup>b)</sup>1 month after  
R. value: a representative value; NA: not available

our review of available data on PFOS and PFOA concentration in tap water and surface water all over the world. The concentrations in tap water were reported only in Japan <sup>9,10)</sup> and the data in surface water are still lacking in many regions. Since a possible pathway of human exposure to pollutant is tap water intake, information of tap water concentration is of important for health risk evaluation.

The study has a primary objective to investigate the concentration of PFOS and PFOA in tap water from different locations in several countries. The contamination levels of PFOS and PFOA in surrounding surface water were also examined. The

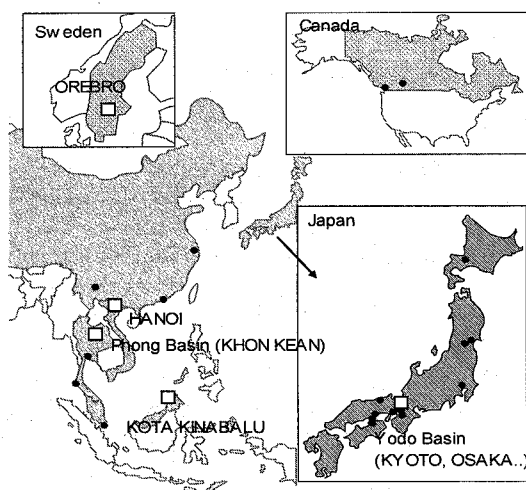
final attempt was to find out if there was any relation between tap water contamination and surrounding surface water contamination.

## 2. SAMPLING AREAS AND SAMPLING PROTOCOL

### (1) Sampling areas

Spot samples of tap water were collected from 7 countries including Japan (18 samples), Thailand and Malaysia (5 samples for each), Vietnam (2 samples), Sweden (2 samples), China (5 samples), and Canada (2 samples). Samples were collected from Jun-05 to May-06. **Figure 1** shows sampling areas of tap water and surface water. **Table 4** shows more details about water sampling sites.

In each of the beginning five countries, one area was selected for systematic survey of surface water contamination. They are Yodo Basin (Japan), Phong Basin (Thailand), Kota Kinabalu City (Malaysia), Hanoi City (Vietnam), and Orebro (Sweden). In addition, spot samples of surface water were also taken from Zhongzhou (China) and Vancouver (Canada). The selected areas were the surroundings of tap water sampling sites which included major water bodies, but some were not always their sources. Sampling was scheduled three times in Yodo Basin (Nov-04, Mar-05, Nov-05), twice in Phong Basin (Jul-05 and Jan-06), twice in Kota Kinabalu City (Aug, Sept-05 and Dec-05), once in Orebro City (Mar-06) and once Hanoi City (Jan-06). The number of samples can be referred in **Table 5**.



**Fig. 1** Sampling areas (●: spot sampling only; □: including systematic samplings of surface water)

## (2) Sampling Protocol

Glass and TEFLON materials were minimized during the whole sampling and analysis procedure because the target analytes may bind to the glass in aqueous solution and TEFLON materials may introduce the interferences. PET bottles (2L) that had been rinsed throughout were used for sampling. Whenever arriving laboratory, samples were preserved under 4°C to avoid the growth of microorganisms.

We had different protocols of pre-treatment for spot samples and systematic surveys samples. Spot samples were brought back our laboratory without any pre-treatment basically within a couple of days. In the systematic surveys except for Yodo River basin, sample pre-treatment including filtration and concentration (loading-to-cartridge step only) was conducted in laboratories of the partner Universities (Khon Kean Univ.; Univ. Sabah Malaysia; Orebro Univ.; and Hanoi Univ. of Tech.) using their Mili\_Q water and high-grade methanol. Mili\_Q water was used as a blank control. Same concentration system and cartridges taken from Japan were used for sample pre-treatment. Sample-loaded cartridges were kept cool (about 4°C) during transportation to Japan.

## 3. ANALYSIS METHOD

The analysis was to find out the concentration of dissolved PFOS and PFOA. Analysis procedure consisted of water concentration by solid phase extraction and LC-MS quantification.

### (1) Water concentration

A collected sample was firstly filtered through a glass fiber filter (WHATMAN GF/B) and about 1000 mL of the pre-filtered sample was loaded on a Presep-C Agri cartridge (WAKO, Japan) using the Sep-Pak concentration system (WATERS, Japan) at a flowrate of 10 mL/min. The cartridge was then eluted with 3 mL methanol and the collected solvent was dried under N<sub>2</sub> gas flow. Finally the sample was reconstituted with a minimum volume of 0.5 mL HPLC solvent into an extract for LC-MS quantification.

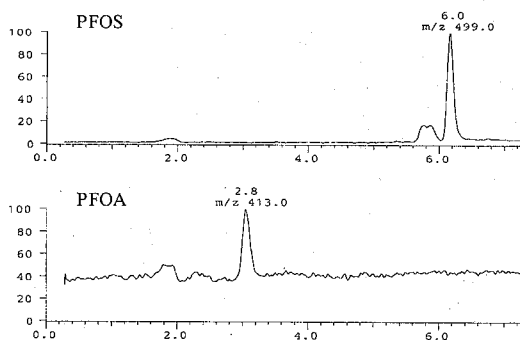
### (2) LC-MS quantification

Table 2 shows information of the instrument and optimized conditions for LC-MS operation. Extracts were chromatographed using HPLC in 14 min. Mobile phases started with 55% solvent B during the first 2 min. After that, linear gradient elution was applied by increasing solvent B to 95% for 7 min.

Finally solvent B changed back 55% during 0.5 min and isocratic elution was maintained until the end. The flow was interfaced with TSQ 7000 which applied selected ion monitoring at  $m/z = 499$  for PFOS anion (C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub><sup>-</sup>) and  $m/z = 413$  for PFOA anion (C<sub>7</sub>F<sub>15</sub>CO<sub>2</sub><sup>-</sup>). Figure 2 shows a typical LC-MS chromatogram of PFOS and PFOA. PFOS peak appeared at 6.0 min, preceded by two small peaks. PFOA was detected at 2.8 min. Quantification of PFOS and PFOA was based on standard curves of standard solution prepared in HPLC solvent.

**Table 2** Instruments and optimized conditions for LC-MS system

HPLC	
Instrument	Ultra Microprotein Analyzer
Column	Agilent Zorbax XDB C-18 (2.1x150 mm, 5mm)
Mobile phase	A: 10 mM CH <sub>3</sub> COONH <sub>4</sub> /H <sub>2</sub> O; B: CH <sub>3</sub> CN
Flow rate	0.2 mL/min
Oven temperature	30°C
Injection volume	10 mL
MS	
Instrument	TSQ 7000 (ThermoQuest, USA)
Ionization	Electrospray ionization
Polarity mode	Negative
Sheath gas	N <sub>2</sub> (70 psi)
Auxiliary gas	N <sub>2</sub> (10 mL/min)
Spray voltage	4200 V
Electron multiplier	1500 V
Capillary temperature	175°C



**Fig. 2** LC-MS chromatogram of PFOS and PFOA (blank sample spiked with 0.25 ng/L PFOS and 0.25 ng/L PFOA with 2000-time concentration)

### (3) Method validation

#### a) Calibration curves and limit of quantifications

PFOA (98% purity) and potassium salt of PFOS (95% purity) (WAKO, Japan) were used to make standard solution. Calibration curves of PFOS (PFOA) from 0.1 µg/L (0.2 µg/L) to 100 µg/L prepared in HPLC solvent were both linear with determination coefficients  $R^2 > 0.997$ .

Limit of detection was set at signal-to-noise ratio

of 3:1. Practically, the limit of quantification ( $LOQ$ ) was used for detecting analytes.  $LOQ$ , which was defined by a coefficient of variation ( $CV$ ) of less than 20%, was originally ranged from 0.05-0.1  $\mu\text{g/L}$  for PFOS and 0.1-0.2  $\mu\text{g/L}$  for PFOA, depending on day of operation. Actual  $LOQ$  was calculated based on the concentration factor, which resulted in 0.025-0.05  $\text{ng/L}$  for PFOS and 0.05-0.1  $\text{ng/L}$  for PFOA in case of 2000-fold concentration.

#### b) Extraction efficiency and recovery

Extraction efficiency experiment was conducted by spiking PFOS and PFOA in Milli-Q water at six different concentrations of 0.5, 1, 5, 10, 50 and 100  $\text{ng/L}$ . These samples were prepared, concentrated and quantified according to the procedure mentioned above. They were calibrated against the calibration curves prepared in HPLC solvent.

Spiking of analytes into environmental samples was conducted in order to investigate the recovery. Tap water samples (a sample in Takatsuki, a sample in Kyoto), and surface water samples (a sample in Yamashina River, a sample in Kizu River, a sample in Yodo River) were spiked with 2, 5, 10, 1, 2  $\text{ng/L}$  of PFOS and 40, 5, 50, 20, 10  $\text{ng/L}$  of PFOA respectively.

## 4. RESULTS AND DISCUSSION

### (1) Analysis results

#### a) Extraction efficiency and recovery

Extraction recovery of analytes in Milli-Q water ranged from 96%-109% for both PFOS and PFOA. The extraction standard curves, for the concentration ranged from 0.5-100  $\text{ng/L}$  for each analyte, were also linear with good determination coefficients ( $R^2 > 0.99$ ).

**Table 3** Analysis results of quality control samples

	PFOS	PFOA
Number of samples	5	5
Field sample concentrations ( $\text{ng/L}$ )	0.8, 2.0, 2.8, 2.7, 5.9	6.7, 18.4, 28.3, 37.1, 42.6
Spiking concentration ( $\text{ng/L}$ )	1, 2, 2, 5, 10	5, 20, 20, 40, 50
Recovery (%)	$87 \pm 14$	$95 \pm 20$

**Table 3** shows the recovery results of environmental samples for several tap water and surface water samples. The mean recovery was 87% and 95% for PFOS and PFOA respectively. In addition, for all systematic surveys, blank control measurement was conducted. Neither of PFOS or PFOA was detected in any of blank controls, which indicated that no contamination happened during sampling and pre-treatment.

#### b) Concentrations in tap water

**Table 4** shows the results of tap water analysis. PFOA was detected in all 18 samples collected in Japan, while PFOS was detected in 16 samples. The concentration ranged from less than  $LOQ$ s to 13  $\text{ng/L}$  for PFOS and 109  $\text{ng/L}$  for PFOA. The highest PFOS concentration, which was found in Kunming tap water, was lower than that in tap water of Tama River basin (Japan)<sup>10</sup>. However, maximum PFOA concentration of 109  $\text{ng/L}$ , found in Hangzhou, was the highest level in tap water reported up to now<sup>9</sup>. PFOS and PFOA concentration in tap water of Osaka City has been reported at 12  $\text{ng/L}$  and 40  $\text{ng/L}$  respectively<sup>9</sup> while we found the corresponding concentrations (mean values) of 1.9  $\text{ng/L}$  and 36  $\text{ng/L}$  in Takatsuki City. Both tap water in Osaka City and Takatsuki City were taken from Yodo River. Among collected samples in Japan, those in Osaka had highest PFOA concentrations. Both PFOS and PFOA were scarcely detected in collected tap water samples in Penang and Kota Kinabalu (Malaysia), Hanoi (Vietnam) and Calgary and Vancouver (Canada).

#### c) Concentrations in surface water

**Table 5** shows a summary of PFOS and PFOA concentration in surface water. Mean concentrations of both PFOS and PFOA in Yodo River basin were significantly higher than those in the other areas ( $p < 0.001$ ,  $t$ -test). The geometric means (geometric standard deviation) of concentration in Yodo River were 3.5  $\text{ng/L}$  (2.8) and 33  $\text{ng/L}$  (2.9) for PFOS and PFOA respectively, while Saito *et al.* (2004) reported corresponding values of 5.7  $\text{ng/L}$  (3.6) and 21  $\text{ng/L}$  (2.3) in Kinki area. The concentrations in the other areas (Phong basin, Kota Kinabalu City, Orebro City, Hanoi City, except Hangzhou for PFOA) were generally less than 5  $\text{ng/L}$  for PFOS and 10  $\text{ng/L}$  for PFOA with the geometric standard deviation of not larger than 1.2 (3.0) for PFOS (PFOA). A surface water sample in Hangzhou was collected from the West Lake, a famous fresh water lake located in central of the City.

### (2) Reproducibility of concentrations

Multiple sampling of tap water was conducted in Shiga, Osaka, Kyoto, Okayama, Shenzhen, Kota Kinabalu, Orebro, Khon Kean, and Hanoi. As shown in **Table 4**, within a sampling area, similar concentrations could be observed. Standard deviations of concentration were below 2  $\text{ng/L}$  for PFOS and 6  $\text{ng/L}$  for PFOA. **Figure 3** shows that fluctuations of concentration within an area were less significant for higher concentrations.

For surface water, repeated sampling was conducted in Yodo River basin, Phong River basin

and Kota Kinabalu. **Figure 4** illustrates differences of the concentrations. Variations were observed but generally limited within one order magnitude. The reproducibility of concentration, therefore, confirmed the contamination levels regardless the seasonal effect. This also indicates that time could be a less important factor for the levels of PFOS and PFOA than the location.

### (3) Relationship of tap water and surface water

#### concentration

Since there was reproducibility of PFOS and PFOA concentration in both tap water and surface water as discussed the above, it would be meaningful to use mean concentrations as representative values for evaluating relation between tap water and surface water contamination. **Figure 5** shows the relationship of tap water and surrounding surface water concentration. The figure depicts positive linear relationships ( $R^2$  equal 0.93 for PFOA and

**Table 4** PFOS and PFOA concentrations in collected tap water samples

Sample Identification			PFOS (ng/L)	PFOA (ng/L)	Sampling Date	Sample Identification			PFOS (ng/L)	PFOA (ng/L)	Sampling Date
Japan	Hokkaido	Sapporo	0.1	0.6	Aug-05	Canada	Alberta	Calgary	-	0.2	Sep-05
	Hyogo	Nishinomiya	-	0.3	Aug-05		BC	Vancouver	-	0.2	Sep-05
	Kagawa	Kotohira	6.8	3.1	Oct-05	China	Shenzhen	Site 1	6.5	3.1	Oct-05
	Kyoto	Sakyo	0.9	6.7	Aug-05		(Guangdong)	Site 2	6.2	2.3	Oct-05
		Yamashina	2.0	15.2	May-06			Site 3	9.9	1.1	Jan-06
	Miyagi	Sendai	0.4	1.2	Mar-06		Yunnan	Kunming	13.2	1.1	Oct-05
	Nara	Yamato	0.1	1.3	Aug-05		Zhejiang	Hangzhou	1.5	109.0	May-06
		-Koriyama				Malaysia	Penang		-	-	Nov-05
	Okayama	Kurashiki	0.6	4.2	Oct-05		Kota Kinablu	Site 1	0.1	0.1	Aug-05
		Okayama	0.1	7.5	Oct-05			Site 2	-	-	Sep-05
	Osaka	Takatsuki	1.9	34.3	Aug-05			Site 3	-	-	Sep-05
		Takatsuki	2.0	37.0	May-06			Site 4	-	-	Nov-05
		Takatsuki	1.9	37.5	May-06	Sweden	Orebro	Site 1	0.3	1.3	Mar-06
	Shiga	Otsu	1.5	8.3	Jul-05			Site 2	0.8	-	Mar-06
	Otsu	-	9.5	Dec-05	Thailand	Bangkok	Site 1	1.9	4.6	Dec-05	
	Otsu	2.5	13.9	May-06		Khon Kean	Site 1	0.2	3.4	Jul-05	
Tokyo	Tokyo	2.7	6.7	May-06			Site 2	0.1	0.2	Jan-06	
Tottori	Tottori	0.1	0.7	Nov-05			Site 3	0.1	-	Jul-05	
Yamagata	Yamagata	0.6	1.1	Mar-06	Vietnam	Hanoi	Site 1	-	-	Jan-06	
							Site 2	-	-	Jan-06	

Note: - : concentration less than LOQ

**Table 5** Statistical description of PFOS and PFOA surface water concentrations

		PFOS Concentration (ng/L)							PFOA Concentration (ng/L)						
Total Sampling Site	Total Sample (N)	Detected Sample /N	Max	Min	GM	Median	GSD		Detected Sample /N	Max	Min	GM	Median	GSD	
Yodo	28	60/60	111.0	0.4	3.5	3.4	2.8		60/60	710.3	4.2	33.4	31.0	2.9	
Phong	29	32/46	1.1	-	0.2	2.1	0.2		36/46	8.8	-	0.8	0.7	2.6	
Kota Kinabalu	21	20/30	3.4	-	0.5	4.0	1.1		15/30	3.2	-	0.7	0.5	2.7	
Orebro	16	14/16	4.6	-	1.2	1.9	1.2		8/16	5.5	-	1.7	2.0	2.3	
Hanoi	12	6/12	1.3	-	0.3	2.5	0.4		10/12	6.6	-	1.1	1.2	3.0	
Hangzhou	1	1/1				1.6			1/1			82.7			
Vancouver	1	1/1				0.1			1/1			0.8			

Notes: - : concentration less than LOQ; GM: geometric mean; GSD: geometric standard deviation (calculated based on detected sample only); for Phong River basin, one exceptionally high concentration of PFOA (473 ng/L) was excluded.

0.81 for PFOS). Low concentrations in tap water of Phong River basin, Kota Kinabalu, Hanoi were in accordance with low surface water concentrations there. High PFOA concentrations of tap water samples taken in Yodo River basin and Hangzhou might be related with the observed concentration in the surface waters, which were in the same levels. Although, the surrounding surface water of an area might not always be tap water source, the main observation was that the contamination levels in tap were similar to those in surface water.

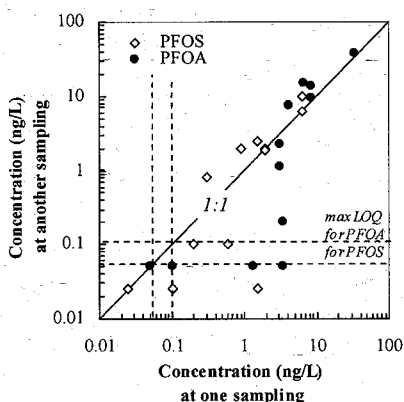


Fig. 3 Comparison of tap water concentration in the same areas

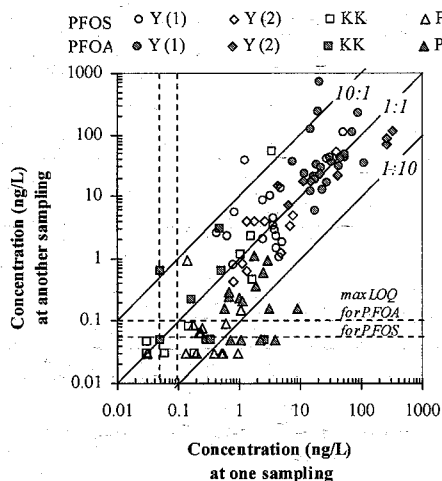


Fig. 4 Comparison of surface water concentrations of PFOS (white) and PFOA (grey) among different sampling periods in two axes. (Yodo Basin: (Y) (1): Mar-05 vs. Nov-05, (2): Nov-04 vs. Nov-05; Phong Basin (P): Jul-05 vs. Jan 06; and Kota Kinabalu (KK): Aug., Sept.-05 vs. Jan 06).

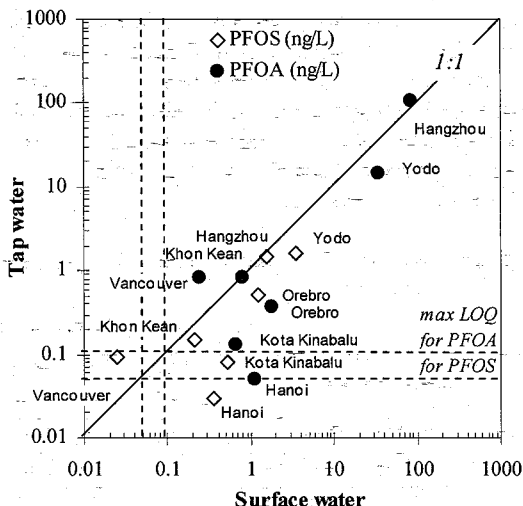


Fig. 5 Mean concentrations of PFOS (white) and PFOA (grey) in tap water against those in surrounding surface water.

#### (4) Tap water contamination in Kinki District (Japan)

Lake Biwa and Yodo River provide water source for about 14 million people in Kinki area. **Figure 6** shows the map of surface water sampling sites whose water could represent the source of tap water. **Figure 7** depicts mean concentrations in tap water samples and in surface samples. Tap water in Otsu and Kyoto depends only on Lake Biwa, and that in Takatsuki does on Yodo River. These concentrations are similar to those of their sources. Yamato-Koriyama, which is not far from these cities geologically but uses a different river system (Yamato River) for its tap water, had completely different levels of PFOS and PFOA from the above cities. Nishinomiya tap water partially depends on Yodo River, but the PFOS and PFOA concentrations were quite lower than those of Yodo river. This may mean that Yodo River was a minor source of the tap water at the date and place sampled. As a conclusion, higher concentration of tap water in Otsu, Kyoto and Takatsuki might be mostly related to contamination of Lake Biwa and Yodo River.

PFOA concentrations were several times higher than PFOS concentrations in tap water of Otsu, Kyoto, Takatsuki. This is corresponding to what is generally found for the basin surface water. Elevated PFOA concentration was noticed in downstream of Yodo River compared to that of upstream Lake Biwa water. As the results, PFOA concentrations in tap water from Takatsuki were higher than those in upstream basin (Kyoto and Otsu).

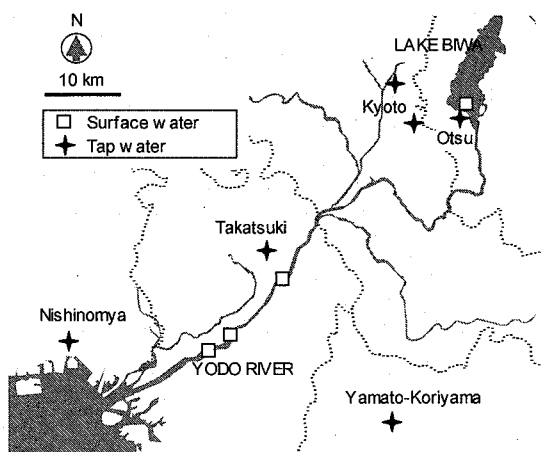


Fig. 6 Sampling sites in Kinki District that are discussed in Fig. 7

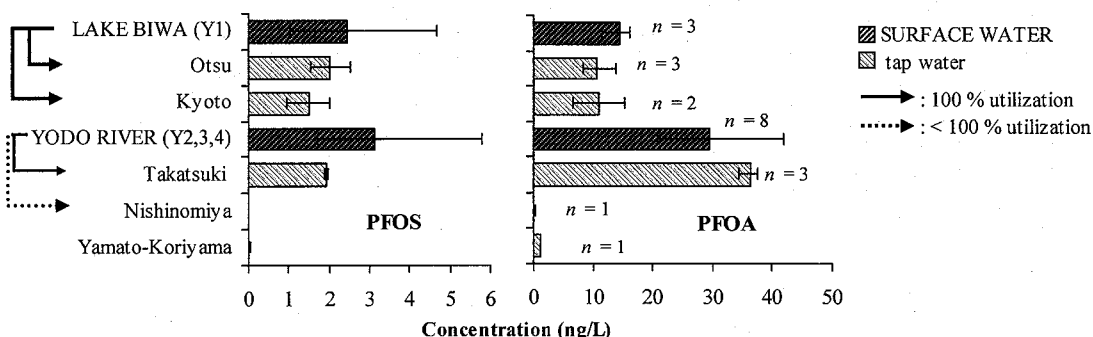


Fig. 7 PFOS and PFOA concentrations of surface water and tap water samples collected from several sites in Kinki District

Research on removal of PFOS and PFOA at trace level of concentration in water was not available. Takatsuki tap water was mainly supplied from a water purification plant which uses the ozone contact followed by activated carbon adsorption as the final processes before distribution. The advanced treatment process might have some limitations of removing the contaminants from water source.

## 5. CONCLUSIONS

This is the first report in the world concerning PFOS and PFOA concentration in tap water in several countries other than Japan, and the relation with that in surface water. The surveys of tap water and surface water contamination were conducted in certain areas of Japan, Thailand, Malaysia, Sweden, Vietnam, China and Canada. It is concluded that:

(1) Most of collected tap water samples were contaminated with PFOS and PFOA with the concentrations ranged from the limit of quantification levels to 13 ng/L for PFOS and 109 ng/L for PFOA.

(2) The level of tap water concentrations was generally related to the level of surrounding surface water concentrations whether the source of tap water was the surface water or not.

(3) In Japan, tap water PFOA concentrations were relatively high in Biwako-Yodo River area (Otsu, Kyoto, Osaka), mostly due to its contamination of Lake Biwa and Yodo River.

Further study is needed to investigate how up-to-date technology of water purification processes can effectively remove the PFOS and PFOA from water source.

## 6. ACKNOWLEDGEMENT

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