Article

The origin of sulfur in the lake Fukami-ike, Japan

Mayuko NAKAGAWA [1]**, Yuichiro U**ENO [2]**, Akiko Y**OKOYAMA [3]**, Akihiko Y**AGI [4]
and Naohiro YOSHIDA [5]

Abstract

Fukami-ike, a eutrophic lake in Japan, has a relatively high sulfate concentration （585 ± 56 μmol L^{-1}） over the entire surface. In order to determine the origin of sulfur in this lake, flow rates and sulfate concentration of five inflows and an outflow were measured and analyzed. The water flux of precipitation in the catchment area is similar to that of surface outflow. Approximately 90 % of precipitation enters to the lake as groundwater inflow. Approximately 20 % of surface sulfur outflux is supplied by surface sulfur influx and the remaining is supplied by groundwater inflow, regardless of the amount of precipitation. The sulfate concentration of groundwater and surface inflow channels on the west side （approximately 400 μ mol L^{-1}） was much lower than on north side （approximately 1400 μmol L^{-1}） of the lake. Such a difference would be caused by the degree of sulfur content in the sedimentary rocks. The sulfate concentration and sulfur content of precipitation and fertilizers contributed little to the sulfur source of the lake, which was also supported by their large sulfur isotopic ratios （+6.1 ‰ to +8.3 ‰）. Thus, the weathered sedimentary rocks surrounding the lake （-28.3 ‰ to +9.1 ‰） are the main source of sulfur in the lake. Furthermore, the sulfur in the coarse-grained sandstone from Oshimojo Formation is estimated to contribute more than 70 % of the sulfur in the lake.

Key words: origin of sulfate, sulfur isotope, fertilizers, sedimentary rocks, lake Fukami-ike

Introduction

Fukami-ike is a monomictic lake located 484 m above sea level in the mountainous area of southern Nagano Prefecture. The lake is stratified from April to November, and hydrogen sulfide produced by sulfate-reducing bacteria can be detected in the hypolimnion. During the stratification period, photosynthetic bacteria grow vigorously in the upper layer of the H$_2$S zone （Yagi et al., 1983）. One previous study showed the sulfate and sulfide concentrations in the anoxic layer of the lake play an important role in the relative activity of sulfate reduction and anoxygenic photosynthesis （Nakagawa et al., 2012）. The sulfur in lakes generally originated from the weathering of sulfur containing rocks in the catchment area. However, some fraction of sulfur from agricultural and industrial origin such as fertilizers and industrial effluents is also

reported （Cook and Kelly, 1992; Robinson, 1997）. The sulfur isotopic ratios can be used to identify the sources such as natural and anthropogenic S contribution.

The objectives of this study were to gain a better understanding of the sulfur cycle and to clarify the source of sulfur in the lake. We investigated the origin of sulfur in the lake by performing chemical and isotopic analyses of inflows, an outflow, lake water, fertilizers, and the sedimentary rocks surrounding the lake.

Methods

For determining water and sulfur fluxes, inflow rates and sulfate concentrations of channels *a-e* （Fig. 1） were measured monthly from June to November in 2011 by a volumetric method. Outflow rates at channel *f* were also measured with an electromagnetic

[1] Academy for Co-creative Education of Environment and Energy Science, Tokyo Institute of Technology, 4259 Nagatsutacho, Midori-ku, Yokohama, 226-8502, Japan
[2] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8551, Japan
[3] Water agency INC., 3-25 Higashigokencho, Shinjuku-ku, Tokyo,162-0813,
[4] Environmental Engineering Course, Aichi Institute of Technology, 1247 Yachigusa, Yakusacho, Toyota, Aichi, 470-0392, Japan
[5] Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259 Nagatsutacho, Midori-ku, Yokohama, 226-8502, Japan
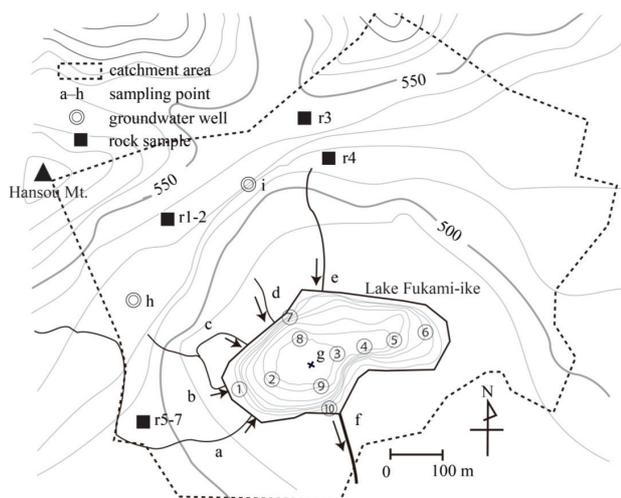
Fig. 1 Bathymetrical map and sampling stations of Lake Fukami-ike. The sampling stations are for (*a-e*) inflows, (*f*) outflow, (*g*) lake water at the deepest point, (*h*) groundwater well, (*i*) spring water, and (r1-r7) sediment rocks.

current meter (model ACM210-D; Alec Electronic, Kobe). The detailed measurement procedures for flow rates and sulfur isotopic ratios are described elsewhere (Nakagawa et al., 2012). The relative standard deviation (RSD) of each inflow rate measurement was approximately 12 %. The RSD of the current meter used for outflow measurements was 2 %. Annual fluxes were estimated by multiplying flow rate by time. Outflow and inflow water samples were collected in polyethylene bottles to measure the concentrations and δ^{34}S values of sulfate. Meteorological data (rainfall at Anan-cho, air temperature and duration of sunshine at Iida-shi) were obtained from the Automated Meteorological Data Acquisition System (AMeDAS) monitored by the Japan Meteorological Agency (http://www.jma.go.jp/jma/indexe.html). Sulfate concentrations in precipitation were obtained from the Limnology Committee of Shimoina Kyoiku-kai (2009).

Lake water was sampled to determine the distribution of sulfate concentration in the surface water of the lake.

For determining the origin of sulfate in the lake, the sedimentary rocks in the catchment area of the lake and fertilizers BBC-284 and NKC-201 (JA Agriyell-Nagano) used in paddy fields were sampled. The rocks were sampled from both the Oshimojo (r1-r4) and Arakida formations (r5-r7) (Fig. 1).

Rock samples were first cut into slabs about 10 cm across using a diamond-tipped saw to remove weathered surfaces. Thereafter, ~10-g slabs were crushed into small chips about 2 mm across using a stainless steel mortar and pestle. The small chips were picked and crushed using an agate mortar and pestle. The fertilizers were crushed using a porcelain mortar and pestle. Total sulfur was

extracted from ~10-g samples using a Kiba method (Kiba et al., 1955). Then, acid volatile sulfur (AVS) and pyrite sulfur were extracted by 6N HCl and CrCl$_3$ (Canfield et al., 1986). These treatments extracted sulfur compounds as H$_2$S, which is then converted to Ag$_2$S. The detection limit of the sulfur contents was 5.5×10^{-5} mg S g^{-1}.

Sulfate concentrations in water samples were measured by ion chromatography (IC; Dionex Qic) equipped with IonPAC AS11-HC column (Dionex). After the sulfur compounds were converted into Ag$_2$S, sulfur isotopic ratios were measured by fluorination and a multiple gas chromatographic (GC) technique. The isotopic composition of SF6 was determined using Thermo-Fishier MAT253 mass spectrometers, both equipped with a dual inlet system. Sulfur isotopic compositions are reported relative to the Vienna Canion Diavro Troilite (VCDT) standard according to

$$\delta^{34}S = \ln\left(\frac{R_{sample}}{R_{standard}}\right) \times 1000 \ [\text{‰}] \qquad (3)$$

where R denotes the isotope ratios (^{34}S / ^{32}S) of samples and standards. The analytical reproducibility of the δ^{34}S value, as demonstrated by the replicate analyses of several working standards, is better than 0.6 ‰.

Results

The 2011 annual water fluxes of evaporation, precipitation, surface inflow, and surface outflow to and from the lake are shown in Table 1. Addition to the water fluxes in 2011, three-year observation from 2008 to 2010 reported in previous study (Nakagawa et al., 2012) were averaged to show the range of each water flux (Table 1). The water fluxes in 2011 showed a similar trend to the hydrological mass balance model suggested in the previous study. Approximately 10 % of the precipitation water flux in the catchment area is surface inflow into the lake, and the remaining would be potential groundwater inflow into the lake. This estimated water flux of groundwater inflow into the lake is almost the same value to the imbalance between the water flux of surface input and output into and from the lake.

The mean sulfate concentrations and annual sulfur fluxes of lake surface water, groundwater, inflows, and outflow are listed in Table 2. Measured sulfate concentrations of inflow channels *a*, *b*, *c*, *d*, and e varied from 360 to 1550 μmol L^{-1}. The annual mean sulfate concentrations of channels *a* and *b* were lower (337-556 μmol L^{-1}) than those of channels *c*, *d*, and *e* (945-1633 μmol L^{-1}). The total surface sulfate influx was 63 kmol yr^{-1}, which was calculated by multiplying the sulfate concentration and monthly water flux of each channel (Table 1). The sulfate concentration of outflow channel *f* was almost equal to that of the lake surface water (①-⑩;

Table 1. Annual water fluxes of precipitation in the catchment area, into and out from the Lake Fukami-ike.

	Sampling point	four-year averaged annual flow[*] ± SD[†] (10^6 L yr^{-1})	Annual flow in 2011 ± SD[††] (10^6 L yr^{-1})
Catchment area	precipitation	423 ± 117	590
Lake inflow	a	11.3 ± 4.1	11.5 ± 0.6
	b	3.5 ± 1.0	0.5 ± 0.2
	c	7.4 ± 2.1	8.7 ± 0.2
	d	14.1 ± 4.7	13.5 ± 0.4
	e	19.2 ± 7.7	19.1 ± 1.6
	total inflow	55.6 ± 10.2	57.8 ± 1.8
Lake outflow	f	443 ± 132	592 ± 12
Lake surface	precipitation	41.3 ± 11.4[**]	57.6
	evaporation	15.0 ± 1.5[***]	14.8 ± 1.4
Net flux of lake	outflux-influx	361 ± 132	492 ± 7

[†] The SD represents annual variability for each flux and error propagation of calculation.

[††] The SD represent measurement errors and error propagation of calculation.

[*] Data showed four-year averaged values from 2008-2011 (2008-2010; Nakagawa et al., 2012, 2011; this study)

[**] Data obtained from the Automated Meteorological Data Acquisition System (AMeDAS).

[***] Data calculated by Makkink method (Nagai et al., 1993).

Table 2. Sulfate concentration, sulfur fluxes and δ^{34}S values for several inputs and outputs of the Lake Fukami-ike in 2011.

	Sampling point (n)	[SO$_4$] ± SD (μmol L^{-1})	Flux ± SD[†] (kmol yr^{-1})	δ^{34}S ± SD[††] (‰)
Inputs	a (6)	360 ± 17	4.1 ± 0.2	− 15.8
	b (6)	468 ± 73	2.3 ± 0.4	− 15.3 ± 0.9
	c (6)	1550 ± 144	13.4 ± 1.3	− 17.3 ± 3.6
	d (6)	1334 ± 238	17.6 ± 3.2	− 18.7 ± 0.5
	e (6)	1372 ± 211	25.3 ± 4.0	− 18.3 ± 0.5
	total surface inflow[*]	1112 ± 92	62.8 ± 5.3	− 18.1 ± 1.5
	precipitation[**]	10 ± 5	0.6 ± 0.1	14.0 ± 1.7
	groundwater h (3)	417 ± 33		− 15.0 ± 0.7
	spring water i (1)	1369		n. d.[‡]
Outputs	outflow f (6)	558 ± 52	309 ± 30	− 12.6 ± 0.7
Lake surface	① - ⑩	585 ± 56		n. d.[‡]

[†] The SD represent propagated error from calculation (flux = [SO$_4$] × annual flow in 2011).

[††] The δ^{34}S values are obtained from Nakagawa et al. 2012.

[*] The sulfate concentration and the δ^{34}S value were weighted according to each annual inflows (a-e). The sulfate flux was the sum of all inflow sulfate fluxes.

[**] Data around Nagano prefecture (Akata et al., 2002)

[‡] The 'n.d.' represent the data not determined

Table 3. Sulfur contents and isotopic values of sediment rocks and fertilizer samples.

Sample name	Formation	Stone group	S content [mg S g^{-1}]	δ^{34}S [‰]
Rock sample				
r1	Oshimojo	Coarse-graind sandstone	5.7×10^{-5}	9.1
r2	Oshimojo	Coarse-graind sandstone	3.0×10^{-4}	-26.1
r3	Oshimojo	Coarse-graind sandstone	2.1×10^{-4}	-28.3
r4	Oshimojo	Coarse-graind sandstone	4.4×10^{-4}	-16.9
r5	Arakida	Tuffaceous sandstone	5.5×10^{-5}	6.7
r6	Arakida	Tuffaceous gravelstone	3.5×10^{-6}	n.d.[‡]
r7	Arakida	Tuffaceous mudstone	3.7×10^{-6}	n.d.[‡]
Fertilizer				
BBC-284 (2)			12.7	8.2 ± 0.2
NKC-201			0.1	6.1

[‡] The 'n.d.' represent the data not determined

Table 2). The annual sulfur surface outflux was approximately five times greater than the surface sulfur influx (309 kmol yr^{-1}). The sulfur flux difference between the surface influx and outflux into and from the lake was calculated to be 245 kmol yr^{-1}.

Sulfur contents and δ^{34}S values of sedimentary rocks and fertilizers are summarized in Table 3. The sulfide compounds (AVS, and pyrite sulfur) in rock samples were below the detection limit. Sulfur contents of sedimentary rock samples varied from 3.5×10^{-6} to 4.4×10^{-4} mg S g^{-1}. The sulfur content in fresh coarse-grained sandstone in the Oshimojo formation (r2-r4) was much higher than in highly weathered sandstone in the Oshimojo formation (r1) and tuffaceous stones in the Arakida formation (r5-r7). δ^{34}S values of r2 and r3 samples were much smaller than those of other rock samples. The sulfur content in the fertilizer BBC-284 was high relative to that in NKC-201. Fertilizer δ^{34}S values ranged from +6.1 ‰ to +8.3 ‰.

Discussions

The sulfur mass balance in 2011 showed similar contributions of surface sulfur influx to surface sulfur outflux, as estimated using the data for 2008, although the precipitation in 2011 was approximately twice as great as in 2008. In order to meet the sulfur mass balance of total sulfur influx to and outflux from the lake, the groundwater sulfur flux is estimated to be 280 kmol yr^{-1}, calculated by the sum of the difference between the surface influx and outflux (245 kmol yr^{-1}) and the total sedimentary sulfur flux of the whole

lake（34.2 kmol yr^{-1}; Nakagawa et al., 2012）. Thus, the sulfur mass balance in 2011 confirmed that most of the sulfate in the lake can be attributed to the groundwater inflow（Table 2）.

The contribution of sulfur in fertilizers can be estimated by the amount used and the isotopic values of the fertilizers. The area of a paddy field is approximately 2000 m^2. According to the rice cultivation protocol of the Japan Agricultural Cooperatives in Minami Shinshu, 0.5 kg m^{-2} of fertilizer BBC-284 is used in April, and 0.1 kg m^{-2} of NKC-201 is used in the end of July. Thus, the sulfur input originating from fertilizers is 0.4 kmol yr^{-1} and forms a very small contribution to the sulfur content in the lake. Furthermore, the δ^{34}S values of fertilizers BBC-284 and NKC-201 were typical values compared to those reported previously（>6.6 ‰ ; Mizota and Sasaki, 1996）. Although the contribution of fertilizers as the origin of sulfur in the lake is small, the δ^{34}S of fertilizers was observed in inflow channel *c* placed in the paddy field. The δ^{34}S values of channel *c* are sometimes larger（approximately -13 ‰）than the others（approximately -20 ‰）in the end of summer （August to October）, when the sulfate concentration is higher.

The average sulfate concentration of precipitation in Shimoina-gun is 10 ± 5 μmol L^{-1}（the Limnology Committee of Shimoina Kyoiku-kai, 2009）and the range of sulfate δ^{34}S value in Nagano Prefecture is 14.0 ± 1.7 ‰（Akata et al., 2002）. The sulfur flux supplied by precipitation in the catchment area is 5.9 ± 3.0 kmolS yr^{-1}, and its contribution to the total sulfur influx（343 ± 30 kmol yr^{-1}）into the lake is less than 2 %.

The δ^{34}S values of sedimentary rocks surrounding the lake showed great variation, from -28.3 ‰ to +9.1 ‰（Table 2）. The δ^{34}S values varied with the degree of weathering in rocks, which correlates with sulfur contents. As the degree of weathering is higher and the sulfur content is lower, the δ^{34}S value（7.9 ± 1.7 ‰）is larger. On the other hand, low δ^{34}S values（-23.8 ± 6.0 ‰）were observed in sedimentary rocks with higher sulfur content. The variation of sulfur content and isotopic values of sedimentary rocks seems to have a relation to the difference between inflow channels *a-b* and *c-e* about the sulfate concentration and isotopic values. The inflow channels *c-e* showed higher sulfate concentration （approximately 1400 μmol L^{-1}）with lower δ^{34}S values（approximately -18 ‰）, and the sedimentary rocks that have high sulfate content with low δ^{34}S values（r1-r4）were sampled around there（Fig. 1）.

The ease of sulfur dissolution from the rocks would be dependent on chemical composition and crystal structure of the minerals although they are still uncertain. Thus, further chemical and mineralogical study of the sedimentary rocks is needed for understanding the cause of the great variation in sulfur content and isotopic values in the sedimentary rocks. However, isotopic fractionation during precipitation and dissolution of sulfate

minerals has been reported to be small（<2 ‰）（Thode and Monster, 1965; Szaran et al., 1998）. Thus the δ^{34}S values of surface water and groundwater input would be the mixing of the sedimentary rocks with high sulfur content in the Oshimojo and the sedimentary rocks with low sulfur content in the Arakida formations. If the isotopic composition of inflows to the lake originates from the sulfate from the weathered rocks of the Arakida formation and the Oshimojo formation, then the contribution of the sulfate originating from the Arakida formation would be estimated using the following equations:

$$f_{p} + f_{high-S} + f_{low-S} = 1$$

$$\delta^{34}S_{input} = f_{p} \times \delta^{34}S_{p} + f_{high-S} \times \delta^{34}S_{high-S} + f_{low-S} \times \delta^{34}S_{low-S}$$

where f_{p}, f_{high-S}, and f_{low-S} are the sulfur contributions of precipitation, high-sulfur-content sedimentary rocks, and low-sulfur-content sedimentary rocks, respectively. $\delta^{34}S_{input}$, $\delta^{34}S_{p}$, $\delta^{34}S_{high-S}$, and $\delta^{34}S_{low-S}$ are the δ^{34}S values of the input to the lake, precipitation, high-sulfur-content sedimentary rocks（-23.8 ± 6.0 ‰）, and low-sulfur-content sedimentary rocks（7.9 ± 1.7 ‰）, respectively. The f_{p} is the fraction of precipitation sulfur flux to the total sulfur influx（0.02）. If $\delta^{34}S_{input}$ is -15.0 ± 0.7 ‰, the f_{high-S} and f_{low-S} are estimated to be 0.73 ± 0.16 and 0.27 ± 0.16, respectively. Further, if $\delta^{34}S_{input}$ is -18.1 ± 1.5 ‰, the f_{high-S} and f_{low-S} are estimated to be 0.83 ± 0.18 and 0.17 ± 0.18, respectively. The geological profile of the lake（Shikama, 1954）indicates that precipitation in the catchment area mainly goes through a longer pathway in the Oshimojo formation than in Arakida formation.

In summary, sulfur mass balance and δ^{34}S analysis reveal the origin of sulfur in the lake originates mainly from high-sulfur-content and low-sulfur-content sedimentary rocks; precipitation contributes to a small fraction of the sulfur content in the lake, while the contribution of fertilizers is negligibly small.

Acknowledgments

References

Akata, N., F. Yanagisawa, R. Motoyama, A. Kawabata and A.

Ueda（2002）: Sulfur isotope ratios of non-sea salt sulfate in wet deposits in Japan. *Journal of the Japanese Society of Snow and Ice*, **64** : 173-184（*in Japanese with English abstract*）.

Cook, R. B. and C. A. Kelly（1992）: Sulfur cycling and fluxes in temperate dimictic lakes, p. 145-188. In Sulfur cycling on the continents, R. W. Howarth, J. W. B. Stewart, and M. V. Ivanov （eds.）: 145-188. John Wiley & Sons.

Kiba, T., T. Takagi, Y. Yoshimura and I. Kishi（1955）: Tin（II）-strong phosphoric acid. A new reagent for the determination of sulfate by reduction to hydrogen sulfide. *Bulletin of the Chemical Society of Japan*, **28** : 641-644.

Limnology Comittee of Shimoina Kyoiku-kai（2009）: Shimoina-shi. Editorial Committee of Shimoina-shi（*in Japanese*）.

Mizota, C. and A. Sasaki（1996）: Sulfur isotope composition of soils and fertilizers: Differences between Northern and Southern hemispheres. *Geodema*, **71** : 77-93.

Nakagawa, M., Y. Ueno, S. Hattori, M. Umemura, A. Yagi, K. Takai, K. Koba, Y. Sasaki, A. Makabe and N. Yoshida（2012）: Seasonal change in microbial sulfur cycling in monomictic Lake Fukami-ike, Japan. *Limnolology and Oceanography*, **57** : 974-988.

Nagai, A.（1993）: Estimation of pan evaporation by Makkink equation. *Journal of the Japan Society of Hydrology and Water Resources*, **6** : 238-243（*in Japanese with English abstract*）.

Robinson, B. W. and S. H. Bottrell（1997）: Discrimination of sulfur sources in prostine and polluted New Zealand river catchments using stable isotopes. *Applied Geochemistry*, **12** : 305-319.

Shikama, T.（1954）: On the Tertiary formations of Tomikusa in south Nagano prefecture. *Science Reports of the Yokohama National University*, **3** : 71-108（*in Japanese*）.

Szaran, J., H. Niezgoda, and S. Halas（1998）: New determination of oxygen and sulphur isotope fractionation between gypsum and dissolved sulphate. *RUDARSKO-METALURSKI ZBORNIK*, **45** : 180-182.

Thode, H.G. and J. Monster（1965）: Sulfur isotope geochemistry of petroleum, evaporites, and ancient seas. In Fluids in Subsurface Environments, Memoirs American Association of Petroleum Geologists, vol. 4, Young, A., Galley, J.E.（eds.）: 367-377.

Yagi, A., I. Sshimodaira, H. Terai, and Y. Saijo（1983）: Seasonal change of chlorophyll *a* and bacteriochlorophyll in Lake Fukami-ike. *Japanese Journal of Limnology*, **44** : 283-292.
（Editor: Dr. Jun Murase, Graduate School of Bioagricultural Sciences, Nagoya University）

摘　　要

深見池（長野県）の硫黄起源推定

中川麻悠子 [1]・上野雄一郎 [2]・横山亜希子 [3]・八木明彦 [4]・吉田尚弘 [5]

　長野県にある富栄養湖、深見池は表層全体の硫酸濃度が 585 ± 56 μmol L^{-1} と一般的な淡水湖より高い硫酸濃度を保持している。この湖の硫黄起源を推定するため、流入河川 5 か所、流出河川 1 か所の水量及び硫酸濃度の測定を行った。深見池の表層流出水量は集水域の降水量とほぼ同量であり、集水域の降水量の約 9 割が地下水として深見池に流入していることが確認された。硫黄収支計算により、年間降水量の多少に関わらず、表層流出硫黄量の約 2 割が表層流入水から供給され、残りは地下からの流入水を通して供給されていることが明確になった。流入河川及び地下水中の硫酸濃度は東側（約 400 μmol L^{-1}）と北側（約 1400 μmol L^{-1}）とで年間を通じて大きく異なっており、堆積岩中の硫黄含有量の影響が示唆された。硫黄源として降水と肥料は濃度及び含有量から寄与は小さく、またそのことは硫黄同位体比が大きい（> +6 ‰）ことからも確認された。つまり、深見池の硫黄は主に深見池周辺岩石中硫黄成分（-28.3 ‰ - +9.1 ‰）が表層水及び地下水に溶出したものが供給されている。特に硫黄含有量が多く、硫黄同位体比が小さい大下条層の砂岩からの寄与が 7 割以上であることが硫黄含有量と同位体比の混合式から見積もられた。

キーワード：硫黄起源，硫黄同位体，肥料，堆積岩，深見池

[1] 〒 226-8502 神奈川県横浜市緑区長津田町 4259 東京工業大学環境エネルギー協創教育院

[2] 〒 152-8551 東京都目黒区大岡山 2-12-1 東京工業大学大学院理工学研究科地球惑星科学専攻

[3] 〒 162-0813 東京都新宿区東五軒町 3-25 ウォーターエージェンシー株式会社

[4] 〒 470-0392 愛知県豊田市八草町八千草 1247 愛知工業大学

[5] 〒 226-8502　神奈川県横浜市緑区長津田町 4259 東京工業大学大学院総合理工学研究科化学環境学専攻

（連絡著者：中川麻悠子 E-mail: nakagawa.m.ae@m.titech.ac.jp）