Estimation of Exchange Rate of Carbon Dioxide Between Air and Lake Surface

Tadashiro KOYAMA, Mitsugu NISHIMURA and Hiromi MATSUDA

Abstract

In order to determine the exchange rate of CO_2 between air and lake surface, a floating box experiment was conducted on an eutrophic lake. The air in the floating box was collected at proper intervals and the CO_2 -concentration in the air was determined by using infrared gas analyser. From the relationship between the CO_2 -concentration and floating time, the exchange rate of CO_2 was determined. The average flux of CO_2 across the air-lake interface through a day was estimated from the diurnal exchange rate of CO_2 .

Introduction

The ultimate source of the carbon which plays a fundamental part in the metabolism of organisms in lakes (autochthonous organic matter), is the carbon dioxide of the atmosphere and the carbonate substances originated from rocks. The allochthonous organic matter is not also an exception in this point.

In general the utilization of total carbon dioxide in the trophogenic layers by the photosynthetic activity of the green plants will produce a marked highering of pH of the lake water. On the contrary, the liberation of total carbon dioxide by respiration of autochthonous matter and microbiological decomposition of autochthonous and allochthonous matters will produce a marked lowering of pH. The pH variation in the surface water may bring exchange of carbon dioxide between air and the lake surface. To estimate the exchange rate of carbon dioxide, therefore, is important to make clear the mechanism of carbon cycle in the lake.

The studies on the carbon dioxide exchange across the air-sea interface have been carried out theoretically by BOLIN (1960), HOOVER and BERKSHIRE (1969), and QUINN and OTTO (1971). A more general account of the processes of interfacial gas exchange has been given by DANCKWERTS (1970). Laboratory studies on the carbon dioxide exchange have been conducted by SUGIURA, IBERT and HOOD (1963), LISS (1973) and KANWISHER (1963) who investigated the exchange of nitrogen, oxygen and carbon dioxide. Direct observation of the carbon dioxide exchange between the atmosphere and the oceans has been carried out by TAKAHASHI (1961), and the dynamics of carbon dioxide and productivity in an Arctic biosphere was discussed by JOHNSON and KELLEY (1970) on the basis of the variation of atmospheric carbon dioxide. Recently, WEILER (1974) calculated the flux of carbon dioxide between the atmosphere and the surface of Lake Ontario from the difference between the partial pressure of carbon dioxide in the air over the lake and the calculated partial pressure in the lake

water multiplied by the transfer coefficient for carbon dioxide.

The purpose of the present study is to

devise a method for the estimation of exchange rate of carbon dioxide between air and lake surface, and to discuss the some results obtained by the method.

Methods

Floating box experiment : A box made of acryl resin ($20 \times 20 \times 7 \text{ cm}^3$) was fixed in the center of a wooden frame as shown in Fig. 1. An air inlet tube which was equipped with a pinch cock was attached to the corner of the box. First the box was filled with the lake water and then 1.2 l of the air was introduced into the box through the inlet tube. The box was previously so adjusted against the frame that the air pressure in the box is equal to that of the outside. The floating box was connected to the anchored boat with a string of more than 5m in length. In practical, two sets of the floating boxes were prepared. At proper intervals (at

Fig. 1. Floating box experiment.

Fig. 2. Apparatus for trapping carbon dioxide in air sample.

intervals of 15 minutes (sometimes of 5 minutes), the air in the box was collected in a vacuum tube having a capacity of about 400ml. After every collecting of air sample, the air in the floating box was replaced with the outside air according to the way mentioned above. Air volume in the sample tube at 0°C and 760mm Hg was calculated from the difference between the weight of the empty tube and that of the tube filled with water as well as water temperature and the atmospheric pressure.

Determination of carbon dioxide in the air samples: Fig. 2 shows an apparatus for trapping carbon dioxide in the air samples. This apparatus consists of dry ice-acetone trap B and liquid nitrogen traps C and D as well as manometer E. Traps B and C are for trapping of water vapour and carbon dioxide in the air sample respectively and trap D is to prevent the apparatus from introduction of the outside water vapour and carbon dioxide. Trap C is a spiral tube and connected to the apparatus by rubber tubes which are equipped with screw cocks(d and e) as shown in Fig. 2. Trap C was placed in a liquid N₂ jar after the air inside the apparatus had been evacuated out through G. Cock a was closed and then cock b was opened. Cock a was now so slightly opened that the air sample was passed through the train of the traps under 10 to 12mm Hg pressure by continuously evacuating it through G. After the air sample had been completely evacuated out, cocks c and b as well as screw cocks e and d were closed and then the trap C with liquid N₂ jar was disconnected from the apparatus. Carbon dioxide condensed in the trap was determined by using an infrared gas analyzer (HITACHI-HORIBA, type EIA-IA) under the following condition: flow rate of nitrogen

as a carrier gas: 0.25 l/min.; chart speed: 20mm/min. and range: 0.2 V. In the case of determination of carbon dioxide-carbon amounted more than 200 µgC, the range is adjusted at 0.5 V.

Preparation of standardization curve of carbon dioxide for the infrared gas analyzer: The standardization curve of carbon dioxide was prepared by using a standard solution of sodium carbonate according to the procedure presented by SATAKE *et al.* (1972).

Determination of pH of water samples: pH of water samples was determined by using a glass electrode pH meter.

An attempt has been made to estimate the exchange rate of carbon dioxide between air and lake surface at the center of Lake Suwa, an eutrophic lake in Nagano Prefecture, Japan (maximum depth: 6.5m; surface area: 14.5km²; height above the sea-level: 759m).

Results and Discussion

Fig. 3 shows the standardization curve for the infrared gas analyzer. This figure indicates that there is a linear relationship between the amounts of carbon dioxide-carbon and the corresponding peak weight of chart within the extent of carbon dioxide-carbon from 0 to 80 µg. It was also confirmed that the linear relationship is observed within the extent up to 200 µg of carbon dioxide-carbon by adjusting the range of the analyzer to 0.5 V.

Fig. 4 shows the relationship between the floating time and the concentration of carbon dioxide in air from the floating box on the surface of Lake Suwa within the time from 6:40 to 7:40 on 29 September, 1972. As a simple method, it was assumed that the tangent line drawn against the curve at zero

time shows the exchange rate of carbon dioxide under the natural condition. This tangent line indicates that the concentration of carbon dioxide in the floating box increases according to the tangent value, $(1,000-290)/16$ (ppm/min.). From the result and the

Fig. 3. Standardization curve for determining carbon dioxide by using infra-red CO₂ analyzer of HITACHI-HORIBA type EIA-IA.

Fig. 4. Relationship between the floating time and the CO₂ concentration in air from the floating box on the surface of Lake Suwa (6:40-7:40, Sept. 29).

Surface water temperature : 17.1°C
pH of surface water : 7.52

following data, the evolution rate of carbon dioxide is calculated at 69 CO₂ ml/m². hr :

Air volume in the floating box: 1, 200ml,
height of the lake surface above the sea-level : 759m, surface water temperature : 17.1°C.

Fig. 5 shows the relationship between the floating time and the concentration of carbon dioxide in air from the floating box within the time from 11:40 to 12:35 on 29 September. The tangent line indicates that the concentration of carbon dioxide in the floating box increases according to the tangent value,

Fig. 5. Relationship between the floating time and the CO₂ concentration in air from the floating box on the surface of Lake Suwa (11:40-12:35, Sept. 29).

Surface water temperature : 15.8°C
pH of surface water : 8.14

Fig. 6. Relationship between the floating time and the CO₂ concentration in air from the floating box on the surface of Lake Suwa (14:28-15:55, Sept. 28).

Surface water temperature : 18.2°C
pH of surface water : 8.72

$(800-290)/35$ (ppm/min.). The evolution rate of carbon dioxide at that time is calculated at $23 \text{ CO}_2 \text{ ml/m}^2 \cdot \text{hr.}$ in the same manner.

Fig. 6 shows the relationship within the time from 14 : 28 to 15:55 on 28 September, 1972. The tangent line indicates that the concentration of carbon dioxide in the floating box decreases according to the tangent value, $(300-10)/40$ (ppm/min.). The absorption rate of carbon dioxide at that time is calculated at $11 \text{ CO}_2 \text{ ml/m}^2 \cdot \text{hr.}$ in the same manner. From the results, the diurnal variation of the exchange rate of carbon dioxide on 28-29 September will be shown in Fig. 7.

From the diurnal variation, the average evolution rate of carbon dioxide on 28-29

September is estimated at $710 \text{ CO}_2 \text{ ml/m}^2 \cdot \text{day.}$ or $0.38 \text{ CO}_2\text{-C g/m}^2 \cdot \text{day.}$ The diurnal variation shows that the exchange rate of carbon dioxide remarkably varies within 24 hours. Therefore, it is a matter of course that the observed data are insufficient to know the actual pattern of the diurnal variation. In order to know the actual pattern, the floating box experiment was conducted at intervals of two hours on the surface of Lake Suwa on November 1-2, 1972.

Fig. 8 shows the diurnal variation of exchange rate of carbon dioxide. The diurnal variation indicates that the peak of absorption rate and that of evolution rate of carbon dioxide correspond to 15 and 3 o'clock respectively and also that the

Fig. 7. Diurnal variation of exchange rate of CO_2 between the lake surface and the air (Sept. 28-29, 1972).

Fig. 8. Diurnal variation of exchange rate of CO_2 between the lake surface and the air (Nov. 1-2, 1972).

Fig. 9. Diurnal variation of pH of the surface water of Lake Suwa (Nov. 1-2, 1972).

observations of carbon dioxide exchange at 15 and 3 o'clock are indispensable to obtain the actual pattern of diurnal variation. From the diurnal variation, the evolution rate of carbon dioxide on November 1-2, 1972 is estimated at $798 \text{ CO}_2 \text{ ml/m}^2 \cdot \text{day}$ or $0.427 \text{ CO}_2\text{-C g/m}^2 \cdot \text{day}$.

Fig. 9 shows the diurnal variation of pH of the surface water.

These findings indicate that the peak of absorption rate corresponds to the highest pH value (8.45) at 15 o'clock on 1 November and the peak of evolution rate corresponds to the lowest pH value (7.08) at 3 o'clock on November 2. The fact suggests that the exchange rate of carbon dioxide between air and lake surface principally depends on the pH value of the surface water.

Seasonal variation of the exchange rate of carbon dioxide between air and surface water of Lake Suwa will be discussed in relation to pH and total carbon dioxide as well as dissolved oxygen in a following paper.

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- (The authors: Tadashiro KOYAMA, Mitsugu NISHIMURA and Hiromi MATSUDA, Water Research Institute, Nagoya University, Chikusa-ku, Nagoya-shi 464, Japan)