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BEHAVIOR AND MASS BALANCE OF FLUORESCENT BRIGHTENING AGENTS IN THE ENVIRONMENT

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The authors have examined how fluorescent brightening agents disappear in an urban river, the Nogawa, after discharge from domestic sources.

The behaviors of two typical fluorescent brightening agents (FBA-1 and FBA-2, see Table 1 for the chemical structures) for detergent in a river were proved to differ from each other. For FBA-1, the main disappearance factor was found to be photofading, on the other hand, for FBA-2, the main factor could not be specified. The transport ratios of the fluorescent brightening agents in the river were 87% for FBA-1 and 15% for FBA-2, respectively.

Mass balance of the fluorescent brightening agents built in detergent was estimated from these results.

1. Introduction

Fluorescent brightening agents (FBA) in natural waters can be analysed by fluorometry¹⁾. In an urban river, the Nogawa which is a branch of the Tama River, two typical FBA's (FBA-1; disodium 4,4'-bis(o-sulfostyryl)biphenyl and FBA-2; disodium 4,4'-[(4-toluidino-6-morpholino-1,3,5-triazin-2-yl)amino] stilbene-2,2'-disulfonate) for detergent were detected in a ratio of 2:1. The average concentration of FBA in the Nogawa river was 15 ppb¹⁾. The amount of FBA run in the Nogawa river was estimated to be 1.8 kg/day on 2-3 August in 1978. Obviously the FBA detected comes from daily home laundering.

The total amount of FBA used in river basin of the Nogawa was estimated to be about 9.98 kg/day from the population, frequency of laundering assessed by a social survey, the detergent's consumption and the average content of FBA in commercial detergents²⁾.

If the customary washing conditions at households that a sudsing bath is used about twice is considered, the uptakes of the two FBA's onto the wash load are estimated to be about 28% for FBA-1 and 55% for FBA-2 respectively, according to the results of a model experiment on cotton materials reported by Ueno *et al.*³⁾. Therefore the amount of FBA which is discharged into the river from households is estimated to be 7.2-4.5 kg/day.

In this paper, the process of disappearance of

FBA in the river water by photofading, biodegradation and adsorption on soils has been studied to clarify the factors to cause the difference between the statistically assessed amount of FBA and the observed one. Furthermore, a field experiment was performed in which for a known amount of FBA thrown in the Nogawa river, the amount transported was measured. The results have been compared with those obtained from the laboratory experiments.

By the multi-cycle Bundle testing⁴⁾⁵⁾, uptake of a FBA onto the wash load was estimated for the washing under controlled conditions with naturally soiled family clothes.

From these results, mass balance of FBA in the environment was elucidated.

2. Experimental

2.1 Materials

FBA's used are shown in Table 1. For laboratory experiments FBA-1 and FBA-2 were applied after the purification by salting out with CH_3COONa and refluxing with $\text{C}_2\text{H}_5\text{OH}$. For the field work and Bundle testing, commercially available FBA samples were applied without any purification.

River water ladled from the Nogawa river was used for the laboratory experiments as it was.

Kanto-loam was used as the model of soils.

2.2 Instrument

A spectrofluorometer (Shimadzu RF-502) which gives corrected excitation and emission spectra,

Table 1 Chemical constitutions of the fluorescent brightening agents (FBA) used.

FBA-1	
FBA-2	
FBA-3	
FBA-4	

was used.

2.3 Analysis

The fluorescence intensity of solution was measured at emission wavelength of 432 nm and excitation of 348–359 nm. The measured fluorescence intensity was linearly correlated to the concentration of FBA in deionized water, on the other hand, the fluorescence intensity in the river water exhibited a tendency to deviate downward in the dilute FBA concentration region. In this respect, the concentration of FBA was calibrated with respective waters.

2.4 Method

2.4.1 Photofading test

Light source: natural sunlight.

Apparatus: glass tube of 25 mm ϕ $\times$ 400 or 1,000 mm, covered with aluminium foil to cut the sunlight from the wall and to help the light to reflect into the FBA solution from the opening at the top of the tube.

Solvent water: deionized water and the river water.

Concentration of FBA: 0.01, 0.1, 0.5, 1.0 mg/l.

Exposure time: 15, 30, 60, 120, 240, 360 min.

Way of sampling: Samples were taken,

- 1,000 mm column; at each levels of 50, 500 and 950 mm below the water surface.
- 400 mm column; mixing the whole volume at each sampling time.

2.4.2 Biodegradation test

Amount of FBA added: 0.1 mg/l (FBA-1), 0.5 mg/l (FBA-2).

Change of the fluorescence intensity of FBA

solution in the river water was measured with and without aeration at 20°C in the dark by the River Die-away⁶⁾ technique.

2.4.3 Adsorption test

Concentration of FBA: 0.01, 0.1, 1.0 mg/l.

Content of loam added: 0.01, 0.1, 1.0, 10 g/l.

Temperature: 30°C.

Incubating time: 15, 30, 60, 120, 240, 480 min.

After incubating at 100 rpm, the sample solution was centrifuged to remove the suspending materials, and the fluorescence intensity was measured.

2.4.4 Transport test of FBA at the Nogawa river

The amount of FBA to be supplied was determined to be 2–10 times of the background fluorescence intensity of the river water.

After being dispersed in 20–30 l of the river water, a known amount of FBA was thrown in the center of the stream instantaneously.

Water samples were ladled over 120 min period after the throw-in at about 1.15 km downstream from the throwing point. The rate of flow and the cross-section of the river at the sampling point were measured to estimate the amount of water in the river. The fluorescence of the samples stored under the dark was measured at laboratory within a couple of days.

Estimation of the FBA transported after the throw-in was made as follows;

(1) The background fluorescence of the river water and the unevenness of the measured fluorescence in the direction of the width of the river (see Fig. 1) were corrected, and the concentration of FBA–time curve was obtained.

(2) The amount of FBA transported (g) was calculated as a product of the integration of the concentration–time curve (g·min/l), and the average flow of water in the Nogawa river (l/min).

2.4.5 Uptake of FBA onto the wash load by

the Bundle testing

Materials applied were commercially available white clothes generally used in households with fiber components 72% of cotton and 28% of synthetic fibers.

The detergent applied was of heavy duty: LAS, Na-tripolyphosphate, Na-carbonate, Na-sulfate, CMC and 0.26% owd of pure FBA-4.

A half of 2 kg of one family's load was washed in a sudsing bath at 20°C for 8 min, after removing the load, the rest load was washed in the same

Fig. 1 Fluorescence intensity-time curve, for throw-in FBA in the Nogawa.

Insert shows the cross-section at the sampling point of the Nogawa.
Water samples were ladled at point A (● ○), B (▲ △) and C (■ □).

bath successively under the same washing conditions. Rinsing was made twice for 3 min on each loads.

Water samples, one from the residual sudsing and four from the rinsing baths, i.e., 5 samples each were filtered with G3 glass filter and analysed. No interference of detergent components in fluorometry was checked previously.

The testing was made on up to 12 cycles of repeating wear and wash for 10 families.

3. Results and discussion

3.1 Photofading of FBA in waters under laboratory conditions

In deionized water solution, it was found that the difference in the depth within 1,000 mm did not affect the photofading of FBA. For FBA-2 the concentration dependence of the photofading was slight within 60 min. On the other hand, it was appreciable for FBA-1, depending on the concentrations, 1 mg/l to 0.1 mg/l and less, differently. (Fig. 2)

In river water solution, the effect of suspended solids and soluble substances in the river water on the photofading was different for FBA-1 and FBA-2 (Fig. 3). For FBA-1, substances in the river water reduced the photofading; on the other hand, the fading of FBA-2 was not affected and got to a steady state in 30 min. It was considered that

this state was reached as a result of the trans-cis isomerization around the ethylene bond⁷⁾ in FBA.

The reduction of the fluorescence intensity was 7% for FBA-1 and 71% for FBA-2, respectively, when they were exposed to sunlight for 60 min in the river water.

3.2 Biodegradation of FBA in river water

Owing to the heavy pollution of the Nogawa river, the water exhibits high BOD and low DO. It was presumed that micro-organisms in the river water would lead to an intensive degradation of FBA. Nevertheless both FBA's were proved to

Fig. 2 Effect of concentration on the photofading of FBA in deionized water.

—— 1.0 mg/l, ——— 0.1 mg/l,
----- 0.01 mg/l

Fig. 3 Photofading of FBA in river and deionized waters.

— river water, ---- deionized water

Fig. 4 Biodegradation of FBA-2 in river water.

resist to the degradation. FBA-1 was especially undegradable. Aeration scarcely affected the degradation (Fig. 4). Such stability of FBA in the water may be attributed to the presence of many aromatic rings in their structure.

Biodegradation in the river water in 60 min was 0% for FBA-1 and 5% for FBA-2, respectively.

3.3 Adsorption of FBA on Kanto-loam

The adsorption of FBA on the loam as a model of the suspended solids in the river water was studied.

The adsorption on the loam has reached a steady state in 30 min (Fig. 5). More pick up took place with FBA-2 than FBA-1, and the extent of adsorption of FBA in the solution was dependent on the content of the loam.

Fig. 5 Adsorption-time curve for FBA on Kanto-loam.

C_0 ; 0.1 mg/l of FBA

loam content; ○ 0.01 g/l ● 1.0 g/l
× 0.1 g/l △ 10 g/l

If the content of the loam in the river water is assumed to be 0.1 g/l or less, 1–2% of FBA-1 and 2–11% of FBA-2 are adsorbed by the loam. When the contact with the stream bed is taken into account, the amount of adsorption may increase with the possibility of contact to the loam.

3.4 Transport of FBA thrown in the river

The FBA was detected over the period of about 2 h after the throw-in.

The ratio of the amounts of FBA transported to thrown in the river is shown in Table 2.

From the comparison of the results obtained in

Table 2 Transport ratios of FBA's in the Nogawa river.

		amount of FBA (g)		transport ratio (%)
		input	transported	
FBA-1	night	271	263.1	97.0
	day	271	236.5	87.2
FBA-2	night	263	76.8	29.1
	day	263	40.1	15.2
FBA-3	night	252	86.0	34.0
	day	252	43.0	17.0

the daytime and at night, the main factor for the disappearance of FBA-1 in the water system can be attributed to the photofading, which is consistent with the results obtained by the laboratory experiments (photofading: 7% in the laboratory and 10% in the field experiment).

On the other hand, much more FBA-2 was lost in the river at night. This result is not consistent with the expectation from the results of the model experiments on the biodegradation and the adsorption on the loam. The photofading factor evaluated from the difference between the data in the daytime and at night found in this throw-in experiment was not so large as obtained by a laboratory experiment (photofading: 71% in the laboratory and 48% in the field experiment). Such a considerable loss is not attributed to the low solubility of FBA-2, because FBA-3 (Table 1), having a high solubility, disappeared to the same extent as FBA-2. Accordingly, for FBA-2 and additionally for FBA-3, some other unclarified factors, for example, the action of activated sludge on the stream bed, must be taken into account.

3.5 Uptake of FBA onto the wash load in washing

The average of the discharge ratio defined as that of the amounts discharged to added in the sudsing bath for 10 families is shown in Fig. 6. This plot shows the summed up value for a sudsing bath and four rinsing baths. The ratio reaches a steady state of about 50% after 8 cycles of the washing, although it is about 90% at 1–2 cycles. This result shows that the uptake ratio in the

Fig. 6 Change of discharge ratio of FBA-4 in washing.

steady state is close to the value assumed previously (55%) from the results on FBA-2 by Ueno³⁾. Since FBA-4 (Table 1) has a structure quite similar to FBA-2, the uptake of FBA's of triazinylstilbene series in washing may be assigned to 50%. Consideration of the less hydrophobic structure of FBA-1 leads to an uptake value about 30% for FBA-1, based on the assumed value of 28% by Ueno³⁾ previously.

4. Mass balance of FBA built in detergent in the environment

The flow time of the Nogawa river from its origin to the junction with the Tama River is about 10 h. Here the results obtained by the field experiments over a period of 2 h was applied to the analysis of the mass balance of FBA in the overall Nogawa river basin, since the photofading and the adsorption of FBA on the loam reached steady states after 60 min, and the rate of biodegradation was not appreciable.

The amount of FBA in each steps in the Nogawa river basin is as follows;

(1) The amount of FBA discharged in the river from households are estimated to be 5.4 kg/day, which is calculated back from the detected value of the amount run (1.8 kg/day), dissolving ratio of the FBA's (2:1) and the transport ratios found by the field experiments in the daytime (87% for FBA-1 and 15% for FBA-2, respectively). So the amount of FBA disappeared in the water is 3.6 kg/day, the difference between 5.4 and 1.8 kg/day.

(2) The amount of FBA supplied in the laundering at household can be estimated to be 10 kg/day according to the discharge ratios in the washing (70% for FBA-1 and 50% for FBA-2). So the difference between 10 and 5.4 kg/day makes the amount of FBA taken on wash load, 4.6 kg/day.

These values are shown in Fig. 7.

The amount of FBA supplied in the Nogawa river basin estimated here is in good agreement with the statistically assessed value, 9.98 kg/day. It is concluded that the transport ratio of FBA estimated from the throw-in experiments can be applied to the overall stream of the Nogawa.

Fig. 7 Flow diagram of FBA from built detergents to the Tama River.

5. Conclusion

1) Model experiments at laboratory

Photofading behaviors of FBA-1 and FBA-2 in the river water are different. By exposure to sunlight for 60 min, the fluorescence intensities of FBA-1 and FBA-2 are reduced to 93% and 29%, respectively.

The rate of biodegradation of both FBA-1 and FBA-2 in the river water is very slow: the former 0%, the latter 5% in 60 min.

Adsorption of FBA on Kanto-loam is modest: 1–2% for FBA-1 and 2–11% for FBA-2 in 60 min at the loam concentration of 0.1 g/l or less.

2) Transport experiments in the Nogawa river

Transport ratios of FBA-1 and FBA-2 in the river are different.

87% of FBA-1 was transported in the daytime; this result is consistent with that obtained by the model experiment. Photofading was a main factor for the disappearance of FBA-1 in the water.

Only 15% of FBA-2 was transported in the daytime, which disagrees with the result obtained by the model experiment; the photofading factor could not explain such a large decay in the water. Some other factors to cause such an extensive loss must be surveyed.

3) Uptake of FBA-4 onto the wash load

The uptake of FBA-4 onto the wash load in washing was found to be about 50% by the Bundle testing.

4) Estimated mass balance of FBA built in detergent

FBA applied in washing was estimated to be 10 kg per day in the river basin of the Nogawa; 4.6 kg of the FBA was adsorbed on the wash load and 5.4 kg was discharged into the river. 3.6 kg of the discharged FBA disappeared from water and the rest 1.8 kg was transported in the river.

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生活環境における蛍光増白剤の挙動と収支

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洗剤に配合された蛍光増白剤が、家庭から排出された後、どのような要因によってどの程度消失して、河川中を流れているか、について研究を行なった。

洗剤用の典型的な蛍光増白剤2種(FBA-1, FBA-2)の河川中における挙動はそれぞれ異なっていた。FBA-1ではその消失の要因は光退色であることが明らかとな

ったが、FBA-2についてはその主要因を解明することができなかった。蛍光増白剤が河川中で消失せずに輸送される割合は、それぞれ、FBA-1で87%, FBA-2で15%であった。

これらの結果にもとづき、洗剤配合蛍光増白剤の物質収支を計算することができた。