

SURVEY OF PERFLUORINATED COMPOUND (PFC) POLLUTION IN THE BASIN OF TOKYO BAY USING THE SIMULTANEOUS ANALYSIS METHOD FOR 35 TYPES OF PFCs

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Introduction

Perfluorooctane sulfonate (PFOS) and its synthetic starting material, perfluorooctyl sulfonyl fluoride (PFOSF), have been designated as persistent organic compounds (POPs) in the world, because they have been listed on Stockholm Convention on POPs held on May, 2009 in Geneva¹. Perfluorooctane sulfonate and their homologues, such as perfluorooctanoate (PFOA), perfluorononanoate (PFNA), and their precursors/derivatives, which are called perfluorinated compounds (PFCs), have been industrially developed and used in our society over 50 years for their special properties (e.g. interfacial activity, resistant property against acid/high temperature, water and oil repellency). However, many reports revealed PFC contamination in the various environmental matrices, such as river/ocean water^{2, 3}, sediment⁴, wildlife⁵, and human body⁶. Even after introduction of restrictions of production/use of PFCs, such as PFOA and its higher homologues under the Stewardship program organized by the USEPA⁷, water guideline values by several institutes⁸, EU directive from 2008⁹, Stockholm Convention on POPs from 2009¹, pollution by PFCs has been continually reported. As mentioned above, many types of PFC homologue exist and they are complexly related to overall PFC pollution. Hence, the research on PFC pollution including PFOS, PFOA, and their precursors/derivatives are necessary. In this study, we developed a simultaneous analysis method of 35 types of PFCs, and applied it to the intensive survey of PFC pollution in the entire of Tokyo Bay basin. The current status of PFC pollution in Tokyo Bay basin is reported.

Materials & Methods

Collected samples

River water and several sewage treatment plant (STP) effluent samples in Tokyo Bay basin were collected during April 3rd to May 1st, 2009. The samplings were carried out when there was no rain on the day of sampling and its previous day. The river water samples (n=50) were collected from the down-stream end of river in each watershed, such that samples should represent the water quality of the watershed. The STP effluent samples (n=6) were collected for purposes of comparison of PFC concentrations in the effluents with the concentrations in the river water samples. All samples were stored in cool box and transported to the laboratory for chemical analysis. The extraction for chemical analysis was conducted within a week after sample collection.

Sample analysis

The target PFC compounds were extracted from 500 ml of water sample by using solid phase extraction cartridge (WAX®, Waters) and Sep-Pak concentrator plus (Waters). The pH of water samples were adjusted to 4 before the extraction by adding 2 ml of 0.5 M tetrabutyl ammonium hydrogen sulfate (TBA), and small amount of 4 M HCl when the pH did not reach 4 after TBA addition. Suspended solid were removed by glass fiber filter and stored in freezer under -20 °C for other analysis. The surfaces of experimental materials which touched individual water sample were washed with methanol, and the obtained solution was combined into the respective sample to avoid any loss of target compounds by sorption onto the surfaces. The sample was loaded onto the cartridge by the concentrator, and 10 mL of 50% methanol was passed to the cartridge 3 times by the concentrator for washing the used materials and cartridge. The loaded cartridges were dried and stored under -20 °C before instrumental analysis. The target compounds were eluted with 7 mL of 1% ammonia methanol, and the extract was concentrated to 200 µL for the analysis by LC-MS/MS (LC: Agilent, MS/MS: Micromass).

QA/QC

The recoveries of 35 PFCs among 45 PFCs analyzed were between 50 and 120%. Nine PFCs whose recoveries were below or above the range, and 1 PFC that suffered from carry-over in separation process by HPLC were omitted in this report, due to lack of accuracy for their concentration. Sampling blank, field blank, instrumental blank and procedural blank samples were also prepared and analyzed. It was confirmed that PFCs

in the blank samples were not detected or of minimal level. The procedural blank value was subtracted from the measured concentration. Also, duplicate measurement and monitoring of water quality change during an 8 day storage in a refrigerator (2 °C) were conducted, which showed good precision in measurement and no significant change during the storage.

Results & Discussion

The results of the survey of PFC pollution in the rivers of Tokyo Bay basin are shown in the map of the basin (Fig. 1). The compounds with high concentration in the river water samples, which were collected from the downstream edge in the watershed (n=50), except for the samples highly affected by point source, were PFNA (median; 20.1 ng/L), PFOA (6.7 ng/L) and PFOS (5.8 ng/L). These predominant compounds were spatially varied in the basin. PFNA was the most dominant among the PFCs; a result that was different from those of many previous reports, and was unexpected because PFOS and PFOA were the two most industrially used chemicals among the PFCs. It might indicate the shift of PFC use by the introduction of restriction. Industrial production of PFNA was recently reported in a special situation of PFCA use in Japan^{10, 11}, such a situation might have contributed to the current trend. Also, the STP effluent contained high level of PFNA compared with river water samples. Such relatively high concentration was specifically observed for PFNA (and PFOA). STP effluent, which is mainly composed of domestic sewage, might have contributed to the river water pollution of PFNA.

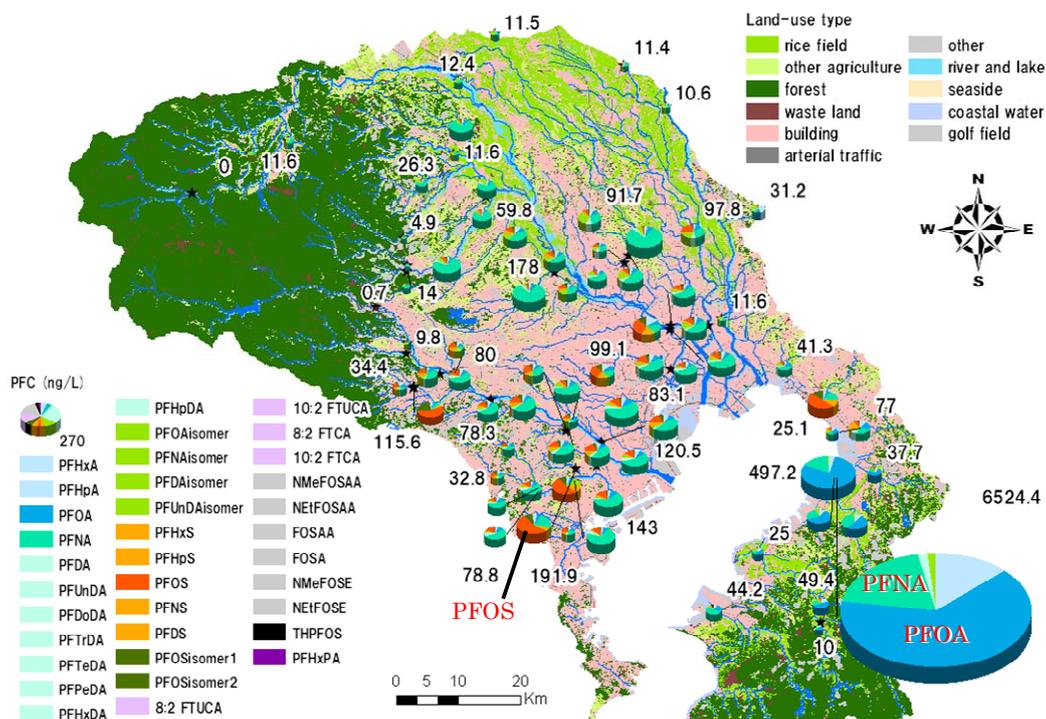


Fig. 1 Spatial distribution of PFCs in Tokyo Bay basin.

The numbers represent the total concentrations of measured PFCs (ng/L).

From Fig. 1, we could see that the PFC pollution was prominent in the area where buildings were dominant. In our previous report, non-point source PFC pollution was identified from the areas with dense commercial and transportation activities³, which is consistent with the current results. The samples obtained near the PFC production plant contained 1-2 order(s) of magnitude higher concentration of PFOA and PFNA (and other short chain perfluorocarboxylates (PFCAs)) compared with river water samples. Such point sources might also have contributed to the environmental PFC pollution.

Detailed PFC concentration in river water and STP effluent samples are presented in Fig. 2. The PFCA with perfluoroalkyls chains longer than 11 (> PFDoDA) were seldom detected in either river water or STP effluent

samples. Also, the precursor of PFCA (8:2 FTUCA, 10:2 FTUCA, 8:2 FTCA and 10:2 FTUCA in Fig. 2) and the precursor of PFOS (NMeFOSAA, NEtFOSAA, FOSAA, FOSA, NMeFOSE and NEtFOSE in Fig. 2) were detected with low concentration compared with transformed compounds like PFOS/PFOA. The PFC that had the highest concentration among precursors was FOSA (0.18 ng/L) in dissolved phase. The 1 order of magnitude lower of concentrations for precursors compared with transformed compounds indicate that the contribution of precursors to total PFC pollution is not significant in Tokyo bay basin. On the other hand, the environmental behavior which depends on their characteristics, such as sediment-water partitioning coefficient, is different between transformed and precursor compounds, thus, it is important that for the future research try to estimate more accurate contribution of precursors.

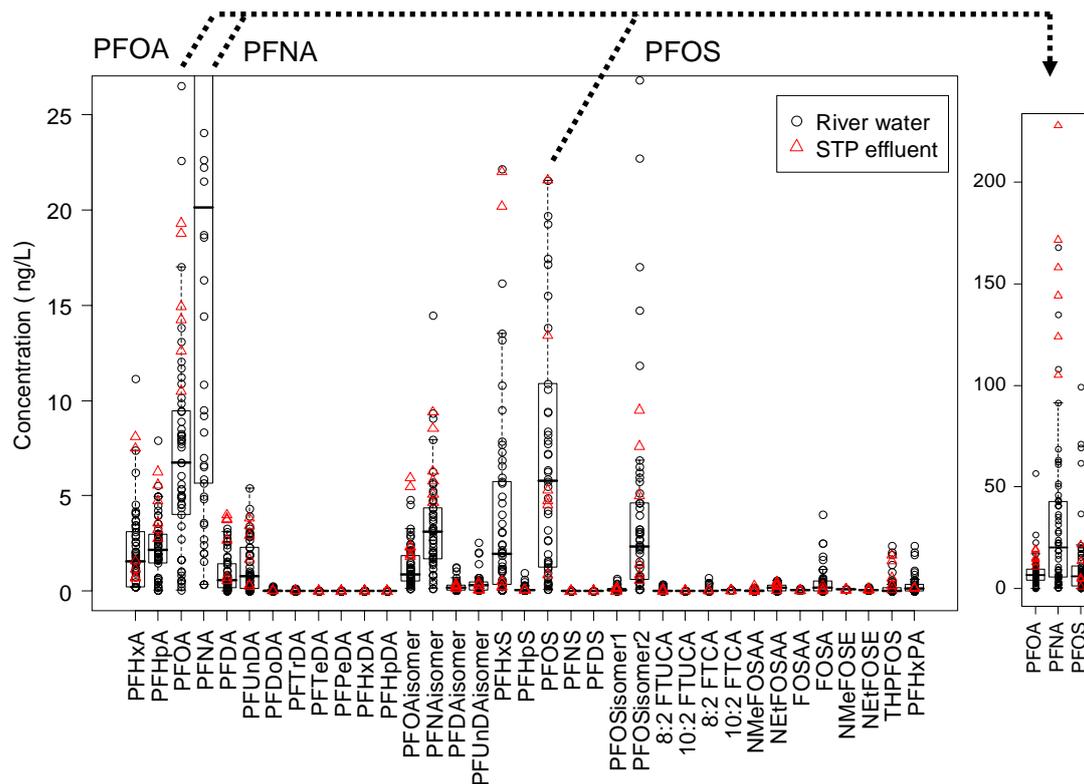


Fig. 2 Box plots of PFC concentrations in the collected samples.

The samples collected from the downstream edge in the watershed (n=50) and STP effluent (n=6) were plotted. Boxplot was constructed only by the data of river water, and plots of STP effluent were just overlapped. Whiskers show $1.5 \times \text{IQR}$ (Interquartile range)

Branched isomers of PFOS and PFCA were separately quantified from linear isomers in this study. Due to the unavailability of standard chemicals of some PFCAs, the signal response ratio of PFNA and isopropyl PFNA, which is available from Wellington Inc. were used for the determination of sum of the PFCA isomer concentration. The comparison between the branched and linear isomers of PFCA exhibited interesting trend of composition. Although, significant correlations between branched and linear PFCAs were not observed, the samples containing high concentration of PFCA showed lower ratio of branched to total PFCA isomers (Fig. 3). In other words, PFCA isomers were prominent in the background area of PFC pollution. It indicates that PFCA branched isomers are widely distributed in the environment. The ratio of PFOA isomer in product (by ECF method) was reported to be around 20-30% (PFNA: 65%)¹², however, the ratio calculated in this study was highly varied from 3% to 65%. These high variabilities might be the result of the introduction of branched PFCA and its precursor production using isopropyl iodide for their alkyl chain⁴. On the other hand, the ratio of PFOS isomers did not vary much in this study, perhaps an indication that a single production method prevailed for PFOS.

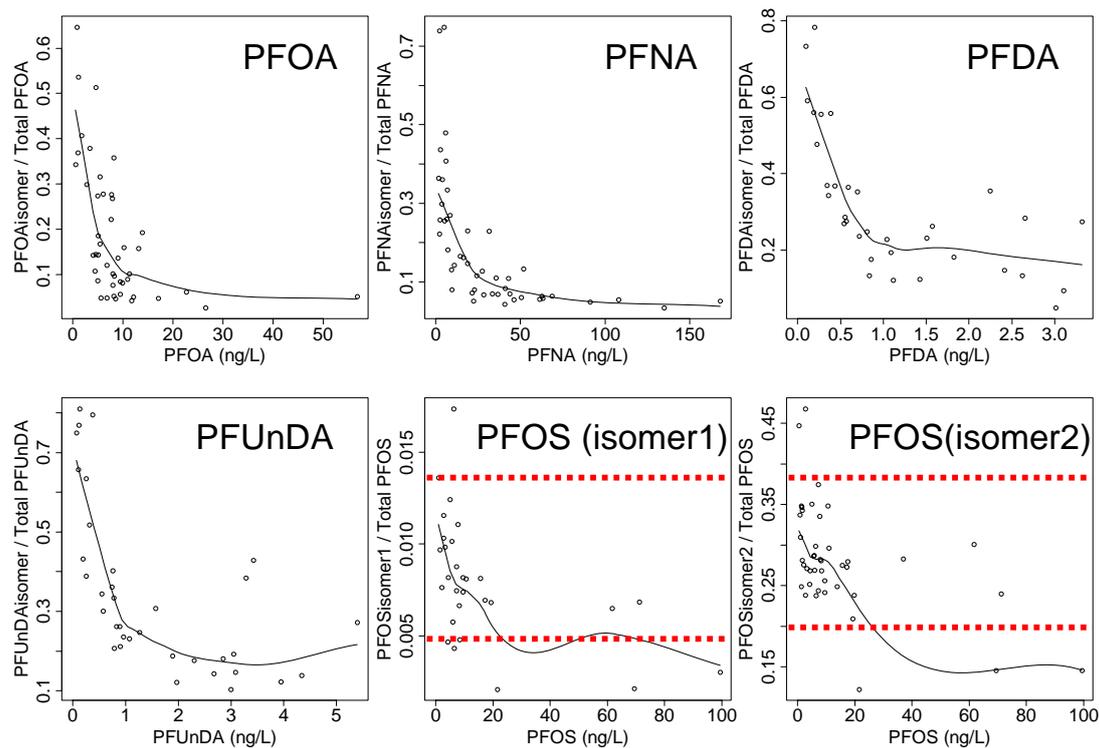


Fig. 3 Shift of the ratio of branched isomer

The developed PFC analysis method and intensive survey conducted in this study revealed various new information concerning PFC pollution, which might be beneficial for source identification and management of PFC pollution.

Acknowledgement

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