

Pollution of perfluorooctanoate and perfluorooctane sulfonate in surface water in Japan and China

Sasaki K¹, Saito N¹, Jin Y², Harada K³, Inoue K³, Koizumi A³

¹Research Institute for Environmental Science and Public Health of Iwate Prefecture, Morioka 020-0852, Japan ; ² Dalian University of Technology, School of Environmental and Biological Science and Technology, No.2 Liggong Load Dalian 116024,China ; ³Kyoto University Graduate School of Medicine, Yoshida Kyoto 606-8501, Japan

Abstract

Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are synthetic surfactants used in a variety of industrial applications. We analyzed their concentrations in surface water samples collected from all over Japan and China by LC/MS in combination with a solid phase extraction method. The quantification of surface water samples collected from Japan showed surface water contamination with PFOA and PFOS. The concentration level of PFOA and PFOS at Tokyo bay which was measured by our research, was correspondent to the result by Odaka and Masunaga¹. Both PFOA and PFOS concentrations were greater in Kinki district than in other districts. Systematic searches of Yodo River and Kanzaki River revealed two highly contaminated sites, a public-water-disposal site for PFOA and an airport for PFOS. In addition, our result of PFOS and PFOA concentration for the Yangtze River in China, were got higher level of concentration than previous report². Moreover, PFOA and PFOS concentration levels in surface water samples collected from China were in almost the same order as the samples from Japan. The present study confirms that these material pollutions diffused widely in China that facilitates industrialization rapidly in recent years.

Introduction

PFOA and PFOS are synthetic surfactants widely used as fire retardants, surface coating materials and synthetic materials and are known as a new class of persistent organic pollutants. We have recently developed a robust, yet simple and sensitive method that enables the determination of trace concentrations of PFOA and PFOS at the pg/ml levels in surface waters by LC/MS³. This method was applied to the determination of PFOA and PFOS in surface water samples collected from various geographic locations around Japan and China.

The major aims of the present study were two-fold. First, PFOA concentrations were determined in surface waters in Japan and China to provide a nation-wide profile of PFOA concentration levels. The second aim was to find source of PFOA, which are associated with geographic difference in PFOA concentration levels. Identified source would suggest a large industrial production of PFOA or other related materials as well as environmental leakages in specific areas. In the present study, PFOS levels were also determined to delineate differences in the contamination profiles between PFOA and PFOS.

Materials and Methods

Standards

Perfluorooctanoic acid (98% purity) was obtained from Wako Pure Chemicals and potassium salt of PFOS (98% purity) was obtained from Fluka. LC/MS-grade methanol was purchased from Wako Pure Chemicals. Presep-C Agri (Short) 200mg cartridges column were also purchased from Wako Pure Chemicals.

Solid phase extraction

Two-L of each of the surface water samples were collected from all over Japan and China. We split a two-L sample into one-L preparations. Individual one-L preparations were processed separately. First, they filtered through a glass fiber filters

(ADVANTEC GA 100, ADVANTEC, Tokyo, Japan) to remove sediments and biota. Samples were passed through a Presep-C Agri (Short) 200mg cartridge column using a Waters Concentrator System (Concentrator Plus, Waters, Tokyo, Japan). Presep-C Agri (Short) cartridges were then eluted with 2mL of methanol and concentrated at room temperature under nitrogen gas flow to 1mL for LC/MS analysis.

LC/MS and quantification

The methanol extracts (10 µL injection volume of the 1mL extract) were chromatographed by HPLC at a flow rate of 0.2mL/min. We employed gradient conditions in the mobile phase: the concentration of CH₃CN (A) in 10mM CH₃COONH₄ buffer (B) started at 35%, then increased to 45% at 2% /min for 5min, and was then maintained at 45% until 20min. The column(Zorbax XDB C-18) temperature was maintained at 40 . Mass spectra were taken on an LC/MS system (Agilent 1100MSD SL) equipped with on orthogonal spray interface, employing electro-spray ionization in the negative mode. The fragmentor voltages were 100V for PFOA and 200V for PFOS and V cap voltages were 4000V for both analytes. The selected ion-monitoring (SIM) mode was employed for quantification of analytes.

The ions for PFOA ion 413(C₇F₁₅CO₂⁻) and for PFOS ion 499(C₈F₁₇SO₃⁻) were monitored for quantification. To avoid interference and ensure complete selectivity, the fragment ions for PFOA ion 369(C₇F₁₅⁻) and for PFOS ion 99(FSO₃⁻) were also monitored.

Results and Discussion

Determination of PFOA and PFOS in surface waters in Japan

The concentrations of PFOA and PFOS in surface water samples from rivers and seas collected from all over Japan (Fig.1) were determined and the results are summarized in Table 1.

Both PFOA and PFOS concentrations were greater in Kinki district than in other districts. The coastal sea water samples also showed: the PFOA and PFOS concentrations were highest in the Koshien Coast (Hyogo). The concentration level of PFOA and PFOS at Tokyo bay which was measured by our research, was correspondent to the result by Odaka and Masunaga¹⁾.

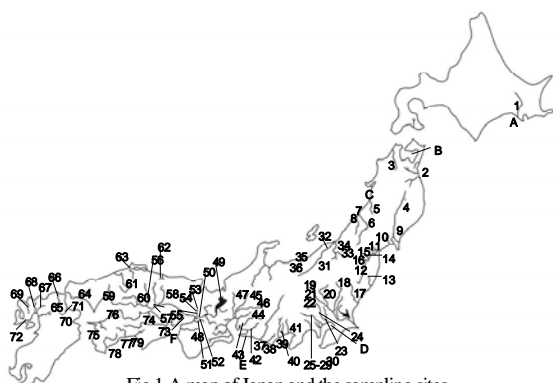


Fig.1 A map of Japan and the sampling sites

Table 1 PFOA and PFOS concentration levels in surface waters in Japan

| Area | n | PFOA (ng/L) | | | PFOS (ng/L) | | |
|-------------------|----|---------------|------|--------------|---------------|------|--------------|
| | | GM | GSD | Range | GM | GSD | Range |
| Hokkaido - Tohoku | 16 | 0.97 | 3.06 | 0.10 4.22 | 1.19 | 2.44 | 0.25 4.62 |
| Kanto | 14 | 2.84 | 3.56 | 0.33 - 15.08 | 3.69 | 3.93 | 0.33 - 31.42 |
| Chubu | 17 | 2.50 | 2.23 | 0.28 - 16.28 | 1.07 | 2.36 | 0.24 6.04 |
| Kinki | 8 | 21.15** | 6.16 | 2.14 - 456.4 | 5.73** | 3.61 | 0.78 - 37.32 |
| Chugoku | 9 | 1.51 | 2.28 | 0.51 8.11 | 1.00 | 3.42 | 0.42 25.1 |
| Kyusyu Shikoku | 15 | 1.93 | 2.4 | 0.20 - 13.82 | 0.89 | 3.09 | 0.24 - 14.86 |

** : Significantlv higher than other areas by ANOVA (nc0.01)

Sources of PFOA and PFOS concentration in the Osaka area

To search for the sources of PFOA, we systematically collected surface water samples from the Yodo River and the Kanzaki River. The Yodo River runs from Lake Biwa to Osaka Bay. The PFOA concentration was high along the shoreline of Osaka Bay. The concentrations increased along the Kanzaki and the Ai River., reaching a maximum at the mouth of the Aigawa Ryuiki water disposal site, where 67,000ng/L of PFOA was recorded. The total PFOA discharged from this site was estimated to be 18kg/day.

PFOS concentrations in the Yodo River were elevated at water discharge site. A systematic search revealed the source of the PFOS contamination, suggesting a source at the airport.

Tap water contamination levels in Osaka area
 Several cities received water from the Yodo River. The water supply for the Hanshin area is a mixture from various sources of water including the Yodo River. In contrast, Osaka city derives its water supply mostly from the Yodo River. The contaminations of PFOA and PFOS are summarized in Table2. PFOA and PFOS were highest in the tap water in Osaka city. PFOA concentrations, in particular, were significantly higher than in other cities.

The quantification of surface water samples collected from all over Japan showed surface water contamination with PFOA and PFOS. We found a large geographical difference in their levels.

Determination of PFOA and PFOS in surface waters in China

The concentrations of PFOA and PFOS in surface water samples from rivers and lakes collected from all over China (Fig.3).

We were determined and the results are summarized in Table 3. The quantification of surface water samples collected from all over China showed surface water contamination with PFOA and PFOS. Moreover, the concentrations of PFOA and PFOS in surface water samples from the Yangtze River were determined and the results are shown in Fig.4-5. In this research, we were added the sampling points between Chongqing and Yichang in the Yangtze River as shown in Fig.4-5, and then our results were got the higher levels of the concentrations (PFOS 37.8ng/L, PFOA 298ng/L) than previous report (PFOS < 0.01 ~ 0.82ng/L, PFOA 2.0 ~ 35ng/L)². This result indicates us that there are some of specific pollution sources between Chongqing and Yichang.

The concentrations of PFOA and PFOS levels in surface water samples from China were in almost the same order as the samples from Japan. The present study confirms that these material pollutions diffused widely in China that facilitates industrialization rapidly in recent years.

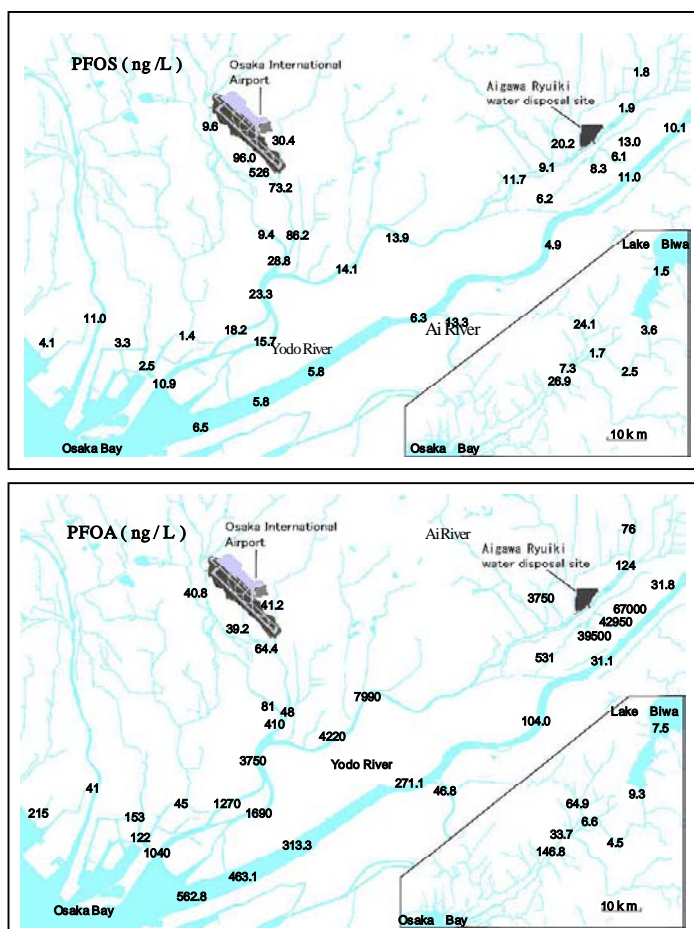


Fig.2 PFOA and PFOS concentrations in rivers in the Osaka area

Table 2 PFOA and PFOS concentration levels in tap water

| District | Prefecture | Local Area | n | PFOA (ng/L) | | PFOS (ng/L) | |
|------------|------------|--------------|---|-------------------|-----|-------------------|-----|
| | | | | GM | GSD | GM | GSD |
| Osaka area | Hyogo | Hanshin Area | 5 | 12.5 ^B | 1.6 | 1.1 ^B | 4.3 |
| | Osaka | Osaka city | 5 | 40.0 ^A | 1.1 | 12.0 ^A | 1.1 |
| | Kyoto | Kyoto City | 5 | 5.4 ^{0C} | 1.5 | 4.9 ^A | 2 |
| Tohoku | Iwate | Morioka City | 5 | 0.7 ^{0D} | 1.5 | 0.2 ^B | 2 |
| | Miyagi | Sendai City | 5 | 0.13 ^E | 1.3 | <LODB | - |
| | Akita | Yokote City | 5 | 0.12 ^E | 1.2 | <LODB | - |

Hanshin Area : Amagasaki City and Kobe City
 Superscript letters indicated the results of Scheffe test after ANOVA. The same superscript letters is not significantly different while the different letters indicate significant differences (p<0.05). Concentrations less than LOD was assumed 0.1 ng/L for calculations.

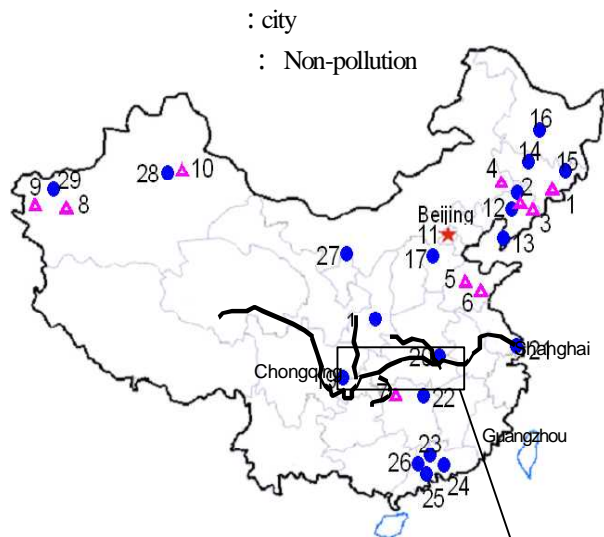


Fig.3 A map of China and the sampling sites

Table 3 PFOS and PFOA concentrations in surface waters in China

| a) River water | | | | |
|----------------|--|-------------------------|-------------|-------------|
| No. in the map | Province or municipality directly under the Central Government | Sample collecting site | PFOS (ng/L) | PFOA (ng/L) |
| 2 | Liaoning | South Canal | 6.2 | 1.4 |
| | | Weigongming Channel (1) | 5.4 | 2.9 |
| | | Weigongming Channel (2) | 6.0 | 3.0 |
| | | Xinkai River | 2.7 | 4.1 |
| | | Nanyun Canal | 0.8 | 1.7 |
| 3 | Liaoning (Berxi city) | Taizi River | 0.6 | 0.3 |
| 5 | Shandong (Jinan city) | Huanghe River | 1.7 | 1.1 |
| 11 | Beijing | Yongding River | 0.8 | 3.7 |
| 15 | Jilin (Tumen city) | Tumen River | 0.7 | 7.8 |
| 22 | Hunan (Changsha city) | Xiang River | 6.6 | 12.6 |
| 23 | Ghangdong (Guangzhou) | Zhujiang (1) | 14.1 | 13.2 |
| 23 | | Zhujiang (2) | 10.4 | 14.3 |
| 23 | | Zhujiang (Estuary) | 5.7 | 6.2 |
| 24 | Changdong (Shenzhen) | Shenzhen River | 10.2 | 30.8 |
| 26 | Changdong (Zhongshan) | Qijiang River | 6.3 | 5.8 |

(Geo. mean \pm Geo. SD): PFOS; (1.79 \pm 2.70), PFOA; (4.63 \pm 2.44)

| b) Lake water | | | | |
|---------------|------------------------|------------------------|-------------|-------------|
| No. | | Sample collecting site | PFOS (ng/L) | PFOA (ng/L) |
| 2 | Liaoning (Shenyang) | Beiling Park | 1.7 | 15.1 |
| 5 | Shandong (Jinan city) | Daming Lake | 4.2 | 3.0 |
| 11 | Beijing | Beihai | 1.2 | 3.2 |
| | | Kuming Lake | 0.8 | 1.2 |
| 12 | Liaoning (Anshan city) | 12.9 Park | 0.4 | 6.6 |
| 20 | Hubei (luhan city) | Dong Lake | 3.8 | 3.3 |
| 24 | Guangdong (Zhuhai) | Hong Lake | 6.0 | 12.2 |

(Geo. mean \pm Geo. SD): PFOS; (3.35 \pm 3.02), PFOA; (4.16 \pm 3.30)

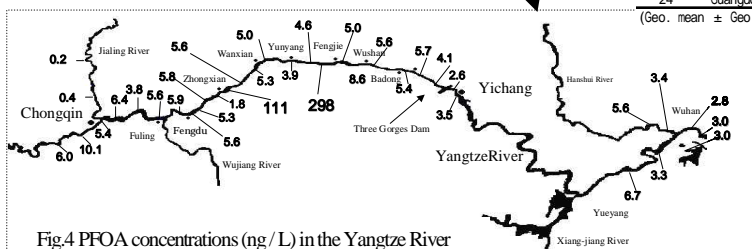


Fig.4 PFOA concentrations (ng/L) in the Yangtze River

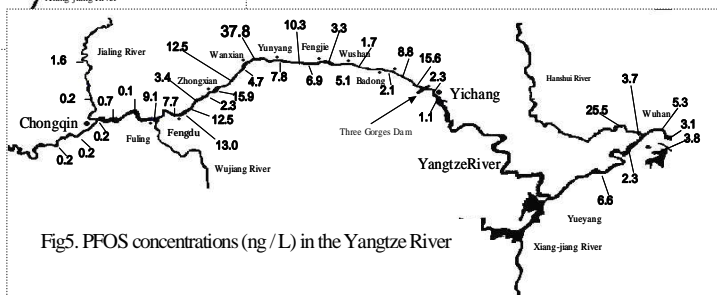


Fig5. PFOS concentrations (ng/L) in the Yangtze River

Acknowledgements

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References

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