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Measurement of Dissolved Oxygen Consumption Rates by Bottom Sediment in an Estuary

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DO(dissolved oxygen) consumption rates by bottom sediments were estimated based on temporal changes in the DO in a closed container under dark conditions. When measuring the DO, the vertical structure of the sampled sediments was maintained as it had been on the bottom in the estuary, and the overlying water was slowly circulated without stirring up the sediments. DO consumption rates were likely to depend on the DO concentration in the overlying water, thus better fitting first-order kinetics rather than a constant rate. Seasonal changes in the DO consumption rates by the bottom sediments in the Ofunato estuary were presented showing high values in the summer. It was suggested that DO consumption rates depended mostly on the biochemical decomposition of organic detritus both on the bottom surface and inside the bottom sediments, leading to a positive correlation with the water temperature of the bottom layer. Empirical regressions of the DO consumption rates versus water temperature were presented.

1 Introduction

The oxygen depletion in the bottom layer in summer has long been a great problem both in environmental conservation and aquaculture in coastal waters. Spatial and temporal changes in DO (dissolved oxygen) concentration C (mg／ℓ) are usually described by an equation of diffusion, which consists of advective, diffusive, and biochemical terms. The biochemical term is given by the sum of the following rates[1).]

$$dC/dt = D_1 - D_2 - D_3 - D_4 - D_5 - D_6 - D_7 - D_8 + D_9 \quad \cdots\cdots(1)$$

where D_1 and D_9 are for DO increase by photosynthesis of phytoplankton and reaeration, D_2 and D_3 for consumption by respiration of phytoplankton and zooplankton, D_4 and D_5 for consumption by oxidative degradation of particulate organic matters and dissolved organic matters, D_6 and D_7 for consumption by nitrification of dissolved inorganic nitrogen compounds from ammoniates to nitrites and from nitrites to nitrates, respectively. D_8 is DO consumption by bottom sediments. For simplification, DO in the bottom layer without reaeration is described by

$$dC/dt = D_1 - D_8 - B_1 \quad \cdots\cdots(2)$$

where B_1 denotes DO consumption rate by

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water, or the sum of D_2, D_3, D_4, D_5, D_6, and D_7 in formula (1).

Several estimated values of DO consumption rates in the bottom layer were reported. The total DO consumption rate($=D_1-D_8-B_1$) of 0.65(g/m^3/day) in Mikawa Bay[2], and 0.15 to 0.72(g/m^3/day) in Dokai Bay[3] were estimated by *in situ* measurements of DO. Also 0.2(g/m^3/day) in Hiuchi-Nada was observed by the light and dark bottle method[4], which agreed well with the calculated value using the heat and oxygen budget model[5]. DO consumption rates by water (B_1) in Suo-Nada were reported 0.10 to 0.67(g/m^3/day) by incubating method in the dark room, and 0.16 to 0.89(g/m^3/day) by the *in situ* dark bottle method[6]. DO consumption rates by water depended significantly upon POC (particulate organic carbon) in the bottom layer[6,7].

DO consumption rates by bottom sediments D_8 has conventionally been given by the constant DO consumption rate K_1 (g/m^2/day) and the depth of the bottom layer H (m), as follows.

$$D_8 = K_1/H \qquad \cdots\cdots\cdots\cdots(3)$$

Several values of K_1 were estimated as 0.49(g/m^2/day) in Hiuchi-Nada (H=6 m)[4], and 0.21 to 0.74(g/m^2/day) in Suo-Nada (H=4 m)[6] by *in situ* methods with the bell-jar. By measuring DO with the experimental apparatus in the laboratory, values of 0.12 to 0.40(g/m^2/day) in Lake Biwa[8], and 30.7(mg/m^2/hr) equivalent to 0.7(g/m^2/day) in Suo-Nada[7] were reported.

As stated above, DO consumption rates by water (B_1) ranged from 0.10 to 0.89(g/m^3/day), and DO consumption rates by bottom sediment (K_1) were reported 0.12 to 0.74(g/m^2/day). DO consumption rates derived from the latter (D_8) seemed to be much less than the former (B_1), if depths of the bottom layer were taken into consideration. Nevertheless, in simulating DO by using an ecohydrodynamic model, DO consumption rates by the bottom sediment are of fundamental importance in the bottom layer. It is the reason that DO consumption by the bottom sediment occurs wherever the bottom sediment exists, while DO consumption by water depends mainly on the changeable concentrations of particulate and dissolved organic matters in the water. In addition to some confusion of definition of DO consumption rate, there has been a lack of the standard method for measuring DO consumption rate by the bottom sediment. This study aims to present the detailed method for measuring DO consumption rates by bottom sediments, and to show their seasonal changes on the bottom in the estuarine waters.

2 Materials

In order to establish the measurement method of DO consumption rates, bottom sediments were sampled around station OFBW in the Ofunato estuary (Fig.1) in October 1992, by diving or by using SM(Smith-McIntyre) mud-sampler(500 cm^2) on board. Ofunato estuary(OF06 at 39°03′ N, and 141°44′ E) is notorious for the anoxic bottom water in summer[9]. Mud samples at OF05, OFBW, OF06, and OF12 were collected monthly from April 1993 to March 1994, to know seasonal changes in DO consumption by bottom sediments. Mud samples(ca. 15cm depth) together with the overlying bottom water were collected by the diver into a tube container with their vertical structure unchanged. When sampled by

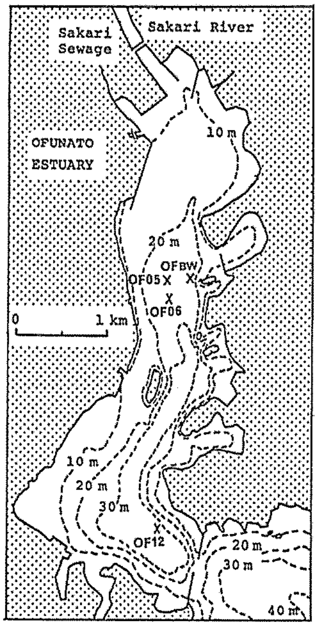

Fig. 1. Sampling stations for bottom sediments in Ofunato estuary, 1993 to 1994.

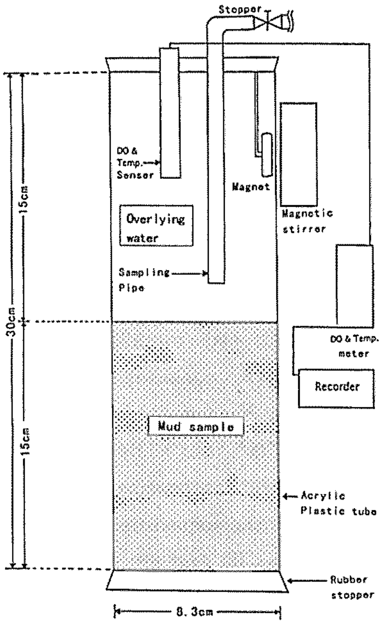

Fig. 2. Experimental container for measuring DO consumption rate. DO in the overlying water was measured with a DO meter every 30 minutes. The stirrer outside the container drove magnet rotation to bring about slow circulation in the water. Sampling pipe was used for calibration of DO meter by Winkler method.

SM mud-sampler, the container was filled with filtered sea water without stirring up bottom sediments(Fig.2). The containers were closed tightly with rubber stoppers and carried back to the laboratory to measure DO consumption.

3 Methods

3. 1 General procedures

After removing the upper stopper, another 15cm long tube with the same diameter as the container was added onto it and the filtered seawater was poured into the jointed container. The overlying water was mixed for 10min.by a magnet stirrer without stirring up any mud sample. Then, the aliquot of the overlying water was taken for control. The container for control was the same as the upper half of the experimental one as shown in Fig.2. These containers sealed were kept in the dark and air-conditioned room. The room temperature was controlled to that in the bottom layer where sediments were sampled. But, in some cases there were some differences between the controlled temperature and the temperature observed in the bottom layer. A magnet(10mm diameter, and 38mm long) was hung 10cm above the surface of the mud, and rotated at 300-350 rpm to make a gentle circulation inside the container without stirring up the mud. Fixed rates of magnet rotation were important for measurement of DO consumption rates.

Temporal changes of DO in the overlying water both in control and in experimental container were measured for more than half day with DO and temperature meters (Model ND-10, Nagashima Shoji Ltd.).

3. 2 Model 1

In this conventional model, DO decreases with a constant DO consumption rate by the bottom sediment K_1 (g/m^2/day) and that by water B_1(g/m^3/day). Because of neither photosynthesis nor reaeration, the temporal change in DO in the experimental container is given by formulas (2) and (3), as follows.

$$dC/dt = -K_1/H - B_1 \quad \cdots\cdots\cdots(4)$$

If DO data are obtained, B_1 and K_1 are given as follows.

$$B_1 = \{C_C(t_0) - C_C(t_0+\Delta t)\}/\Delta t \quad \cdots\cdots\cdots(5)$$

$$K_1 = \{C_E(t_0)+C_C(t_0+\Delta t)-C_E(t_0+\Delta t)-C_C(t_0)\}\cdot H/\Delta t \quad \cdots\cdots\cdots(6)$$

where C_C and C_E are DO's in control and an experimental container, respectively. Initial time is t_0 and time lapse is Δt.

3. 3 Model 2

Decrease in DO is assumed to depend on DO concentration and coefficients of DO consumption rate by the bottom sediment K_2(m/day) and that by water B_2(ℓ/day), as follows.

$$dC/dt = -(K_2/H + B_2)\cdot C \quad \cdots\cdots(7)$$

By using DO data, B_2 and K_2 are given as follows.

$$B_2 = (1/\Delta t)\cdot \ln | C_C(t_0)/C_C(t_0+\Delta t) | \quad \cdots\cdots(8)$$

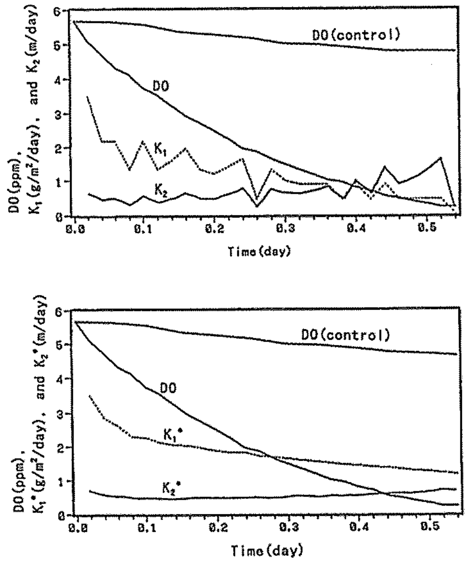

Fig. 3. Upper; Temporal changes in DO, DO in control(solid lines), DO consumption rates K_1 (broken line), and coefficients of DO consumption rate K_2(solid line).
Lower; Same as the upper, except that K_1^* (broken line), and K_2^*(solid line) denote averaged K_1, and averaged K_2 for the period during which DO was measured, respectively.

$$K_2 = (H/\Delta t)\cdot \ln | \{C_E(t_0)\cdot C_C(t_0+\Delta t)\}/\{C_E(t_0+\Delta t)\cdot C_C(t_0)\} | \quad \cdots\cdots(9)$$

Recorded data of DO were plotted every 30 min., giving K_1 and K_2 calculated from formulas (6) and (9). Averaged K_1 and K_2 for the period T(day) during which DO had been measured, were given by substituting zero for t_0 and T for $t_0+\Delta t$.

4 Results and discussion

Fig.3 shows temporal changes every half an hour in DO in control, DO in an experimental container, DO consumption rates K_1, and coefficients of DO consumption rate K_2. K_1 was found much more changeable than K_2, and it was shown that high values of ca. 3(g/m²/day) at the start declined to less than 0.5(g/m²/day) at the end. High values of K_1 were likely to come from high DO concentration in the beginning of the experiment. On the other hand, K_2 was less changeable, ranging 0.3 to 0.6(m/day), although it increased up to 1.5(m/day) after 0.4 days passed. It was suggested that these high values of K_2 were associated with some degradation of benthic animals that could not be alive due to DO depletion in the end of the experiment. Less changeable K_2 values indicated that DO consumption by the bottom sediment obeyed approximately first-order kinetics. Averaged K_2 (shown as K_2^* in Fig.3) for less than 0.4 days could give a parameter estimation of DO consumption rate by the bottom sediment.

Three methods for DO consumption rates by the mud were presented by Satoh[10], including the experiments 1) with the mud fully mixed with the seawater, 2) with the mud not mixed and only the seawater circulated, and 3) with the mud and the seawater in no motion. It was reported that the first-order reaction was observed and DO consumption rates depended on COD(chemical oxygen demand) of the mud in the experiment 1), and consumption rates in the experiment 2) were ca. 1.5(g/m²/day), while lower values of ca. 0.55(g/m²/day) in the experiment 3). These results suggested DO consumption rates were affected by both movements of the overlaying seawater and labile organic contents on the surface and inside the mud. Berner[11] presented the general diagenetic equation for the concentration inside the bottom sediment, which consisted of diffusive, advective and biochemical terms. This equation suggested that the turbulent flows on the bottom and the vertical profile of DO in the interstitial water inside the mud would affect the flux of DO between the overlying seawater and the mud. Vertical profiles would be affected directly by sulfides that were produced from organic compounds in the mud through some biochemical degradation processes, and reaction rates of these processes would depend on temperatures. It follows that

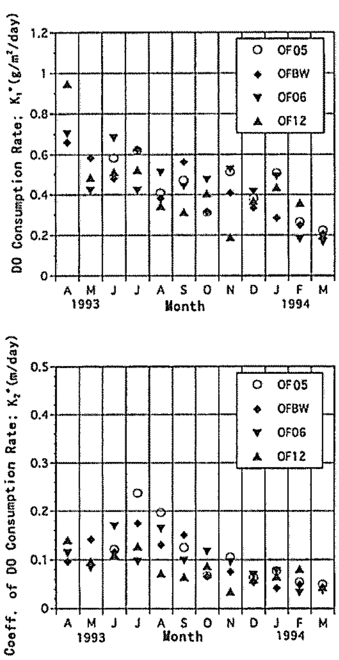

Fig. 4. Seasonal changes in averaged DO consumption rate K_1^*(upper), and averaged coefficients of DO consumption rate K_2^*(lower) of bottom sediments in Ofunato estuary, 1993 to 1994.

DO consumption rate by the bottom sediment would depend on the movement of the overlying water, labile organic content inside the mud, and the temperature.

In numerical calculation of DO in the bottom layer, the product of DO and K_2^* divided by H could give the rates of the consumed DO by the bottom sediment, as formula (7) shows. Constant rates K_1^* might give the negative DO in calculation. But, the resultant DO in calculation using K_2^* would not become negative any more, which would be useful when calculating the autumn recovery of DO from summer DO depletion.

Fig.4 showed seasonal changes in averaged DO consumption rate K_1^*, and averaged coefficients of DO consumption rate K_2^* of bottom sediments in Ofunato estuary, 1993 to 1994. Values of K_2^* were relatively high in summer, ranging ca. 0.05(m/day) in winter to more than 0.2(m/day) in summer, while no remarkable seasonal changes in K_1^* were found. This 0.2(m/day) would be equivalent to 1.2 (g/m^2/day) if DO in the bottom layer was 6(mg/ℓ). However, there might have been some overestimation of K_2^* in summer, because the water temperatures in the experiment containers sometimes exceeded those observed in the estuarine bottom layer.

No seasonal changes in K_1^* would be attributed to the initial DO concentrations in the container that varied from measurement to measurement. Low DO in the container tended to lead to lower values of K_1^*, vice versa. Values of K_2^* were likely to depend on the organic contents and the temperature inside the muds, since DO consumption by the bottom sediment was associated with the biochemical degradation processes.

Fig.5 showed averaged DO consumption rates K_1^* and K_2^* against the temperatures t (℃). Their regressions were given by the least squares method as follows.

$$K_1^* = 0.165 \cdot \exp(0.0455 \cdot t) \quad \text{--------(10)}$$

$$K_2^* = 0.0158 \cdot \exp(0.0855 \cdot t) \quad \text{--------(11)}$$

where the correlation coefficients (r) of K_1^* and K_2^* were 0.41 and 0.65, respectively.

Thus, each of regressions might give an empirical equation for estimation of DO consumption rates by the bottom sediment under a given temperature. Estimated K_1^* and K_2^* at 20(℃) that was the maximum temperature

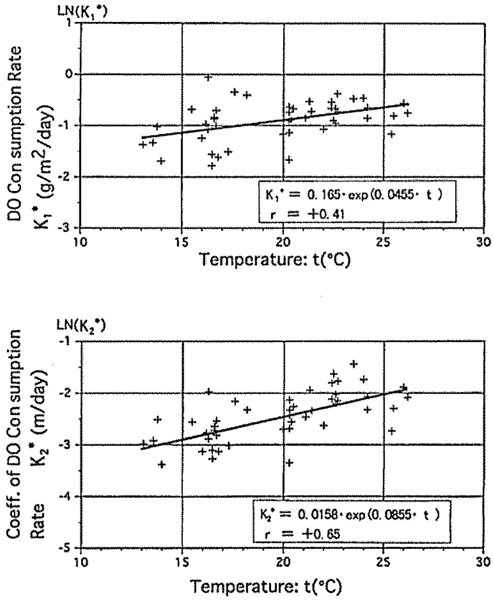

Fig. 5. Plots of averaged DO consumption rates K_1^* and averaged water temperatures during the experiment, and their regression (upper). The same as the upper except for rate K_2^*(lower). Each of regressions may give an empirical equation for estimation of DO consumption rates under a given temperature. DO consumption rates are shown on the scale of natural logarithm.

observed in the bottom layer, are 0.41(g/m^2/day) and 0.09(m/day) equivalent to 0.54 (g/m^2/day) if 6(mg/ℓ) of DO in the bottom layer. These were within the range of reported values. Corrected rates with the observed temperatures could give better estimates if the organic contents were the same. Effects of the water movement and the organic content inside the bottom sediment on DO consumption rates would have to be considered quantitatively.

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内湾底泥の溶存酸素消費速度

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内湾底泥による底層水中のDO（溶存酸素）消費速度を測定する方法を示した。室内実験装置を用いて，密閉・水中攪拌・暗条件下での，鉛直構造を保持したままの底泥によるDO消費速度をDO時間変化から測定した。その結果，DO消費は，従来用いられてきた一定数値よりも，水中のDO濃度に依存する１次反応式に良く一致した。この方法を大船渡湾の底泥に適用してDO消費の季節変化を示した。DO消費は夏期に増加したが，これは底泥によるDO消費が，底泥表面および内部における有機物の分解速度に依存するゆえに，水温と正相関するためである。DO消費速度を水温の関数とした実験式を示した。