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AUTHOR(S):
Yoshida, Hiroo; Kudari, Shunsuke; Hori, Toshitaka; Sugiyama, Masahito

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Distribution and Geochemical Behavior of Anionic Surfactants Determined as Ethyl Violet Active Substances in Lake Biwa, Japan
Hiroo Yoshida, Shunsuke Kudari, Toshitaka Hori, Masahito Sugiyama

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan

Correspondence to: Masahito Sugiyama, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: sugiyama.masahito.5s@kyoto-u.ac.jp

Telephone: +81-75-753-6836; fax: +81-75-753-7879
**Abstract**

The distribution and geochemical behavior of anionic surfactants (AS) determined as ethyl violet active substances (EVAS) were studied in Lake Biwa, Japan. We determined the vertical distributions of dissolved EVAS (DEVAS), suspended particulate EVAS (PEVAS), particulate organic carbon (POC), and the PEVAS/POC ratio. Statistical analyses conducted using plots of PEVAS vs. POC and PEVAS/Chlorophyll-a (Chl-a) vs. POC/Chl-a revealed that the distributions of DEVAS and PEVAS were affected by the concentrations of freshly produced POC and aged POC and by the pH of the lake water. Adsorption and desorption of EVAS onto the POC phase were found to be important mechanisms regulating the distribution and environmental/geochemical behavior of EVAS in the lake. The organic carbon-normalized particle–water partitioning coefficient, $K_{oc}$, for EVAS was also estimated and compared to that for nonylphenol.

**Keywords**
Introduction

Linear alkylbenzene sulfonate (LAS) is the primary anionic surfactant found in Japan. This compound is listed as Class I in the Pollutant Release and Transfer Register Law of Japan. A Class I Designated Chemical Substance is defined as continuously occurring throughout much of the environment based on its physical and chemical properties, manufactured volume, and importation and usage, and having risks to human health and the ecosystem (Japan Ministry of the Environment 2013). Production of LAS was 72 kt in 2002 and the amount of LAS discharged to the sewage in Japan was 64 kt in 2001 (National Institute of Technology and Evaluation 2005). The degree of discharge is related to the environmental risk.

Research on anionic surfactants (AS) in the aquatic environment has been carried out globally. In Japan, AS concentrations have been reported to range...
between 50–8500 µg/L in river water (Kobayashii and Yamauchi 1979; Kobuke 1981; Yoshimura et al. 1984; Hirayama et al. 2006), 0–264 µg/g in river sediments (Ambe 1972; Uchiyama 1982; Yoshimura et al. 1984), and 10–50 µg/g in lake sediments (Ambe 1972). LAS concentrations ranged between 0.6–79 µg/L in river water in Japan (Kobuke 2004; Miura et al. 2008), 0–342 µg/L in South Africa (Gordon et al. 2009), and 2–126 µg/L in the Philippines (Dyer et al. 2003). LAS concentrations also ranged between 60–2300 µg/g in suspended particles in rivers in Japan (Takada and Ishiwatari 1987) and between 0.03–17.76 µg/g and 0.101–0.186 µg/g in river sediments in Portugal (Hampel et al. 2009) and South Africa (Gordon et al. 2009), respectively.

As noted above, most limnological and environmental studies of AS have been focused on rivers, but few studies have been conducted of AS in lakes. The distribution of AS in rivers is important in determining anthropogenic pollution levels and discharges to the natural environment of AS by human activities. However, these studies alone are not sufficient to fully delineate the
environmental and geochemical processes of AS, because water masses are frequently renewed by flows from upstream. On the other hand, water masses may stagnate in lakes and thus, studies on partitioning of AS between lake water and suspended and sediment particles are more feasible.

Several authors have studied removal processes for AS in laboratory experiments (Ou et al. 1996; Perales et al. 1999; Doi et al. 2002; Garcia et al. 2002). These compounds are generally known to be degraded by microorganisms (Perales et al. 1999) and adsorbed by solid phases (Ou et al. 1996; Doi et al. 2002; Garcia et al. 2002). The former depends on the water temperature, while the latter is related to the organic carbon content of the solid phase, known as the particulate organic carbon (POC) content. To date, there have been few studies of adsorption and partitioning of AS to POC in lakes. Although some authors have addressed POC, they treated it as a homogeneous material despite being a mixture of various organic materials (Yoshida et al. 2009). In our previous study (Yoshida et al. 2009), we clarified that POC in lakes
could be classified into two fractions, freshly produced POC (f-POC) and aged POC (a-POC), based on differences in the affinity of nonylphenol (NP) to POC; its affinity to a-POC was approximately 4 times higher than that to f-POC. A similar evaluation is also needed for AS. Colorimetric methods have often been used for analysis of AS. Among these methods, methylene blue, which offers the advantage of being an easy-to-use and convenient technique, is widely used. In recent years, the methylene blue reagent has been replaced by an ethyl violet reagent (Soejima 1982). The ethyl violet colorimetric method is more useful than methylene blue as it has: (1) high sensitivity, (2) a very simple and less time-consuming procedure, (3) little interference by coexisting ions, and (4) good reproducibility and quantification of trace amounts of anionic surfactants (Matomizu et al. 1982). It is also used as a standard method in Japan (Japan Standards Association 1998). Therefore, we quantified AS as ethyl violet active substances (EVAS). In this study, we determined the distribution and geochemical behavior of AS in
Lake Biwa as EVAS. Using plots of suspended particulate EVAS (PEVAS) vs. POC and PEVAS/Chlorophyll-\(a\) (Chl-\(a\)) vs. POC/Chl-\(a\), we evaluated adsorption and partitioning of EVAS to POC in Lake Biwa. The average PEVAS/POC ratio and organic carbon-normalized particle–water partitioning coefficient \((K_{oc})\) of EVAS to f-POC and a-POC were estimated and compared to those of NP.

Materials and methods

Solvents and standards

Sodium sulfate and sodium hydroxide were purchased from Nacalai Tesque (Kyoto, Japan). Acetic acid, toluene, disodium ethylenediaminetetraacetate (EDTA), and sodium dodecyl sulfate (SDS) were obtained from Wako Chemicals (Osaka, Japan). Ethyl violet was obtained from Tokyo Chemical Industry (Tokyo, Japan).

Sampling site and sample collection
The sampling sites for this study were located in Lake Biwa (35°15' N, 136°05' E) and the Yasu River. Lake Biwa, which is the largest lake in Japan, is divided into two parts, the northern and southern basins. The former has a volume of 27.3 km³ with an average depth of 44 m. Thermal stratification typically occurs from May to January and vertical convection of the entire water column in the lake occurs regularly from February to April. The southern basin of the lake has a volume of 0.2 km³ with an average depth of 3.5 m. The water in this basin is not thermally stratified and is more or less saturated with atmospheric oxygen throughout the year (Sugiyama et al. 2005). Field surveys were conducted at Station Ie-1 (35°12.58' N, 135°59.55' E) between September 2000 and August 2001.

The Yasu River is a large river that flows near Station Ie-1 in Lake Biwa. It has the largest drainage area and the second highest water discharge among the more than 110 rivers flowing into Lake Biwa (Lake Biwa Environmental Research Institute 1986; Kunimatsu 1988). Several towns are located along this
river with a total population of 220,000. The river water is generally used for industrial water, domestic supply, and irrigation, and then the discharge is released to the river (Kimaro et al. 2002). Field surveys of the river were conducted at Stations YS-1 (35°09.70' N, 135°99.30' E) and YS-2 (35°02.37' N, 136°01.12' E) on 5 September 2000 and 9 March 2001.

Lake water samples were collected vertically with a Van Dorn water sampler and river water samples were collected with a glass bottle. The samples were filtered through a Whatman GF/F filter (diameter 47 mm, pore size 0.7 µm) to separate suspended particles from the water. The water samples were analyzed within 3 days of sampling. Suspended particle samples collected on the filter were kept frozen until they were analyzed.

**Analytical procedures**

Sample treatment for AS determination was carried out as follows. Forty milliliters of a water sample was transferred into a glass centrifuge tube. Two
milliliters 1 mol/L sodium sulfate solution, 2 mL acetic acid–EDTA buffer (pH 5.0),
0.8 mL 1 mmol/L ethyl violet solution, and 2 mL toluene were added to the tube.
The tube was shaken for 60 min and then centrifuged for 5 min. After phase separation, the absorbance of the toluene phase was measured at 611 nm (UV-1600; Shimadzu, Kyoto, Japan) and calibrated against an SDS solution.
Suspended particle and sediment samples were dried at 60 °C and ultrasonicated twice with 10 mL methanol for 45 min at room temperature. The obtained extracts were evaporated until they were dry using a centrifugal vaporizer (Model CVE 2wd; Tokyo Rika Kikai, Tokyo, Japan). The residue was redissolved in 40 mL water and the solution was then treated as a water sample.
POC was quantified with a CHN analyzer (Model 2400; Perkin Elmer, Tokyo, Japan). The temperatures of the combustion and reduction chambers were set to 925 °C and 640 °C, respectively.
Chl-a was quantified spectrophotometrically according to the methods of UNESCO and Lorenzen (Lorenzen 1967).
Results and discussion

Method validation

In the analyses using the ethyl violet colorimetric method, sodium sulfate was used to accelerate phase separation and EDTA was used to reduce interferences from multivalent metal ions. AS were determined as EVAS.

Method validation was carried out to evaluate the suitability of this method. SDS was used as a standard material for analysis of AS. The linearity of its calibration curve was evaluated by taking measurements at four different concentrations of SDS. The correlation coefficient $r$ of the curve was $>0.999$ from 0 to 38 $\mu$g/L SDS.

The detection limit was determined as the concentration of SDS that gave a signal three times the background noise, which was 0.27 $\mu$g/L.

Accuracy and precision were calculated based on recovery of SDS from sediments, since sediments have a more complex matrix. For this evaluation, 101 $\mu$g/g SDS was spiked into a sediment sample containing 235 $\mu$g/g of EVAS.
The recovery rate and precision were 115% and 3.3% \((n = 3)\). Thus, this method was found to be suitable for analysis of AS in environmental and geochemical studies.

Distribution and geochemical behavior of EVAS in Lake Biwa

Figure 1 shows the vertical distributions for water temperature, pH, and EVAS concentration in Lake Biwa. During the circulation period (2 April 2001), the vertical distribution of dissolved EVAS (DEVAS) was relatively constant, because the lake water was well mixed due to the vertical convection that occurs in early spring. Conversely, the DEVAS concentration during the stagnation period (12 September and 5 October 2000, 11 April 2001) had higher values at the surface and decreased at the thermocline. The concentration in the hypolimnion was nearly constant except near the bottom and was similar to that during the circulation period. The high DEVAS concentrations in the epilimnion are believed to be due to river water with high DEVAS concentrations flowing
only into the epilimnion and/or to desorption of AS from the POC phase due to
the increase in pH in the surface water during the stagnation period. Average
DEVAS concentrations in the Yasu River were 18.2 µg/L on 5 September 2000
and 55.7 µg/L on 9 March 2001. These values were higher than those in the
epilimnion during the stagnation period and in the entire water column during the
circulation period. Weighted average concentrations in the epilimnion were 12.2
µg/L on 12 September 2000, 14.6 µg/L on 5 October 2000, and 12.2 µg/L on 11
April 2001. During the circulation period (2 April 2001), the weighted average
concentration over the entire water column was 10.5 µg/L. These results indicate
that the DEVAS concentration in the surface water is increased by the Yasu and
other rivers flowing into the epilimnion during the stagnation period.
In addition, the pH in the epilimnion increases with active biological
productivity in the summer in many lakes, including Lake Biwa (Lake Biwa
Research Institute and National Institute for Research Advancement 1984;
Sugiyama et al. 2005). It has been reported that AS desorb from the suspended
POC phase when the pH of the aqueous phase increases (Yoshimura and Nakae 1982). Therefore, the DEVAS concentration in the surface water may have increased by desorption of AS from the POC phase in the suspended particulate matter and the sediments in shallow and littoral area of the lake when the pH of the water increased. This hypothesis was supported by the results for PEVAS vs. POC (see below).

The concentration of PEVAS decreased from the surface to the thermocline or the middle layer. However, at any given sampling time in Fig. 1, the vertical distribution of PEVAS/POC, which represents the organic carbon-normalized concentration of EVAS in the suspended particles, was neither uniform nor similar to those of PEVAS or POC. Figure 2 plots PEVAS vs. POC. The correlation coefficient $r$ was relatively low at 0.619. There are believed to be two reasons for this result. The first is the treatment of POC as a homogeneous material despite actually being a mixture of various organic materials. The second is not considering changes in the pH of the lake water, although AS is
known to desorb from the suspended POC phase when the pH of the aqueous phase increases.

The first issue can be explained further based on the results of our previous environmental and geochemical study on NP in Lake Biwa (Yoshida et al. 2009).

In that study, POC was mathematically classified into two fractions, f-POC and a-POC, based on the affinity of NP to these fractions. The differences between f-POC and a-POC are likely associated with their chemical structure and the nature of the organic matter. Therefore, in the present study, we examined the distribution of PEVAS and POC in a similar manner. The total concentration of POC, [POC], can be expressed as:

\[ [POC] = [POC]^f + [POC]^a \]

where \([POC]^f\) and \([POC]^a\) are the concentrations of f-POC and a-POC, respectively. If the EVAS concentration accumulated by f-POC and a-POC are defined as \([PEVAS]^f\) and \([PEVAS]^a\), respectively, then the total PEVAS concentration, \([PEVAS]\), can be expressed as:
[PEVAS] = [PEVAS]_f + [PEVAS]_a

= R_f[POC]_f + R_a[POC]_a

= R_f[POC]_f + R_a([POC] - [POC]_f)

where $R_f$ and $R_a$ are the average PEVAS/POC ratios for f-POC and a-POC, respectively.

Phytoplankton is typical of freshly produced organic matter in a lake and the Chl-a concentration is an index of phytoplankton abundance. Therefore, if Chl-a is regarded as an index of the f-POC concentration, [POC]_f can be expressed as:

[POC]_f = \alpha\text{[Chl-a]}

where $\alpha$ is the average f-POC/Chl-a ratio. The following relationship can be obtained from the above equations:

[PEVAS] = R_ao[Chl-a] + R_a([POC] - \alpha[Chl-a])

= R_a[POC] + \alpha(R_f - R_a)[Chl-a]

[PEVAS]/[Chl-a] = R_ao[POC]/[Chl-a] + \alpha(R_f - R_a)

The obtained equation can be interpreted as follows. The plot of PEVAS/Chl-a
vs. POC/Chl-\(a\) is predicted to be linear, with a slope and intercept of \(R_a\) and \(\alpha(R_f - R_a)\), respectively. If AS accumulates in a-POC more than in f-POC (i.e., \(R_a > R_f\)), the intercept will be negative. Figure 3 plots PEVAS/Chl-\(a\) vs. POC/Chl-\(a\). The plot showed good linearity and its correlation coefficient (\(r = 0.916\)) was higher than that of the PEVAS vs. POC plot (\(r = 0.619\)). These results suggest that classification of POC into f-POC and a-POC is possible through this method and is important for understanding the behavior of AS in the lake. As expected, the intercept \(\alpha(R_f - R_a)\) of the plot was negative (-1.27×10^{-2} g/g). Therefore, the affinity of AS to a-POC was higher than to f-POC. These results are consistent with our previous study showing that NP also has stronger affinity to a-POC than to f-POC (Yoshida et al. 2009).

The slope \(R_a\) and intercept \(\alpha(R_f - R_a)\) of the linear regression line in Fig. 3 were 5.5×10^{-3} g/g and -1.27×10^{-2} g/g, respectively. Using 87.8 g/g as the average \(\alpha\) value (Yoshida et al. 2009) based on the average POC/Chl-\(a\) value in culture experiments of phytoplankton from Lake Biwa (Tezuka 1985), \(R_f\) can be
estimated as $5.4 \times 10^{-3}$ g/g. According to the definition given above, $R_f$ and $R_a$ are the average EVAS/POC ratios for f-POC and a-POC, respectively. Therefore, these values indicate that the affinity of AS to a-POC is somewhat higher than that to f-POC.

The second reason for the poor correlation coefficient ($r = 0.619$) between PEVAS and POC in Fig. 2 can be explained by the PEVAS vs. POC plots shown in Fig. 4. Based on the pH of the lake water, the data can be classified into 3 groups: Group A, samples of the epilimnion in September and October 2000 (pH 7.6–7.8; 0–13 m in September and 0–17 m in October); Group B, samples of the hypolimnion in September and October 2000 (pH 6.9–7.1; 20–72 m); and Group C, samples at all depths on 2 and 11 April 2001 (pH 7.1–7.4). The correlation coefficients for the three groups were 0.690, 0.926, and 0.908, respectively. The PEVAS/POC value (3.38) for the epilimnion with high pH values was smaller than those (5.57 and 7.84) for the hypolimnion and at all depths with low pH values. These results are consistent with the increase in the DEVAS
concentration in the epilimnion with high pH values during the stagnation period,
and also indicates that PEVAS concentrations in the POC decreased with an
increase in the pH of the lake water. In other words, EVAS is desorbed from the
suspended POC phase when the pH of the aqueous phase increases.

We previously reported that some oxyanions are also released from solid
phases such as sediments and suspended particulate matter with an increase in
the pH of lake water (Harita et al. 2005), similar to the present results. Therefore,
adsorption and desorption of chemical components onto solid phases with
changes in the pH of lake water are considered to be important mechanisms
regulating their distribution and environmental/geochemical behavior in lakes.

However, such a trend was not observed in our previous study of NP. This is
likely because NP, as a non-ionic compound, is not affected by changes in pH.

As shown in Fig. 4, the PEVAS/POC value (5.57) in the hypolimnion in
September and October was smaller than that (7.84) at all depths in April. This is
believed to be due to degradation of PEVAS in the hypolimnion during the
Comparison of $K_{oc}$ values for EVAS and NP

The partition coefficient $K_{oc}$ is calculated using the following equation, which uses the DEVAS concentration and the PEVAS/POC ratio ($R_{f}$ and $R_{a}$):

$$K_{oc}(\text{mL/g – POC}) = \frac{[\text{PEVAS/POC}(\text{g/g – POC})]}{[\text{DEVAS}(\text{g/mL})]}$$

The average DEVAS concentrations were $15.9 \times 10^{-9} \text{ g/mL}$ and $9.1 \times 10^{-9} \text{ g/mL}$ in the epilimnion and hypolimnion, respectively. Using these concentrations, log $K_{oc}$ was determined to be 5.5 and 5.8 for $R_{f}$ and $R_{a}$, respectively. These values are within those (2.5–5.9) obtained in a previous study (Vincent and Glenwood 1987).

The log $K_{oc}$ values for EVAS (5.5–5.8) were higher than those for NP (4.8 and 5.4). The high $K_{oc}$ values for EVAS are likely due to formation of a bulky ionic pair with cationic organic compounds such as quaternary ammonium ions as well as its high affinity to POC. Cationic surfactants, which typically contain...
quaternary ammonium ions, are widely used in industrial and household
detergents and are discharged into lake and river waters. Their production in
Japan was 70 kt in 1997 (Japan Surfactant Industry Association 1997). Cationic
surfactants easily form a stable ion pair with coexisting anionic surfactants in
environmental waters (Utsunomiya et al. 1998) and this ion pair is quickly
absorbed onto sewage sludge and sediments with a high partitioning coefficient
(Sun et al. 2003; Sütterlin et al. 2008).

Conclusions

We studied the distribution and geochemical behavior of EVAS in Lake Biwa,
Japan. The distributions of DEVAS and PEVAS were clearly affected by the
concentrations of the two POC fractions, f-POC and a-POC, and by the pH of the
lake water. Thus, adsorption and desorption of EVAS onto the POC phase were
found to be important mechanisms regulating their distribution and
environmental/geochemical behavior in lakes.
Acknowledgements

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References


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Figure captions

Fig. 1. Vertical distributions of WT, pH, DEVAS, PEVAS, POC, PEVAS/POC, and Chl-a at Station le-1 in Lake Biwa. WT: water temperature.

Fig. 2. Plot of PEVAS vs. POC. The regression line for the plot of PEVAS vs. POC was constrained to pass through the origin to estimate an average PEVAS/POC ratio. The correlation coefficient $r$ was estimated from the PEVAS and POC data.

Fig. 3. Plot of PEVAS/Chl-a vs. POC/Chl-a. The correlation coefficient $r$ was estimated from the PEVAS/Chl-a and POC/Chl-a data.

Fig. 4. Plot of PEVAS vs. POC. The data were classified into 3 groups: Group A, samples of the epilimnion (squares) in September and October 2000 (pH...
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7.6–7.8; 0–13 m in September and 0–17 m in October); Group B, samples of the hypolimnion (triangles) in September and October 2000 (pH 6.9–7.1; 20–72 m); and Group C, samples from all depths (circles) on 2 and 11 April 2001 (pH 7.1–7.4). The regression line for the plot of PEVAS vs. POC was constrained to pass through the origin to estimate an average PEVAS/POC ratio. The correlation coefficient $r$ was estimated from the PEVAS and POC data.
Fig. 1.
Fig. 2.

\[ y = 5.20x \]
\[ r = 0.619 \]
Fig. 3.

\[ y = 0.0055x - 0.0127 \]

\[ r = 0.916 \]
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Fig. 4.