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Distribution of Fluorescent Whitening Agents as an Indicator of Domestic Wastewater

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The distributions of fluorescent whitening agents (FWA) in the water of the Yasu River and their tributaries flowing into Lake Biwa (Japan) were surveyed on winter and summer. The FWA fluxes had linear correlation with the corrected resident population in catchments of the tributaries of Yasu River. Therefore, the FWAs in the rivers come from domestic wastewater, and those fluxes in the tributaries depended on the human population of their catchments. As an application of the FWA indicating domestic wastewater, we could assess seasonal changes in the sources of dissolved organic matter in the tributaries.

Key words : fluorescent whitening agents, domestic wastewater, dissolved organic carbon

INTRODUCTION

Fluorescent whitening agents (FWAs, Fig. 1) used in laundry detergents have long residence time in aquatic environment, since these compounds are resistant to microbial decomposition, and are eliminated partly during sewage treatment (Poiger *et al.*, 1998). Hence, they are potential sources of organic pollution in rivers and lakes. For assessing influence of the FWAs to river and lake waters, we need to clarify distribution and behavior of the FWA in their environments.

In this study, we surveyed the distribution of FWAs in the Yasu River and their tributaries flowing into Lake Biwa using a high-performance liquid chromatography (HPLC) with a fluorescent detector after solid-phase extraction, and clarified relationship with domestic wastewater and organic pollution and assessed seasonal changes in the sources of dissolved organic matter in the tributaries.

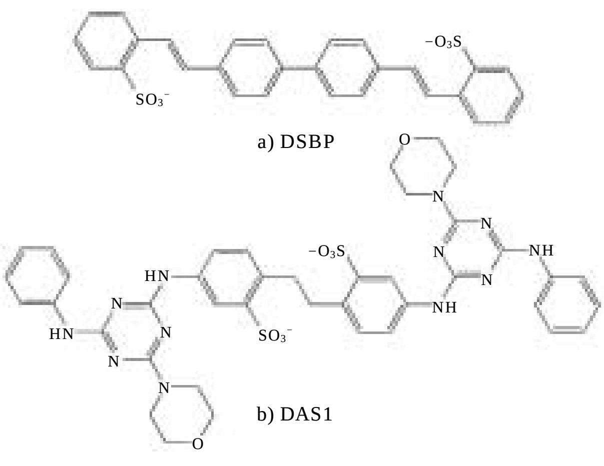

Fig. 1. Structures of the two fluorescent whitening agents. Full names: DSBP: 4,4′-bis (2-sulfostyryl)-biphenyl; DAS1: 4,4′-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2-disulfonate.

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FIELDS AND METHODS

Yasu River flows to Lake Biwa, and has a 65 km length and 382 km^2 catchment area (Fig. 2). Its watershed is occupied by residential area, industrial area, farms and forested mountains (approximately 134,000 total populations). It is a typical land−use in the watershed of Lake Biwa.

The measuring method of FWAs was slightly modified from earlier studies (Poiger *et al.*, 1996, Hayashi *et al.*, 2002). All sample treatments were undertaken in a dark room under yellow light to prevent from photodegradation. Sample waters were collected from 14 sampling stations of Yasu River and its tributaries on November, December 2002 (three times in winter), July and August 2003 (two times in summer). The collected water was filtered through pre−combusted glass fiber filters (Whatman GF/F, UK). The filtrate was used as our dissolved matter sample. Dissolved organic carbon (DOC) concentrations in the filtrates were measured by the high temperature catalytic oxidation method using a total organic carbon analyzer (Shimadzu TOC−5000A, Japan). FWAs in the 500 ml filtrate were extracted using an octadecyl silica (ODS) cartridge (Sep−Pak Environmental tC18 plus, Waters, USA) at a rate below 10 mL min^{-1}. The FWAs absorbed in the ODS cartridge were eluted with 20 mL of 0.01 M tetrabutylammonium hydrogensulfate−methanol. The eluent was evaporated to dryness and re−dissolved in 1 mL N,N,−dimethylformamide−water−methanol (1 : 1 : 2). Aliquots of the solution were injected into HPLC. The HPLC analysis was performed using Agilent 1100 fluorescence detector system with a reversed phase column (HP ODS Hypersil, 4.6 mm i.d., 200 mm, USA), and an online postcolumn UV irradiator (irradiation for 6s at 254 nm: PHRED photochemical reactor, Spelco, USA). The FWAs were quantified by absolute calibration method based on peak area.

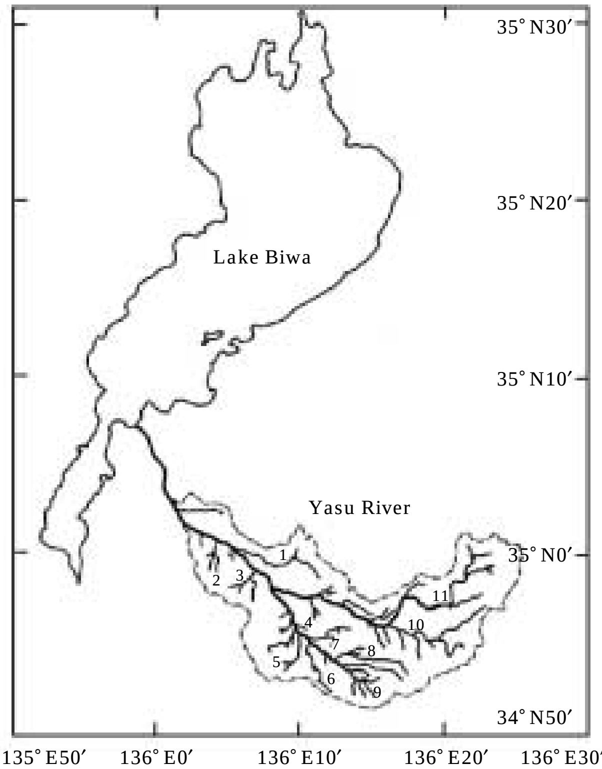

Fig. 2. Map of Yasu River and its watershed. Numbers of tributaries on the map refer to Table 2.

Water discharge of each river was determined by multiplying the flow velocity by the cross−sectional area, which is measured directly using a meter survey rod and tape. The flow velocity was measured with a current meter (Dentan TK−105K, Toho Dentan, Japan) at the sampling period.

RESULTS AND DISCUSSIONS

1. FWAs as a domestic wastewater indicator

The DSBP and DAS1 concentrations in the Yasu river and its tributaries were averagely 483 and 298 ng L^{-1} in winter respectively, and 145 and 138 ng L^{-1} in summer (Table 1). These data were lower than those of Tamagawa River, major rivers in Tokyo, reported previously by Hayashi *et al.* (2002). Although the catchment basin of the Yasu River has residential and industrial areas which are potential sources of the FWAs, the water of Yasu River did not have serious FWA

Table 1. FWAs and DOC concentrations in the tributaries of Yasu River.

	Range (mean)	
	Winter (n = 31)	Summer (n = 21)
DSBP	26～1275 (483)	6～527 (145)
DAS1	13～1502 (298)	8～717 (138)
FWAs (DSBP＋DAS1)	38～2777 (789)	19～1220 (283)
DOC	0.49～4.0 (1.7)	0.60～3.9 (1.8)

Unit; FWAs: ng L^{-1}, DOC: mgC L^{-1}

Table 2. Population covered by sewerage system in tributaries.

No.	Branch river name	Total population	Large centralized sewerage	Rural sewerage	On−site treatment technology	Non−treatment
1	Omoi R.	20600	11007	2066	3413	1222
2	Ochiai R.	6476	4153	0	491	507
3	Arakawa R.	3370	141	0	883	777
4	Hiedani R.	6571	121	32	6349	23
5	Iso−o R.	5678	2589	687	914	494
6	Asano R.	1101	502	133	177	96
7	Saji R.	3641	953	1797	348	182
8	Ohara R.	4125	1968	1974	183	0
9	Aburahi R.	1737	56	780	184	0
10	Tamura R.	3443	0	1015	848	0
11	Upper Oduchi dam	831	0	820	11	0

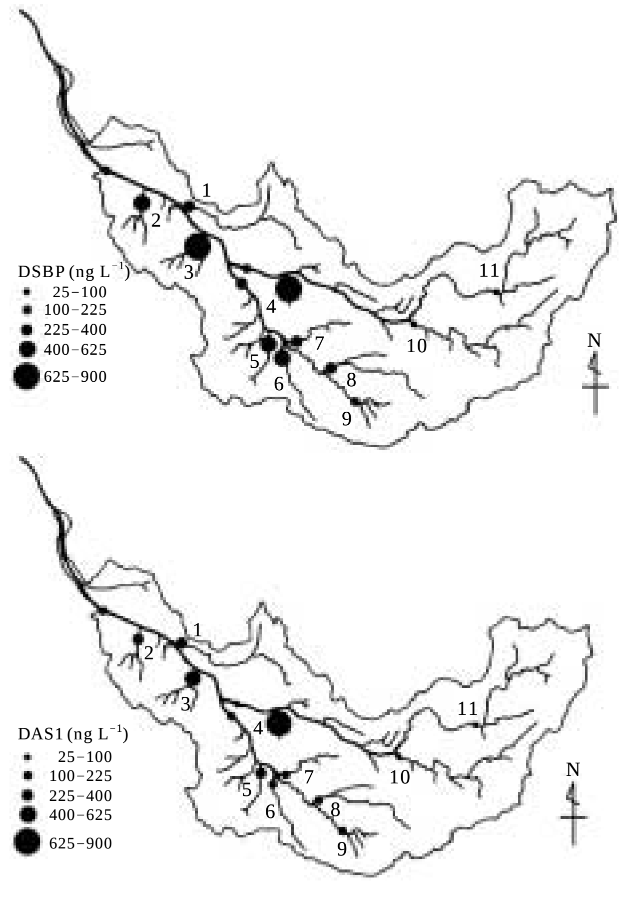

Fig. 3. a) DSBP and b) DAS1 concentrations of the tributary waters in Yasu River on the winter observation.

pollution, like the Tamagawa Rivers.

The DSBP and DAS1 fluxes of Yasu River (main river) at Ishibe sampling−site were averagely 1632 and 992 mg $hour^{-1}$ in winter (n = 3) respectively, and 2534 and 2113 mg $hour^{-1}$ in summer (n = 2). Although the water flows of Yasu River in the summer (8.33 m^3 s^{-1}) were 4 times higher than those in winter (2.08 m^3 s^{-1}), the DSBP and DAS1 fluxes of Yasu River in summer were close to those in winter. Hence, there is no seasonal variation of the DSBP and DAS1 fluxes. The FWAs (= DSBP plus DAS1) concentrations of the tributary waters in summer were lower than those in winter (Table 1), indicating that the FWA concentrations in the summer were diluted by high water−mass flow.

Higher DSBP and DAS1 concentrations are appeared in the Arakawa and Hiedani Rivers (Fig. 3a, b), which have non−treatment domestic wastewater from residential area as river water sources. Then, we compared the FWAs in the tributary waters and resident population in their catchments. As an assumption that the FWA fluxes of the tributaries are related with the population in their catchments, following equation is expressed.

$$F = k * P_T \tag{1}$$

where F: FWA flux (= DSBP flux + DAS1 flux); k: discharge rates of FWA by one person; P_T : total population in catchment. The drainage basin of the Yasu River has some kinds of sewage system, such as large centralized sewage, rural sewage, on−site treatment technology, and non−treatment systems (Table 2). The centralized sewage system does not flow to the Yasu River and their tributaries, but other sewage systems flow to them. The rural sewage and on−site treatment technology systems can remove the FWA concentrations in the effluents moderately. Hence, Equation (1) can be transformed

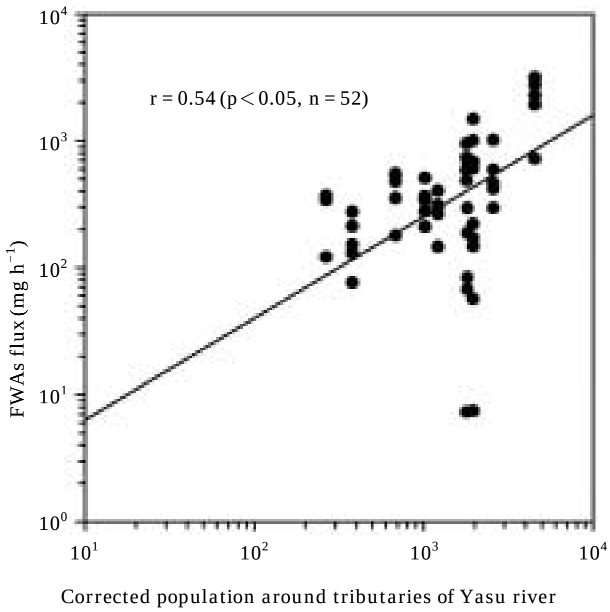

Fig. 4. Relationship between FWA fluxes in the tributaries and corrected resident population based on Equation (2) in the catchments on the summer and winter observations.

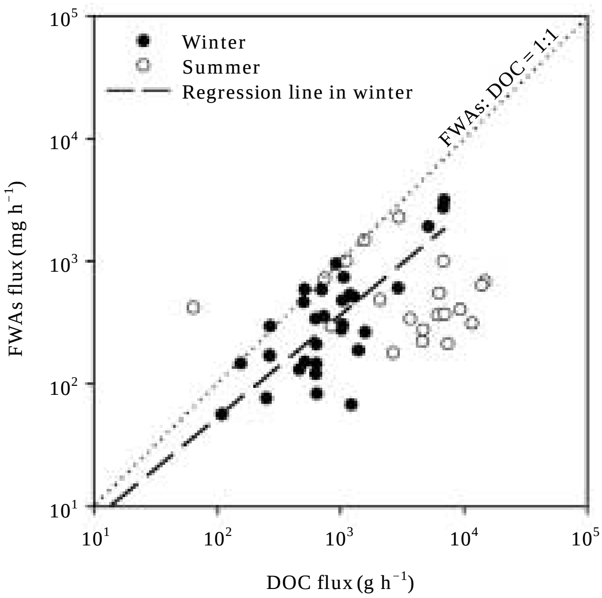

Fig. 5. DOC and FWA fluxes of the tributary waters in Yasu River on the summer and winter observations. Open circles denote the data on the summer (n = 21), and solid circles denote the data on the winter (n = 31).

into following equation

$$F = k * \{P_R * (1-\alpha_R) + P_O * (1-\alpha_O) + P_N\}$$
$$= k * [\text{corrected population}] \quad (2)$$

where P_R: population depended on rural sewage system; α_R: removal rates of FWAs by rural sewage system; P_O: population depended on on-site treatment technology system; α_O: removal rates of FWAs by on-site treatment technology system; P_N: population of non-treatment sewage. The removal rates are measured in Shiga Prefecture reported by Yamaji *et al.* (In preparation). As a Fig. 4, we found linear relationship significantly ($r = 0.54$, $p < 0.05$, $n = 52$) between the FWA fluxes and the corrected population in the tributaries of Yasu River. Therefore, the FWAs in the rivers come from domestic wastewater, and those fluxes in the tributaries depended on the population of their catchments. The slope indicates FWAs flux per inhabitant in this study area. The recalculated DSBP and DAS1 fluxes in the tributaries of Yasu River were 1.53 and 1.02 mg inhabitant day^{-1}, which are barely higher value than those in Swiss rivers (DSBP: 0.51～1.24 mg inhabitant day^{-1}, DAS1: 0.47～0.95 mg inhabitant day^{-1}) reported by Poiger *et al.* (1996). The rates in Tamagawa River could be one order of magnitude higher (Hayashi *et al.*, 2002).

2. Application of FWAs for organic pollution assessment

As an application of FWAs for organic pollution assessment, we compared FWAs and DOC concentrations in the tributaries of Yasu River. DOC concentrations in the tributary waters were in the range of 0.49～4.0 mg C L^{-1} in winter and 0.60～3.9 mg C L^{-1} in summer (Table 1). Although the DOC concentrations of the tributary waters in the summer and the winter were almost equivalent, the DOC fluxes of the tributary waters in the summer increased more than those in the winter (Fig. 5). It indicates the DOC increasing in the rivers during the summer. The FWA fluxes of the tributaries in summer and winter were almost equivalent (Fig. 5), depend on the human population in the catchments above mentioned. As the results, the DOC and FWA fluxes in the winter had linear correlation significantly ($r = 0.62$, $p < 0.05$, $n = 31$), however the both in the summer had no correlation (Fig. 5). It indicates that the potential sources of riverine DOC in the winter come from domestic wastewater, but those in the summer may be added other sources like as soil, plant and other anthropogenic organic matter. As a summary of the application, we can obtain that the dissolved organic pollution of the tributary waters, and suggest that the FWA is a useful indicator of domestic wastewater.

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