TRAIN STATION AS AN INDICATOR OF THE NONPOINT SOURCE OF PERFLUORINATED COMPOUNDS IN URBAN RIVER BASIN

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Introduction

Pollution by perfluorinated compounds (PFCs) has recently been reported and found to be ubiquitous. PFCs are also accumulated even in Arctic wildlife [1, 2].

The major sources of PFCs reported are industrial plants [3, 4], airports [5, 6] and sewage treatment plants (STPs) [7, 8]. In our previous study, the source of PFCs in the Tsurumi River, which is the most PFC-contaminated river among the major rivers flowing into Tokyo Bay, was investigated and STP was found to be one of the PFC sources. Furthermore, a nonpoint source (NPS) of PFCs has been found to exist by comparing the PFC loads in the river [9]. It was considered that NPS pollution was occurred by eluting from commercial products which were used in the river basin. However, the pathways of PFC emissions from consumer products containing PFCs have not been clarified.

In this study, we attempt to identify the nonpoint source of PFC using geographic information system (GIS). GIS has been applied to studies of the relationship between nonpoint sources (such as special land use) and river water pollution, for example, heavy metal [10], total nitrogen and total phosphorus [11]. We selected the Hayabuchi River as a model to examine the relationship between geographic information, such as land use (cropland, residential distinct, commercial land, road, train, etc.) and population density, and PFC pollution. The results will help us to understand the nonpoint source of PFCs and to carry out cost-effective management regarding PFC regulation.

Materials and methods

Study area and sampling

The study was carried out for the Hayabuchi River, a tributary of Tsurumi River in Yokohama, Japan (Fig. 1). The Hayabuchi River is a typical urban river running through a populated area. No fluoropolymer- or related-product-manufacturing plants exist in the basin. A separated sewerage system serves the basin, except for some terminal parts of the basin, and no wastewater treatment plant exists in the river basin. Additionally, the coverage of the sewer system is 99.6% in Yokohama. Thus, in this basin, no sewage flows into the river. However, rain water drainages are connected to the river and storm runoff water flows into the river through these drainages. In this basin, 13 drainages exist throughout the river stretch. River water and drainage effluent samples were collected at each sampling station (Fig. 2) on January 9th, 2007. Fixed-point monitoring was also conducted using an automatic sampler (Water sampler-3700) during the time of river water and drainage effluent sampling (11:00 - 21:00, 10 hours, 11 samples). The fixed-point monitoring was conducted at Mineoo Bridge (Fig. 2) to grasp the time trend of PFC concentration. On the sampling day, the weather was fine and no rain had been observed for the preceding 2 days.

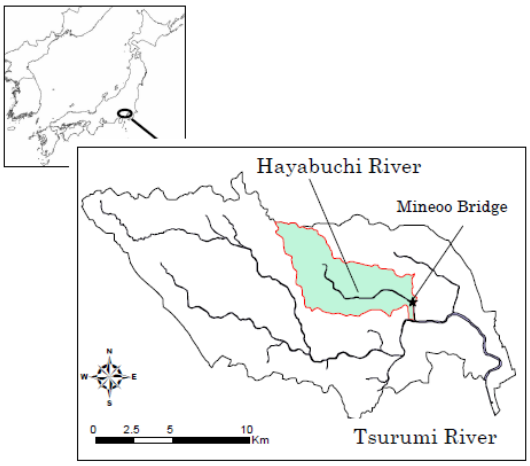

Fig. 1 Study area: the location of Hayabuchi River basin

Target compounds

Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA) were measured in this study.

Sample preparation

The river water and drainage effluent were extracted according to a method previously described [12].

Instrumental analysis

The concentrations of PFCs in the water samples were analyzed using a HPLC interfaced with MS/MS operated in the electrospray negative-ion mode (HPLC-MS/MS).

Preparing geographic information

The software ArcGIS 9.1 was used for geographical analysis. The watershed map of Hayabuchi River was made using Digital Elevation Model (DEM) data of 50 m mesh. Then the drainage areas were re-created. The population distribution and land use maps were then overlapped as layers, and these layers were intersected with the watershed layer.

The watersheds constructed by GIS and sampling sites are shown in Fig 2. Although the drainages at St. F and St. I actually existed, they were not drawn from DEM data. Moreover the drainage simulated from DEM data, situated between St. 9 and St. I, could not be found in the field survey. In spite of these differences however, the map shown in Fig. 2 reflects the real situation of the Hayabuchi River basin very well on the whole.

Statistical analysis for nonpoint source identification

The sampling sites were selected on the basis of data geographically displayed by GIS. Then river monitoring was conducted and the concentration of PFCs in water was analyzed. Finally, the source identification of PFCs was conducted by correlation and regression analysis between GIS data and PFC concentration. The Mann-Whitney U test was used to evaluate the impact of certain factors on the PFC concentration.

Correlation analyses among the land use variables showed that there are significant correlations among themselves. The presence of these correlations, which are called multi-collinearity, may affect the regression analysis between land use and PFC concentration in the basin. As one of the best ways to overcome this problem, principal component analysis (PCA) was performed for the land use variables [10]. PC scores of those principal components for each watershed were used as the variable representing respective land uses in the watershed. Then, correlation and regression analysis (principal component regression analysis (PCR)) was performed between the PC score and the PFC concentration for each watershed. The PFC concentration data for St. F and St. I, and the PC score data at stations in the watershed were not included in the correlation and regression analysis because, as mentioned above, those drainages were not drawn from DEM data and the proportion of land use area in the watershed that was considered to reflect the water quality of drainage effluent could not be extracted.

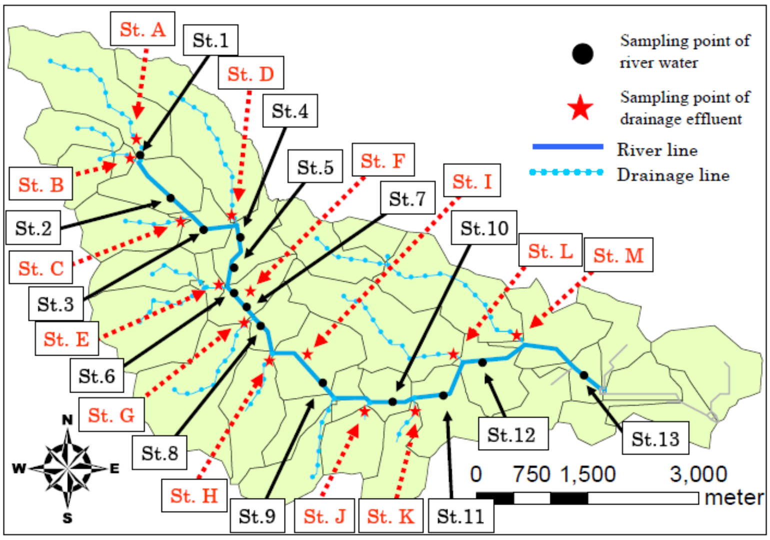

Fig. 2 Sampling site in Hayabuchi River

The Mann-Whitney U test, which is a nonparametric test, was selected by considering the existence of outliers or the failure of normality in the data of PFC concentration. All the water quality data of drainage effluent were used for the Mann-Whitney U test. The PFC concentration at St. F and St. I, whose watersheds were not drawn appropriately from DEM data, were included in the Mann-Whitney U test. In these cases, riverward watershed fragments which contained St. F and St. I were regarded as the respective watersheds (Fig. 6). This was acceptable because only the existence or nonexistence of railway stations in the watershed was important in this analysis and accurate watershed boundaries were not necessary.

Results and discussion

Trend of PFC concentration during sampling at fixed point

The trend of PFC concentration during sampling at the Mineoo Bridge, which is located 400 m downstream of St. 13 in Hayabuchi River (Figs. 1 and 2), was studied to see whether water quality change significantly with time or not (Fig. 3). Thus, it can be regarded that PFC concentrations of the river water and drainage effluent during the sampling were in the steady state condition.

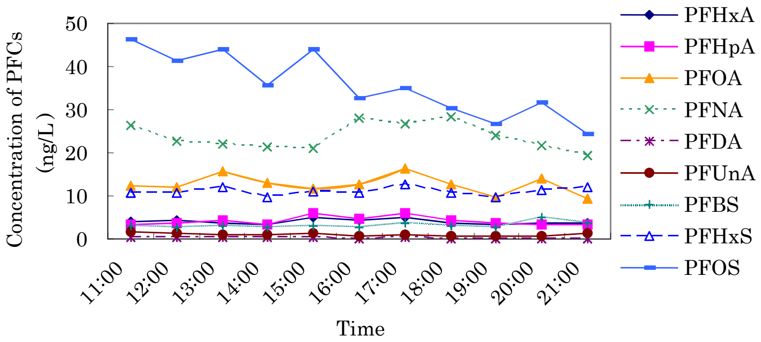

Fig. 3 Trend of PFC concentrations at the fixed sampling point located downstream of St. 13

Regression analysis between land use identified using GIS and PFC concentration

The correlation and regression analyses between the land use in each watershed and the PFC concentration in each drainage effluent were performed.

Correlation coefficients between PC1, and PFOA, PFNA, PFUnA and PFOS were 0.77, 0.94, 0.82 and 0.74, respectively. Thus, PFOA, PFNA, PFUnA and PFOS had a significant correlation with PC1, which reflects commercial and transportation-related land use. Other PCs did not show any significant correlation with any of the PFCs. No PFCs had significant correlations with population density. The values of population density here are based on nighttime population density. This may be the reason why no significant correlation between population density and PFC concentrations was observed.

The linear regression lines between PC1 and PFOA, PFNA, and PFOS, which are shown to be significantly correlated, are shown in Fig. 4. The slopes (and coefficients of determination: R^2) of the regression lines for PFNA, PFOA, and PFOS are 6.21 (0.88), 1.54 (0.59), and 18.0 (0.56), respectively. These results show that PFCs have their source in commercial and/or transportation-related land use, where human activities are dominant. A large amount commodities, such as car wax, paint, paper and cloth, that contain PFCs as components or as impurities are used in those areas.

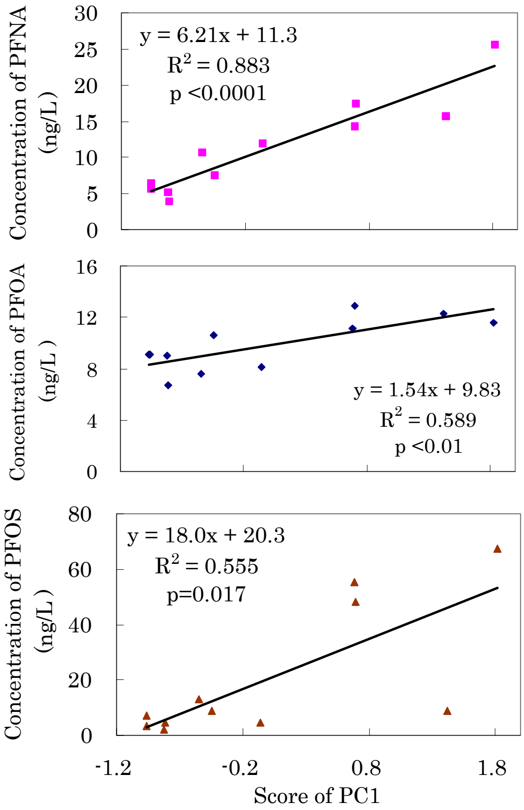

Fig. 4 Linear regressions between PC1 (which reflects commercial and transportation land use) and PFC concentrations

Relationship between PFC concentration and existence of station

Table 1 shows the result of the Mann-Whitney U test. All the PFCs show significant differences in the concentration ($p < 0.05$; two-sided p-value) between the watersheds with and without stations. The results indicated that high concentrations of PFCs were discharged from the watersheds with train stations. Commercial and transportation-related land use tends to be high around the station. Thus, the train station could be regarded as an indicator of a nonpoint source of PFCs.

The results showed that ionic substances (measured by EC) and DOC were not discharged in large amounts from stations in contrast to PFCs. The greater emission of PFCs from watersheds with stations is considered to be a very specific phenomenon of PFCs.

The results of this study showed that to taking measures against drainage water discharged from a watershed with a station is an effective management strategy against nonpoint-source-type PFC pollution.

Table 1 Mann-Whitney U test results of differences in PFC concentrations, EC and DOC on the basis of existence or nonexistence of train stations in watersheds

Existence of train stations	Measured value (±SD) Nonexistent (n=7)	Measured value (±SD) Existent (n=6)	Rank sum Nonexistent (n=7)	Rank sum Existent (n=6)	p-value (two-sided)
PFHxA	3.0 ± 0.6	8.5 ± 6.0	32.0	59.0	< 0.05
PFHpA	4.3 ± 1.4	7.6 ± 5.9	34.0	57.0	< 0.05
PFOA	8.5 ± 1.4	13.9 ± 3.7	28.0	63.0	< 0.01
PFNA	7.7 ± 3.1	20.4 ± 8.1	28.0	63.0	< 0.01
PFDA	0.2 ± 0.1	0.4 ± 0.1	28.0	63.0	< 0.01
PFUnA	0.3 ± 0.2	1.2 ± 0.4	28.0	63.0	< 0.01
PFBS	2.6 ± 2.3	6.1 ± 3.7	33.0	58.0	< 0.05
PFHxS	4.8 ± 3.8	28.6 ± 26.8	31.0	60.0	< 0.05
PFOS	7.0 ± 3.7	145.6 ± 256.2	30.0	61.0	< 0.01
EC (mS/cm)	5.2 ± 0.6	6.2 ± 1.3	40.5	50.5	0.22
DOC (ppm)	5.4 ± 0.5	6.8 ± 2.9	41.0	50.0	0.25

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