Supporting Information

Role of photodegradation in the fate of fluorescent whitening agents (FWAs) in lacustrine environments

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Includes : 18 pages; one sheet of text, 10 tables, 6 figures,

Supporting Information-1

Analytical procedure of FWAs

The samples were analyzed according to methods developed by Poiger et al. (1). All sample treatments were undertaken in a darkroom under yellow light to prevent photodegradation. Water samples were filtered through glass fiber filters (Whatman, GF/F). FWAs in the filtrates (10 mL – 1000 mL) were extracted using an octadecyl silica (ODS) cartridge (Sep-Pak Environmental tC18 plus, Waters; 900 mg of resin weight) at a rate below 30mL/min. The ODS cartridge had been previously washed with 40 mL of methanol (MeOH) and 20 mL of distilled water. FWAs were eluted with 20 mL of MeOH. The eluent was roto-evaporated to dryness and re-dissolved in an appropriate volume (1 mL – 100 mL) of N, N-dimethylformamide/water/MeOH (1:1:2) and, a 100 µL aliquot was injected onto the HPLC.

Particulate samples (suspended particles, sediment trap samples, and sediment samples) were freeze-dried before analysis. The glass fiber filters containing the particles or the sediments were placed into 50 mL amber centrifuge tubes and were extracted with 10mL of 0.03 M tetrabutylammonium/MeOH using ultrasonicator (UT-15, SHARP) for 30 min. The extraction was repeated 4 times, and the combined extracts were percolated through quartz wool, roto-evaporated, and re-dissolved into 30mL of distilled water. The aqueous solution containing FWAs were extracted and analyzed by the same procedure as the filtrate samples.

HPLC analyses were performed using Hewlett-Packard G1310. FWAs were separated on a reversed phase column with precolumn (HP ODS Hypersil, 5 µm, 4.8 mm I.D. x 200 mm) operated at 25 °C with an eluent flow rate of 1mL/min. The mobile-phase solvents were acetonitrile/MeOH (1:1) (eluent A) and 0.1 M aqueous ammonium acetate buffer of pH 6.5 (eluent B). A 25 min linear gradient from 30% A/70% B to 70%A/30% B was employed. An initial eluent composition was re-established after a 2-min linear gradient, followed by an equilibrium time of 5 min. Stilbene-type compounds have trans (E) and cis (Z) geometric isomers and only trans isomers fluoresce and, therefore, cis isomers were partially converted to trans isomers through isomeric equilibrium using on-line post-column UV irradiation for 5 seconds at 254 nm (Photochemical Reactor; Aur Industry). The irradiated eluent was monitored with a fluorescence detector (Hitachi F1000; excitation wavelength: 350 nm; emission wavelength: 430 nm).

FWAs were quantified by the external standard method based on peak area. The linearity of the calibration curve ($r^2 > 0.99$) was confirmed for the concentration range of 0.4 ng/mL – 200 ng/mL for DAS1 and 0.05 ng/mL – 20 ng/mL for DSBP. Analytical standards were kindly supplied by Dr. J. Kramer of Ciba-Geigy AG, Switzerland.

Reference

- (1) Poiger, T.; Field, J. A.; Field, T. M.; Giger, W., Occurrence of Fluorescent Whitening Agents in Sewage and River Water Determined by Solid-Phase Extraction and High-Performance Liquid Chromatography. *Environ. Sci. Technol.* **1996**, *30*, (7), 2220-2226.

(a) **DSBP**

(b) **DAS1**

Figure S1. Structures of DSBP and DAS1.

Figure S2. Study area and sampling locations of Lake Biwa.

Figure S3. Concentrations of dissolved FWAs and DSBP/DAS1 ratio in sewage, sewage effluents, river water, and lake water in Lake Biwa catchment.

Figure S4. Correlation between solar radiation and DSBP/DAS1 ratio.

Figure S5. Time-course of FWA concentrations (left) and DSBP/DAS1 ratio (right) during sunlight-exposure experiment.

Figure S6. Correlation between $\ln R_t$ and $\ln B_t$ in photodegradation experiment. R_t and B_t mean DSBP/DAS1 ratio and remaining proportion of FWAs, respectively, during sunlight-exposure experiment.

TABLE S1. Geographical parameters of Lake Biwa

Surface area (km ²)	670
Max depth (m)	104
Mean depth (m)	41
Volume (km ³)	27.5
Catchment area (km ²)	3174
Inhabitants in catchment	1.3×10^6
Inflow river	121
Outflow river	1
Mean residence time of water (year)	5.5

Table S2. Concentrations of FWAs in river water (Station Y of R. Yasu)

	DSBP				DAS1				DSBP/DAS1		
	Dissolved	Adsorbed	Total	%Dissolved	Dissolved	Adsorbed	Total	%Dissolved	Dissolved	Adsorbed	Total
14:00	0.269	n.a.	n.a.	n.a.	0.115	n.a.	n.a.	n.a.	2.35	n.a.	n.a.
17:00	0.144	0.0361	0.181	80.0%	0.090	0.00604	0.096	93.7%	1.61	5.98	1.88
20:00	0.169	0.0151	0.184	91.8%	0.111	0.00699	0.118	94.1%	1.52	2.16	1.56
23:00	0.259	0.0402	0.299	86.6%	0.122	0.00596	0.128	95.3%	2.13	6.74	2.34
2:00	0.224	0.0126	0.237	94.7%	0.117	0.00685	0.124	94.5%	1.91	1.83	1.91
5:00	0.262	0.0221	0.284	92.2%	0.116	0.00857	0.124	93.1%	2.26	2.58	2.29
8:00	0.278	0.0217	0.300	92.8%	0.126	0.00958	0.135	92.9%	2.21	2.27	2.22
11:00	0.297	0.0136	0.310	95.6%	0.130	0.00674	0.137	95.1%	2.28	2.02	2.27
Average	0.238	0.023	0.257	90.5%	0.116	0.007	0.123	94.4%	2.05	3.18	2.08
SD	0.054	0.011	0.056	5.5%	0.012	0.001	0.014	0.9%	0.32	2.07	0.29

n.a. : not analyzed

Table S3. Phase-distribution of FWAs in some of the water samples from Lake Biwa

Sample	DSBP				DAS1			
	Dissolved (ng/L)	Adsorbed (ng/L)	Total (ng/L)	%Dissolved	Dissolved (ng/L)	Adsorbed (ng/L)	Total (ng/L)	%Dissolved
July 2.5m	0.31	0.0113	0.317	96.4%	2.49	0.0279	2.52	98.9%
July 15m	1.90	0.0114	1.914	99.4%	4.07	0.0305	4.10	99.3%
July 30m	0.83	0.0131	0.840	98.4%	3.94	0.0321	3.97	99.2%
July 70m	1.34	0.0256	1.370	98.1%	4.35	0.0709	4.42	98.4%
Feb. 2.5m	1.74	0.1100	1.850	94.1%	3.53	0.2005	3.73	94.6%
Feb. 30m	1.88	0.0947	1.978	95.2%	3.36	0.2112	3.57	94.1%
May 2.5 m	0.26	0.0338	0.295	88.5%	1.88	0.0766	1.95	96.1%
May 30m	0.85	0.0261	0.875	97.0%	2.42	0.0713	2.49	97.1%
Average				95.9%				97.2%
SD				3.5%				2.1%

Table S4. Concentrations of FWAs in Wastewater Influent and Effluents

		Population in the catchment	Influent										Effluent										per-capita-load* (mg/person/day)		Removal Efficiency																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
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*Total (Dissolve + adsorbed)-FWAs-based calculation . For samples in Dec. 2001 and Feb. 2002, Total FWAs concentrations were estimated based on %dissolved for the sample in Aug. 2001.

TABLE S5. Cumulative Input of FWAs Per Water Volume in Lake Biwa and Greifensee

	Input (g/d)		Cumulative input per water volume (kg/km ³)	
	DSBP	DAS1	DSBP	DAS1
Lake Greifensee	156	114	415	303
Lake Biwa	8667	2033	633	148

※1. Data of Lake Greifensee were calculated from data reported in ref-11).

(residence time: 1.1 year, water volume 0.151 km³)

※2. Input to Lake Biwa was calculated from Tables S8.

Table S6. Variation of %photodegradation estimated by various degradatoin experiments

Data Source reference		The present study	Hayakawa et al. (2007) ref-25	Kramer et al. (1996) ref-12	Kramer et al. (1996) ref-12
Condition		Lake water/Sewage (14:1)	River water	Lake water	bidistilled water with phosphate buffer
DOC (mg-C/L)		25.9 mg/L	0.77 mg/L	3.3 mg/L	0
K1		0.0088	0.0058	0.0080	0.0128
K2		0.0019	0.0014	0.0025	0.0021
% Remaining	DSBP	30	28	25	32
	DAS1	77	74	65	83
% Degradation	DSBP	70	72	75	68
	DAS1	23	26	35	17

*R0 : 5.41, Rt : 2.08

Table S7. Applied parameters for the calculation of load to Yasu River

Parameter	Abbreviation	unit	Applied parameter	
			DSBP	DAS1
Per-capita-load of FWA	A	(mg/day/person)	11.0	2.0
Population in the catchment	B	(capita)	78859	
percent population covered by regional STP	C1	(%)	26	
percent population covered by local STPs	C2	(%)	14	
percent population covered by on-site treatment system	C3	(%)	16	
Removal Efficiency of FWA in local STPs	D2	(%)	65	63
Removal Efficiency of FWA in on-site treatment system	D3	(%)	43	42

Table S8. Mass Balance of FWAs in Lake Biwa

	DSBP		DAS1	
	Mass flow		Mass flow	
	(kg/month)	(%)	(kg/month)	(%)
<i>Input*</i>	260±43		61±19	
<i>Output</i>				
Riverine outflow**	17	6.5	6	9.8
Photodegradation***	93 - 99		44 - 63	
Sedimentation****	0.49	0.2	0.28	0.5

*Details are available in Table S9.

**Based on hydraulic flow and measured FWA concentrations in the outflowing river.

***Based on DSBP/DAS1 ratio using Eq. (5)

****Based on the FWAs determination of sediment trap sample.

Table S9-1. Calculation of Total Load of DSBP to Leke Biwa (riverine inlets and direct discharge of secondary effluents from regional STP)

[illegible]

Table S9-2. Calculation of Total Load of DAS1 to Leke Biwa (riverine inuts and direct discharge of secondary effluents from regional STP)

[illegible]