A MASS BALANCE OF PERFLUOROOCTANE SULFONATE AND PERFLUOROOCTANOIC ACID IN THE TAMA RIVER, TOKYO

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Abstract

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were measured at 21 sites in the Tama River basin. Site E was especially characterized by high concentration of PFOS, and its composition reached approximately 97%. Considering the flow rate and PFOS concentration in the site U that is located the most downstream among the investigated sites, it was cleared that the site E strongly contributed to the PFOS pollution from wastewater treatment plants (WWTPs) in the Tama River. On the other hand, high contribution of PFOA was found in the site F, and PFOA was detected with 120 micro g/sec as pollution loading amount ([pollution loading amount] = [flow rate]*[concentration]). Samples of both sites are effluents of WWTPs; therefore, it may be assumed that PFOS and PFOA are present in wastewater with high concentration as well as other chemicals such as linear alkylbenzenesulfonate and nonyl phenol. A balance of the Tama River's flow was satisfactory, and we estimated a mass balance of PFOS and PFOA in the Tama River.

Introduction

Some fluorinated alkyl compounds are used for industrial purposes, such as in surface-active and fire-extinguishing agents, and also for producing water-repelling and antifouling coatings that exploit the chemical properties of the fluoro groups that remain on the processed surfaces.[1]. Perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoic acid (PFOA, $C_7F_{15}CO_2^-$) are believed to be the final decomposition products of fluorinated alkyl compounds, and studies have been conducted on the route through which people are exposed to these compounds and the mechanisms by which they contaminate the environment. Persistent organic pollutants (POPs) and other chlorinated organic compounds are highly soluble in lipids, and are only slightly soluble to water, and thus readily accumulate in the lipids of organisms. On the other hand, PFOS and PFOA are both water-repelling owing to their perfluoro groups and water-soluble due to their functional groups, suggesting that they should be easily removed from the bodies of organisms. However, PFOS and PFOA accumulate in organisms and are thus likely to have a unique accumulation mechanism that is different from those of other environmental pollutants. The aquatic environment appears to be an important route via which PFOS and PFOA are discharged to the environment. Possible routes of contamination include sewage and the contamination of underground water by PFOS and PFOA in the soil. Foam fire-extinguishing agents used at airports and the hydraulic oil used in aircraft have also been reported to contain PFOS, and actual contamination by PFOS has been detected in accidental release of fire-extinguishing agents.[2,3] Thus, PFOS and PFOA concentrations in the aquatic environment need to be continuously monitored, and effective measures for controlling pollution sources should be drawn up to limit contamination.

In this study, the actual states of PFOS and PFOA contamination were monitored in the Tama River basin in Tokyo, where diverse types of industries are concentrated and the population density is high. Further, we tried estimating a mass balance of PFOS and PFOA by using the flow rate and the concentration obtained from each site.

Materials and Methods

Methanol and acetonitrile were of HPLC grade available (Wako Pure Chemical Industries, Osaka, Japan) and were used without further purification. Ammonium acetate for LC/MS was of molecular biology grade available. PFOS potassium salt (98%) and PFOA (98%) were purchased from ABCR GmbH & Co. KG (Germany). Authentic $^{13}C_4$ labeled PFOS and $^{13}C_4$ labeled PFOA were purchased from Wellington Laboratories Inc. (Ontario, Canada). Purified water was obtained by passage through a Milli-Q® water purification system (Gradient A10, Nihon Millipore, Tokyo, Japan).

We collected samples of surface river water (the depth: 20 cm) in the Tama River on November 2005 (Fig. 1). Two liters of samples were collected from each location by using a stainless steel bucket which was pre-cleaned by rinsing with methanol and purified water. Samples were stored at 5°C in two polypropylene bottles (1 L). All

Teflon®-containing laboratory materials were avoided during the experimental and sampling procedures to prevent possible contamination of the samples. The flow rate was also measured at each site.
All samples including $^{13}C_4$ labeled PFOS (2 ng) and PFOA (2 ng) were extracted using OASIS® HLB plus cartridge (Waters Corp., Milford, USA). The cartridge was firstly pre-conditioned by passing through the cartridge in the sequence of 3 ml of methanol and 3 ml of purified water. One liter of samples was passed through the pre-conditioned cartridge at a rate of 10 mL/min. PFOS and PFOA were eluted with 3 ml of methanol/purified water (1:1 v/v). The eluate was evaporated and replaced with 1 ml of acetonitrile-water (40:60 v/v). This extract passed through a nylon mesh filter (0.2 μm) into a polypropylene vial for LC/MS. Ten μl of extract was injected onto a ZORBAX Eclipse XDB-C18 column (150 mm length, 2.1 mm i.d., 3.5 μm particle size; Agilent Technologies Inc., Palo Alto, USA) with a 10 mM ammonium acetate/acetonitrile mobile phase at a flow rate of 0.2 mL/min. The column was maintained at 40°C. Quantitative analyses were performed by using LC/MS/MS (Applied Biosystems Japan Ltd., Tokyo, Japan) equipped with an 1100 series liquid chromatograph (Agilent Technologies Inc., Palo Alto, USA), and the mass spectrometer operated in the electrospray ionization under negative mode. The ionspray voltage, nebulizer gas pressure, turbo gas pressure, and ion source temperature were held -4500 V, 40 psi, 80 psi, and 400°C, respectively. For PFOS analysis, declustering potential (DP) and collision energy (CE) were maintained at -105 V and -86 eV, respectively. For PFOA analysis, DP and CE were maintained at -35 V and -16 eV, respectively.

Results and Discussion

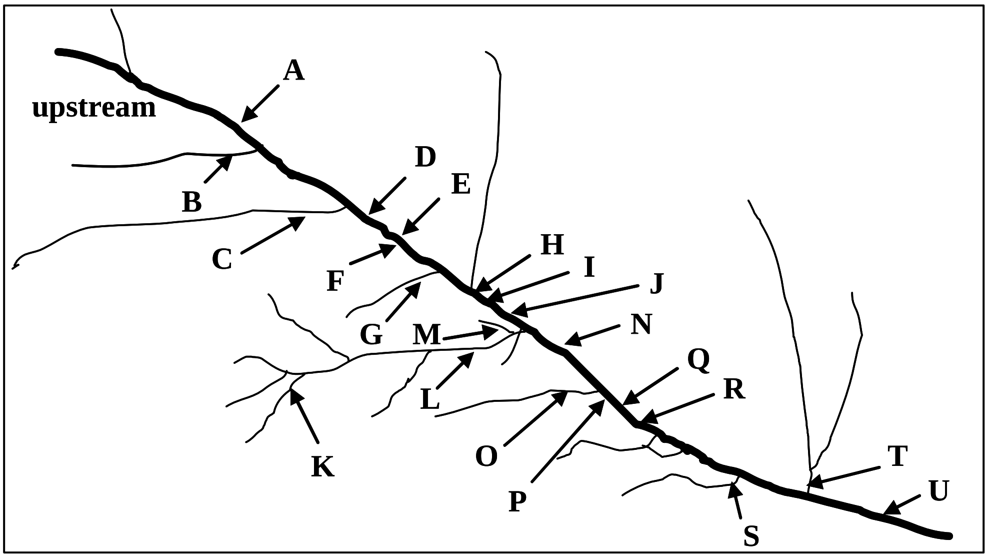

Fig. 1 Map of the Tama River (bold line) showing sampling sites

Twenty-one sampling sites were composed of “effluent of wastewater treatment plant (WWTP, 7 sites: E, F, H, J, M, P, and Q)”, “major branches (2 sites: C and L)”, “minor brunches (6 sites: B, G, K, O, S, and T)”, and “mainstream of the Tama River (6 sites: A, D, I, N, R, and U)”. The sampling frequency a day was 2 times in WWTP and minor branches. The frequency for major branches and mainstream was 3 or 4 times a day. Figure 2 indicates average pollution loading amounts of PFOS and PFOA in each sampling time. The sum of PFOS and PFOA was remarkable in the Site E, I, N, R, and U; PFOS was dominant. Judging from the PFOS amount of Site U that is located in the most downstream among the investigated sampling sites in the Tama River, the release of PFOS in the Site E (effluent of WWTP) strongly contributed to overall PFOS pollution in this river. As seen in Fig. 3, we notice that the Site E possesses a high PFOS ratio (> 97%) compared with other sites. On the other hand, Site F corresponding to effluent of WWTP provided the high contribution of PFOA, and the relative composition of PFOA reached 79%. It follows from this that difference of relative composition between Site E and F is reflected in characteristics of WWTPs.

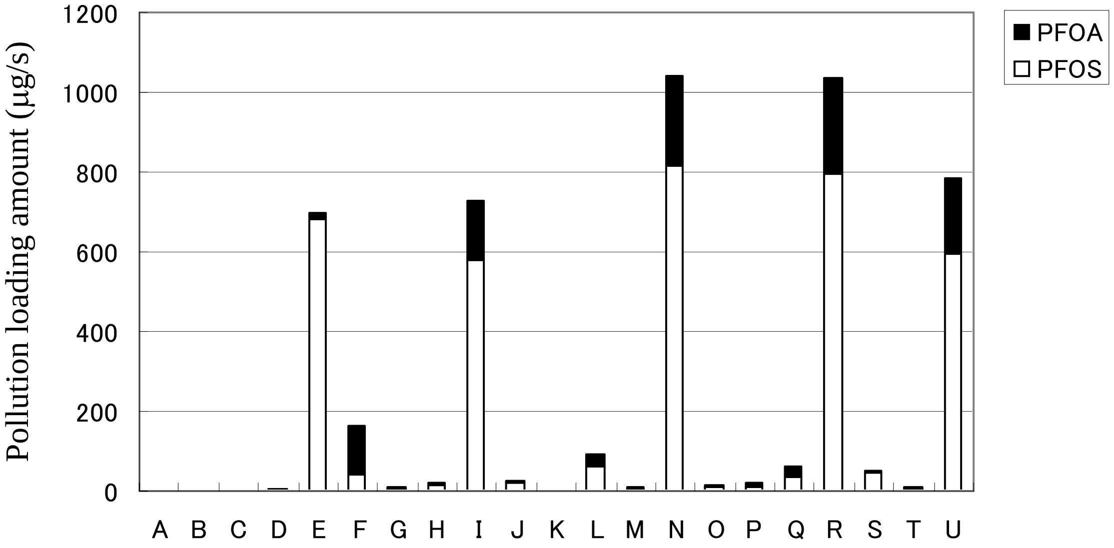

Fig. 2 Pollution loading amount of PFOS and PFOA

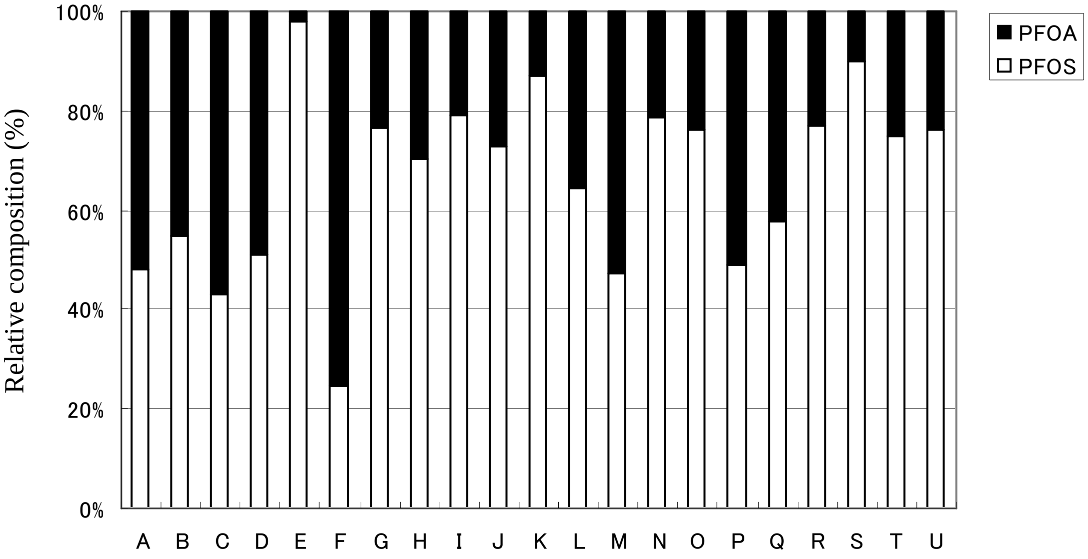

Fig. 3 Relative composition of PFOS and PFOA

A mass balance of PFOS and PFOA is shown in Fig. 4. We compared the contribution of PFOS and PFOA between WWTPs and the Tama River's branch. As a result, the release from WWTPs was dominant, and the total amounts of PFOS and PFOA from WWTPs were calculated as 800 micro g/sec and 190 micro g/sec, respectively; on the other hand, PFOS and PFOA flowed into the Tama River from the Tama River's branches were 130 micro g/sec and 48 micro g/sec, respectively. On the Tama River's branches, PFOS and PFOA were detected in Site L and S, and Site L also showed the high contribution of PFOA. Therefore, the sum of amounts of WWTPs and branches reached 930 micro g/sec for PFOS and 240 micro g/sec for PFOA. Inflow load amounts to Tokyo Bay from the Tama River calculated by the amounts in Site U were estimated as 51.8 g/day for PFOS and 16.4 g/day for PFOA.

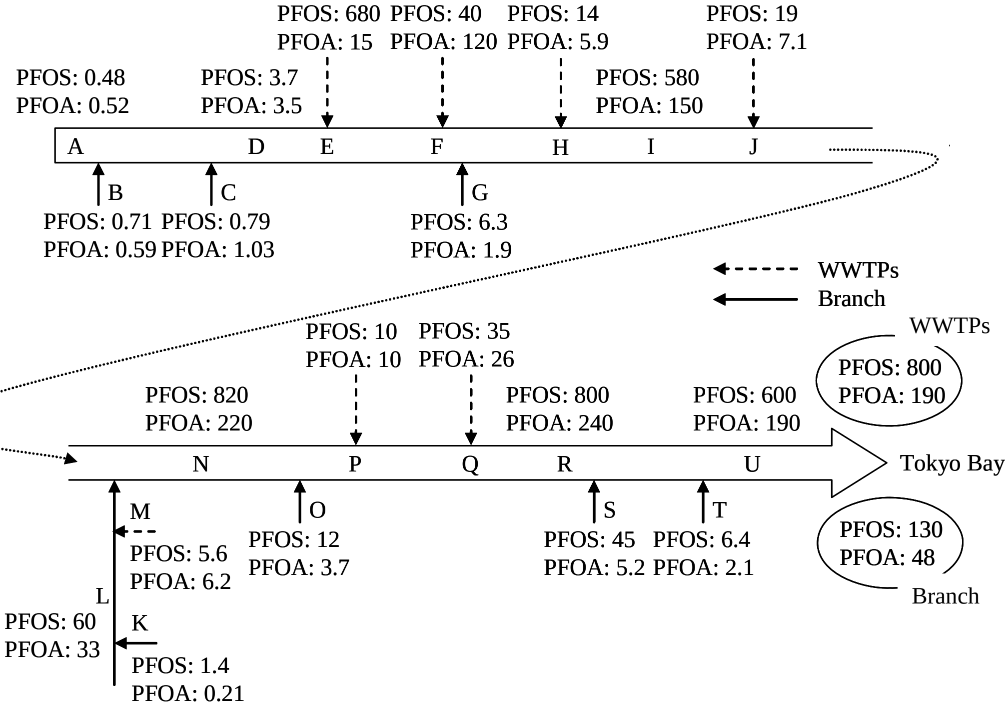

Fig. 4 A mass balance of PFOS and PFOA (unit: micro g/sec) in the Tama River Basin

Acknowledgements

This work was supported by the Ministry of the Environment, Japan. We express our gratitude to colleagues for their assistance in collecting samples.

References

1. Kissa E. Fluorinated surfactants and repellents, 2nd Revised and Expanded, Marcel Dekker, 615p.
2. Moody CA, Herbert GN, Strauss SH, Field JA. *J Environ Monit.* 2003; 5:341.
3. Moody CA, Martin JW, Kwan WC, Muir DCG, Mabury SA. *Environ Sci Technol.* 2002; 36:545.