Oxygen Consumption in the Bottom Water Related with the Production of Sulfides in the Bottom Sediments

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The dissolved oxygen consumption of the overlying water was studied in the north and south basins of Lake Biwa. DO consumption due to the bottom sediment was estimated from the dissolved oxygen uptake in the core tube. Chemical oxygen uptake in the bottom sediment core were measured separately from total uptake by supplementation of formalin or mercury chloride. Total DO consumption rates in the north and south basins averaged 0.4 g O₂/m²/day and 0.02 g O₂/m²/day, respectively. Chemical oxygen uptake accounted for about 80% and 17% of the total oxygen uptake in the north and south basins. The sulfides accumulation was found to be much higher in the north basin than in the south basin.

In both the basins, the concentration of sulfides in the bottom sediment was correlated with chemical DO consumption in the overlying water. Regression analysis suggests that sulfide formation in the bottom sediment is the dominant factor controlling chemical DO consumption in each basin.

One of the most undesirable environmental conditions in water regions might be "deficiency of dissolved oxygen" in the water, or the formation of anoxic layer in the bottom water. Mainly, dissolved oxygen in sufficient level is essential not only for the growth of fish and shellfish, but also for keeping appropriate quality of water. The concentration of dissolved oxygen in the water is governed by the difference in the rates of the diffusion from atmosphere and consumption in the water body.

Although a certain amount of oxygen is used in the process of oxidative decomposition of organic materials in eutrophicated water, the consumption of dissolved oxygen seems largely to be responsible for the oxidation of sulfides which are produced microbiologically in bottom sediments followed by liberation into the overlying water.

The major process of producing sulfides is thought to be dissimilatory sulfate reduction by microorganismus,¹⁾ whereas they are partly produced microbial decomposition of sulfur-containing organic compounds. The former process is performed by sulfate reducing bacteria, which reduce sulfate to sulfide in coupling with the hydrogen donation from some organic compounds. In addition to the physiology and biochemistry of

each species of the bacterial group, thier sulfide formation in the bottom sediments of various water regions has been studied in details.^{2,3)} The organic compounds which can be utilized directly and served as hydrogen donors in the bacterial sulfate reduction are reported to be acetic, formic, pyruvic and lactic acids, etc.^{2,4)}

Despite these findings, actual circumstances as to *in situ* contribution of organic acids to the sulfide production in bottom sediment are still obscure. From the viewpoint, the authors have intended to reveal the mechanism of the formation of oxygen deficient layers in coastal and inland water, focusing the studies on the *in situ* productions of sulfides and organic acids in connection with decomposition of organic matter, and further on the consumption of dissolved oxygen in the water-sediment interface.

This paper deals with the actual distribution and seasonal variation of dissolved oxygen in the water as well as the sulfide concentration in the bottom sediment, in the north and south basins of Lake Biwa. Further, *in situ* rate of oxygen consumption in the bottom water has been estimated by the use of a newly devised technique.

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Materials and Methods

Outline of the Water Regions Studied

Lake Biwa is the largest lake in Japan, whose area is approximately 690 km² and maximum depth is 104 m. The lake is divided limnologically into two basins, i.e. the large, deep, oligotrophic north basin and the small, shallow eutrophic south basin. The lake has numerous inlet streams and an outlet, the Seta River, at the southwestern end of the south basin. In this experiment, two sampling stations, Station A (depth, ca. 80 m) and Station B (depth, ca. 3 m), were set up in each basin as shown in Fig. 1.

Collection of Samples

The bottom sediment samples were collected by

Fig. 1. Stations set up at the north and south basins of Lake Biwa.

Fig. 2. Experimental apparatus for measuring dissolved oxygen consumption by Winkler's method (a) and DO meter (b).

the use of a KK core sampler (the original design was reported Kimata⁵⁾) equipped with a plastic tube of a 5 cm inside diameter. For the chemical analysis, the sediment column was sliced into each 0.5 cm or 1.0 cm thickness on board, and put into a plastic bottle, sealed tightly, then brought into the laboratory keeping at 0°C in the ice box.

Measurement of DO Consumption

Following two methods were employed in the measurement of *in situ* rate of oxygen consumption in the overlying water of the tubes.

(1) Measurement of oxygen consumption by the Winkler's method

Just after collecting a core sample on board, the upper end of a core tube was sealed with a rubber stopper connected with a rubber tube (Fig. 2a), to intercept the bottom water from atmosphere. The core tubes were kept at the definite temperatures throughout the experiment. At a definite interval bottom water was collected into Winkler's oxygen bottles, then determined the decrease of dissolved oxygen in the overlying water.

(2) Measurement of oxygen consumption by DO meter

The core tube collected were sealed with a rubber stopper at each end on board. At the measurement of dissolved oxygen, the rubber stopper at the upper end was replaced with the stopper equipped with a DO sensor and a stirrer (Fig. 2b). Time course of DO concentration in the overlying water was traced using DO meter (Toshiba Beckman Fieldlab Oxygen Analyzer) at various temperature.

Physical and Chemical Analyses

The *in situ* temperature and dissolved oxygen of the water were measured by Portable Water Pollution Monitor WP-2 (Kyoto Denshi Kogyo). Total Sulfides in the bottom sediment was trapped into Zn acetate solution by the steam distillation under acidic condition.⁶⁾ The trapped sulfide was determined colorimetrically by the method of Shinra.⁷⁾ Free sulfide in the bottom sediment was released by steam distillation without acid supplementation.

Results

Seasonal Changes in Water Temperature and DO Concentration

The seasonal and vertical distributions of temperature and dissolved oxygen in the water of north

Fig. 3. Seasonal and vertical distributions of temperature (a) and dissolved oxygen (b) in the water of north basin in 1981.

○: March, ●: July, △: August, ▲: September.

basin were shown in Fig. 3a and Fig. 3b. In the summer, the stratification due to temperature was recognized clearly in the water column of the north basin, whereas the water temperature was almost constant all the year round in the hypolimnion (Fig. 3a). On the other hand, DO in the hypolimnion fluctuated seasonally, and DO in the bottom water fell down as low as 38 saturation % in the summer season, which may be ascribed to that the DO consumption in the bottom water exceeds the diffusion of atmospheric oxygen into the bottom water across the thermocline.

Seasonal changes in water temperature and DO in the water of south basin were shown in Table 1. The temperature of bottom water fluctuated

seasonally, maximum temperature of 26°C was observed in August and decreased to below 8°C in December. Despite a marked seasonal change in the bottom temperature, DO value was almost constant in the bottom water. This may be due to the diffusion of atmospheric oxygen into such shallow bottom water in the south basin.

Fig. 4. Dissolved oxygen consumption by the bottom sediment in the overlying water of the north basin.

○: incubated at 0°C, ⊙: incubated at 0°C in the presence of formaldehyde, ●: incubated at 0°C in the presence of mercury chloride, △: incubated at 8°C, ▲: incubated at 8°C in the presence of formaldehyde, ▲: incubated at 8°C in the presence of mercury chloride.

Fig. 5. Dissolved oxygen consumption by the bottom sediment in the overlying water of the south basin.

○: incubated at 0°C, ●: incubated at 0°C in the presence of mercury chloride, △: incubated at 25°C, ▲: incubated at 25°C in the presence of mercury chloride.

Table 1. Dissolved oxygen in the south basin of Lake Biwa in 1981

Month	Dissolved oxygen (saturation %)				
	April	June	August	October	December
Surface water	105	106	100	110	113
Overlying water	95	97	97	102	104

Fig. 6. Seasonal and vertical distribution of total and free sulfides in the north (a) and south (b) basins.

□ total sulfides, ■ free sulfide.

Table 2. The rate of biological and chemical DO consumption in the north and south basins of Lake Biwa in 1981

Station	North basin				South basin			
Month	Mar.	Jul.	Aug.	Sep.	Mar.	Jul.	Aug.	Sep.
Biological DO consumption (g O ₂ /m ² /day)	0.08	0.09	0.11	0.12	0.02	0.05	0.16	0.17
Chemical DO consumption (g O ₂ /m ² /day)	0.28	0.29	0.31	0.32	0.01	0.02	0.03	0.01

Consumption of Dissolved Oxygen in the Overlying Water

The DO consumption by the bottom sediment in the overlying water of the north basin was shown in Fig. 4. To measure the oxygen consumption based on chemical processes separately from total oxygen uptake in the overlying water, sufficient amount of formaldehyde (5% in final concentration) or mercury chloride (2 ppm in final concentration) was added to the core tubes, then incubated at 0°C. Under this condition, the lowest oxygen consumption was observed. The DO consumption incubated at 0°C without the inhibitor was slightly higher than that with the inhibitor. This shows that the biological oxygen uptake was al-

most inhibited and that oxygen uptake under such condition may be due to chemical oxidation. The DO consumption at *in situ* temperature (8°C) was a little higher than that in the presence of the inhibitor at 0°C. The difference may be attributed to biological process. From these results, it is evident that the DO consumption in the overlying water in the north basin is performed mainly by the chemical oxidation rather than biological oxygen uptake.

The DO consumption in the overlying water in the south basin was shown in Fig. 5. The result shows that the biological respiration occupied the most part of *in situ* DO consumption.

In comparison with south basin, the total DO

consumption was higher in the north basin, but biological oxygen uptake was almost at the same level in both basin. From this finding, it is clear that the difference between north basin and south basin in the DO consumption in the overlying water was ascribable to the difference of chemical oxidation based on the bottom sediment.

Distribution of Sulfides in the Bottom Sediment

Seasonal and vertical distribution of total and free sulfides in both basins were shown in Fig. 6a and Fig. 6b. In the north basin, the concentration of total and free sulfides did not change vertically all the year round. The ratio of free sulfide to total sulfide was almost constant, i.e. about 30% in the bottom sediment from near surface until ca. 10 cm depth. In the south basin, total and free sulfides were found to increase in summer at the surface layer of bottom sediment and decrease in winter at near surface of bottom sediment. With regard to the ratio of free sulfide to total sulfides, the bottom sediment of south basin had a similar tendency as that of north basin.

The Rate of DO Consumption in Overlying Water

Table 2 shows the rate of biological and chemi-

cal DO consumption in the north and south basins in different seasons. The rate of DO consumption calculated using equation of Michealis-Menten. As a result, the values of north basin hardly change all the year round. The chemical oxygen uptake was approximately three times higher than the biological oxygen uptake in the north basin. In south basin, the DO consumption was found to increase in summer and decrease in winter. Thus, in contrast with north basin, the DO consumption in south basin was largely responsible for the biological respiration.

Discussion

Average annual oxygen uptake of bottom sediment in Lake Biwa (south basin 0.12 g O₂/m²/day and north basin 0.4 g O₂/m²/day) seems to be as the similar level as the already reported values (0.02–3.9 g O₂/m²/day) (Table 3).

In the south basin, average biological oxygen uptake could account for about 80% of total oxygen uptake. Since the epiphytic algae and benthic animals were scarcely found in the core tube, bacterial oxygen uptake would be most part of the

Table 3. Respiration of various sediment systems

Community	Average Respiration g O ₂ /m ² /day	Reference
River mud	2.4	Edwards and Rolley ¹⁴⁾
Freshwater lake	0.35	Hargrave ¹⁵⁾
Georgia sublittoral	2.6 biological 2.8 total	Smith ¹⁶⁾
Atlantic slope	0.017	Smith and Teal ¹⁷⁾
San Diego trough	0.04 biological 0.08 total	Smith ¹⁸⁾
Intertidal salt marsh, Ga.	3.9	Teal and Kanwisher ¹⁹⁾
Salt marsh mud, La	0.45 biological 0.8 total	Hopkinson <i>et al.</i> ⁹⁾
Danish fjord	1.2	Jørgensen ¹⁾
South basin of Lake Biwa	0.10 biological 0.12 total	This study
North basin of Lake Biwa	0.10 biological 0.40 total	This study

Table 4. The diffusion coefficient calculated from the rate of DO consumption and the concentration of free sulfide

Station	Rate of DO consumption (μmol/cm ² /sec)	Concentration of free sulfide* (μmol/g wet mud)	Diffusion coefficient (cm ² /sec)
North basin	1.4×10^{-6}	3.1	6.0×10^{-6}
South basin	0.4×10^{-6}	0.8	6.3×10^{-6}

* concentration of free sulfide in the sediment of 0~0.5 cm depth.

biological oxygen uptake. Hargrave⁸⁾ reported that bacterial respiration was directly related to temperature in Marion Lake. Further, Hopkinson⁹⁾ suggested that the magnitude and temporal patterns of benthic respiration are a function of rate to supply of organic material in Louisiana saltmarsh. In agreement with their finding, seasonal change in DO consumption rate in the south basin, as shown in Table 2, may support a correlation between oxygen uptake and water temperatures which increase in summer and decrease in winter.

In the north basin, the chemical process occupied most part of DO consumption. The rate of DO consumption in the north basin scarcely changed all the year round. The rate of chemical oxygen uptake to whole DO consumption was nearly constant (Table 2). Gardner and Lee¹⁰⁾ have reported that the rate of chemical DO consumption was found to be dependent on temperature and ferrous iron content of sediment in Lake Mendota. On the other hand, Nikaido¹¹⁾ demonstrated that the oxygen consumption by reduced sulfur compound in the lake sediment depends on the amounts of sulfide-S and humic substances. In this study, the concentrations of total and free sulfides as well as temperature in the sediment of north basin were found to be scarcely changed as shown in Fig. 6a. From these findings, the chemical DO consumption in the overlying water in the north basin might be mainly responsible for reduced sulfur compounds liberated from the sediment. In the chemical process of sulfide oxidation, there forms stable elemental sulfur.¹²⁾ If the reduction $2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + \text{H}_2\text{O}$ proceeds in the sediment-water interface, 1 mole of oxygen should be consumed by 2 moles of hydrogen sulfide. Then, DO consumption rate in the overlying water by hydrogen sulfide may be a function of its liberation rate, $L = \phi D(\text{Ca} - \text{Cb}/dZ)$ where L: rate of sulfide liberation; ϕ : porosity; D: diffusion coefficient; Ca: concentration of free sulfide in the bottom sediment of depth dZ; Cb: concentration of free sulfide in the overlying water (assumed as 0 in the bottom water of the south and north basin). Table 4 shows the diffusion coefficient calculated from the equation, in which the 1/2 rate of DO consumption was given as L. The obtained values were

6.0×10^{-6} in the north basin and 6.4×10^{-6} in the south basin, respectively. Kamiyama *et al.*¹³⁾ have already found the diffusion coefficient of ammonium nitrogen in the bottom sediment in Lake Biwa to be $4 \sim 2 \times 10^{-6}$. This value coincides with the diffusion coefficient calculated from the DO consumption in this study, which suggests that the rate of chemical DO consumption in the overlying water in the both basins depends mainly on the amount of sulfides in the bottom sediment.

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