Diurnal and Seasonal Variations of Exchange Rate of Carbon Dioxide across an Air-Lake Water Interface

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Abstract

The exchange rate of CO₂ between the atmosphere and Lake Suwa, a eutrophic lake in Nagano Prefecture (Japan), was estimated based on a floating box experiment.

The diurnal variation of the exchange rate of CO₂ indicated that the ratio of photosynthetic rate to respiratory rate including organic matter decomposition is highest at 15 o'clock and lowest at 3 o'clock.

The seasonal variation of the average daily exchange rate of CO₂ indicated that the absorption flux of CO₂ occurred during the period from early spring to middle summer and the evolution flux of CO₂ during the period from late summer to late autumn.

The average daily absorption rate of CO₂ on 17-18 July 1973 was estimated at 1.3 CO₂-C g/m²/day, when the water bloom of *Microcystis* developed.

1. Introduction

In general the utilization of total carbon dioxide in the trophogenic layers by the photosynthetic activity of the green plants will produce a marked elevation in pH of the lake water. On the contrary, the liberation of total carbon dioxide by respiration of autochthonous organisms and microbiological decomposition of autochthonous and allochthonous matters will produce a marked lowering of pH. The pH variation in the surface water may cause an exchange of carbon dioxide across the air-lake water interface.

The ultimate source of the carbon which plays a fundamental role in the metabolism of organisms in lakes is the carbon dioxide in the atmosphere and the carbonate substances originating from rocks. To estimate the exchange rate of carbon dioxide, therefore, is an important means to clarify the mechanism of the carbon cycle in a lake.

Recently, WEILER (1974) reported a study on the air-water exchange of carbon dioxide on Lake Ontario through one year.

The flux of CO₂ between lake and atmosphere was calculated from the difference between the partial pressure of CO₂ in the air and the calculated partial pressure of CO₂ in the lake water (KANWISHER, 1963; HOOVER and BERKSHIRE, 1969; LISS, 1973). KOYAMA et al. (1972) discussed the seasonal variation of the net fixation rate and net formation rate of CO₂ in Lake Suwa, which were estimated from a relationship between pH and total CO₂ and the seasonal variation of pH values.

In a previous paper (KOYAMA et al., 1975), a floating box experimental method for determining the exchange rate of carbon dioxide across an air-lake interface was presented and some results obtained from Lake Suwa (maximum depth: 6.5 m; surface area: 14.5 km²; height above sea level: 759 m), a eutrophic lake in Nagano Prefecture, Japan, were discussed.

The present study is an attempt to ascertain the diurnal and seasonal variations of exchange rate of CO₂ between the atmosphere and Lake Suwa determined based on the floating box experiment and to clarify the relationship between the seasonal
variation and those of net fixation and net formation rates of CO₂ in the lake water, which latter were presented in a previous paper (KOYAMA et al., 1972).

2. Methods

The exchange rate of CO₂ across the air-lake water interface was determined by the floating box experiment (KOYAMA et al., 1975). The principle of the floating box experiment may be summarized as follows: a box made of acrylic resin (20 x 20 x 7 cm³) was fixed to the center of a wooden frame and floated on the lake surface. First, the box is filled with lake water and then 1.2 l of air is introduced into the box. At suitable intervals (15 minutes, sometimes 5 minutes) the air in the box is collected in a vacuum tube. After collecting the air sample, the air in the floating box is replaced with the outside air. The carbon dioxide in the collected air sample is determined by an infrared gas analyzer, after being trapped in a glass tube cooled with liquid N₂. Plotting of the carbon dioxide concentration of the air sample against the floating time gives a convex or concave curve when carbon dioxide is being liberated into the air or absorbed across the air-lake water interface, respectively. It was assumed that the tangent line of the convex curve or of the concave curve at zero time represents the evolution or the absorption rate of carbon dioxide, respectively, under the natural condition at the start of the experiment. The reliability of the exchange rate estimated by the method was discussed in another earlier paper (KOYAMA, 1976).

Total carbon dioxide (Total CO₂) of water samples was determined using Koyama’s method (KOYAMA, 1954). Total CO₂ of water samples equilibrated with air at the prevailing temperature was defined as original total carbon dioxide (Orig. CO₂).

Dissolved oxygen and the other gases combined except Total CO₂ were analysed using the carbon dioxide method (SUgAWARA, 1939) modified by OANA (1957) and KOYAMA et al. (1968).

The pH of the water samples was determined using a glass electrode pH-meter, and pH of the water samples equilibrated with air at the prevailing temperature was defined as original pH (Orig. pH).

3. Results and discussion

The diurnal and seasonal variations of pH, Orig. pH, Total CO₂ and Orig. CO₂ in the surface water as well as the exchange rate of CO₂ across the air-lake water interface at the center of Lake Suwa were measured 7 times at varying intervals from November 1972 to November 1973. Among the diurnal variations, those of July, September and November will be

Fig. 1. Diurnal variations of pH and Total CO₂ of the surface water of Lake Suwa (July 17-18, 1973).
discussed as the representative examples.

Figure 1 shows the diurnal variations of pH, Orig. pH, Total CO₂ and Orig. CO₂ of the surface water on 17-18 July 1973, when water bloom of Microcystis developed. All the pH values remained in a high range of 10.5 to 10.0 throughout the day. The highest values (10.4-10.5) were observed at about 15 and 11 o’clock and the lowest values (10.0) were at 23 and 3 o’clock.

Total CO₂ showed its lowest values (1.0-1.2 CO₂ ml/l) at 15 and 11 o’clocks and its highest value (7.0 CO₂ ml/l) at 3 o’clock. The diurnal variation of Total CO₂ is a contrast to that of pH. These findings may be attributable to the ratio of CO₂ fixation by photosynthesis to CO₂ formation by both respiration and microbial decomposition, which was highest at about 15 o’clock and lowest at about 3 o’clock.

Figure 1 also shows that the observed pH values were higher than Orig. pH values (8.1-8.2) and Total CO₂ values were lower than Orig. CO₂ values (15.0-15.1 ml/l). This means that the photosynthetic utilization rate of CO₂ was higher than the catabolic formation rate of CO₂ through the experimental period.

Figure 2 shows the diurnal variations of absorption rate of CO₂ and pH-difference value of the surface water on 17-18 July 1973. The highest absorption rate, which was observed at 15 o’clock, amounted up to 260 CO₂ ml/m²/hr; the lowest absorption rate, which was observed at 3 o’clock, amounted to 28 CO₂ ml/m²/hr, respectively.

The average daily absorption rate of CO₂ was calculated at 2420 CO₂ ml/m²·day or 1.30 CO₂-C g/m²·day from the diurnal variation of absorption rate of CO₂. The pH-difference values ranged from -2.35 to -1.8 and its diurnal variation was similar to that of absorption rate of CO₂.

The diurnal variations of pH, Orig. pH and degree of saturation of O₂ of the surface water on 21-22 Sept. 1973 were shown in Fig. 3. The pH values during the period from 17 o’clock on 21 Sept. to 1 o’clock on 22 Sept. as well as at 15 o’clock on 22 Sept.
were higher than Orig. pH values, whereas the pH values during the period from 3 o'clock to 11 o'clock on 22 Sept. were lower than Orig. pH values. In contrast to the pH values, Orig. pH values remained at about 8.0. The degree of saturation of O₂ varied as a function of time in parallel with the pH values.

Figure 4 shows the diurnal variations of exchange rate of CO₂ and pH-difference value of the surface water on 21-22 Sept. 1973. They parallel each other, and are sharply contrasted to the diurnal variation of saturation degree of O₂ (Fig. 3). Thus, the rate of CO₂ fixation during the period from 17 o'clock on 21 Sept. to 1 o'clock on 22 Sept. as well as at 15 o'clock on 22 Sept. was higher than the rate of CO₂ formation by respiration and microbial decomposition. Also during the period from 1 o'clock to 13 o'clock on 22 Sept., the fixation rate of CO₂ was lower than the formation rate of CO₂. The average daily evolution rate of CO₂ was calculated at 1,280 CO₂ ml/m². day or 0.69 CO₂-C g/m². day from the diurnal variation of exchange rate of CO₂ as shown in Fig. 4.

The diurnal variations of pH and pH-difference values of the surface water on 1-2 Nov. 1972 were shown in Fig. 5. The highest and the lowest pH values were observed at 15 o'clock on 1 Nov. and 3 o'clock on 2 Nov., respectively. The pH-difference value varies with time in a clear contrast to the pH values.

The diurnal variation of the exchange rate of CO₂ on 1-2 Nov. 1972 was shown in Fig. 6. The maximum absorption rate of CO₂ and the most remarkable evolution rate of CO₂ were observed at 15 o'clock on 2 Nov., respectively. The average daily evolution rate of CO₂ was calculated at CO₂ 798 ml/m². day or CO₂-C 0.43 g/m². day. The diurnal variation of exchange rate of CO₂ is practically parallel with that of pH-difference value as shown in Fig. 5. This suggests that the pH-difference value provides important information on the exchange of CO₂ across an air-lake water interface.

In addition to the foregoing results, the diurnal variations of various components were measured at the center of Lake Suwa in April, May, October and November 1973. All the results with an exception of those on 29-30 October when the lake was thickly clouded over, indicated that the ratio of CO₂ fixation to CO₂ formation was highest at about 15 o'clock and lowest at about 3 o'clock as mentioned above.

The seasonal variation of the average daily exchange rate of CO₂ was summarized in Table 1 and Fig. 7. Findings show, that the absorption flux of CO₂ is observed during the period from early spring to middle summer, while the evolution flux of CO₂ is seen during the period from late summer to late autumn in Lake Suwa. On
Fig. 5. Diurnal variations of pH and pH-difference value (Orig. pH-pH) of the surface water (Nov. 1-2, 1972).

Fig. 6. Diurnal variation of exchange rate of CO$_2$ between the atmosphere and Lake Suwa (Nov. 1-2, 1972).
the assumption that the exchange rate of CO₂ in the winter season is not important to estimate the average yearly exchange rate of CO₂, the average rate was estimated at 0.32 CO₂-C g/m²·day as the average yearly absorption rate of CO₂ from the absorption and evolution areas in Fig. 6.

The seasonal variations of the average daily absorption rate and evolution rate of CO₂ are similar to those of the average net fixation rate and net formation rate of CO₂ presented in the previous paper (KOYAMA et al. 1972) in which the rates of CO₂ in the lake water were estimated from a relationship between pH and Total CO₂ and the seasonal variation of pH values determined by OKINO et al. (1969). The principles of the method are as follows:

1). From the results of Total CO₂ and pH of water samples from various depths in Lake Suwa in different seasons, the pH and Total CO₂ curves corresponding to different seasons are deduced.

2). Values of total CO₂ are estimated from pH values using the pH and total CO₂ curves.

3). Preserved amounts of net fixation and net formation of CO₂ in the lake water are calculated as the difference between Orig. CO₂ and Total CO₂. The difference value corresponds to the former and the latter in cases of positive and negative values, respectively.

4). A large number of data of the average preserved amount of net fixation of CO₂ (A. P. A. N. fix. CO₂) and that of net formation of CO₂ (A. P. A. N. form. CO₂) are obtained through all seasons. From the seasonal variation, a histogram of these amounts is constructed against the months.

5). On the assumption that the average exchangeability of CO₂ between air and lake water in a month is similar to those of the adjacent months, the difference between A. P. A. N. fix. CO₂ or A. P. A. N. form. CO₂ of a month and that of an adjacent month corresponds to the average net fixation rate of CO₂ during the two months in the case of a positive value and to the average net formation rate of CO₂.
in the case of a negative value.

From the seasonal variations of the average net fixation and net formation rates of \( \text{CO}_2 \), the net formation rate of \( \text{CO}_2 \) was estimated at 0.8 gC/m\(^2\) day as a result of the yearly balance sheet (Koyama et al., 1972). From the result, an evolution rate of \( \text{CO}_2 \) as an average yearly exchange rate of \( \text{CO}_2 \) has been expected in Lake Suwa. Contrary to the expectation, however, an absorption rate of \( \text{CO}_2 \) (0.32 CO\(_2\)-C g/m\(^2\)/day) was estimated in the present study as an average yearly exchange rate of \( \text{CO}_2 \) between the atmosphere and Lake Suwa. One reason may be the inaccurate estimation of the average yearly exchange rate of \( \text{CO}_2 \), because the diurnal and seasonal variations of the exchange rate of \( \text{CO}_2 \) fluctuate remarkably in terms of environmental factors. In order to obtain the average yearly exchange rate of \( \text{CO}_2 \), therefore, it is desirable to have at least the continuously observed data of pH in addition to the data of the diurnal and seasonal observations of the exchange rate of \( \text{CO}_2 \).

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References


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