Kasetsart J. (Nat. Sci.) 35 : 74 - 84 (2001)

Kinetic Model for Describing Oxygen Fluxes Across the Sediment-water Interface

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ABSTRACT

The oxygen uptake rate of coastal sediments has been investigated. The method which has been used for measuring the oxygen uptake of sediment consisted in transferring undisturbed sediment cores to laboratory and measuring oxygen depletion in overlying water by using stirring oxygen probe (YSI Model 5739). Changes in amount of dissolved oxygen over the sediment cores can be calculated as oxygen fluxes, and expressed as mg O_2 m^{-2} hr^{-1}. The oxygen fluxes across the sediment-water interface was noticed to be dependent upon oxygen concentrations of the overlying water. By modifying Fick's Law of diffusive fluxes, one dimension diffusion of dissolved oxygen in the sediment has been described and the mathematical approximation of total benthal oxygen uptake (BOU) was proposed to be $BOU = F + \sqrt{L^2+2\phi^2(D/\theta^2)\,B\,C_0}$. In the case of the benthal sediment in which contained only a few macroinvertebrates, a linear relationship can be obtained when the square of BOU rates were plotted against the oxygen concentrations of overlying water. It seemed that differences in slopes and intercept constants of such regression lines implied the differences in relative importances of microbial and inorganic oxidation reaction that varied seasonally and depended on sampling locations of benthal sediments. The expression of respiratory activity of active macroinvertebrates was also discussed.

Key words: coastal sediments, oxygen fluxes, kinetic model

INTRODUCTION

Because of the fact that the transfer of material across the sediment-water interface in benthic ecosystem has an important influence on biological activity in both aquatic and sediment environment, several ways of investigations on sediment-water interactions have been conducted. In the past two decades, many mathematical water quality models have been developed to simulate chemical, physical and biological processes occurring in river and coastal waters. Their possible applications ranged from identifying processes affecting water quality to forecasting the quality of operational processesed (Walker and Snodgrass, 1986 and Zeillinski, 1988). Ullman and Aller (1982) and Hammon *et al.* (1996) have performed investigations relative to bulk sediment coefficient that was necessary to calculate fluxes from the sediments. It has been reported that the fluxes from sediments supply about 80% of nutrients during certain times of the year in Narragansett Bay (Nixon, 1976), about 60-100% and 30-50% of the requirement of primary production in coastal and offshore area of the North Sea (Billen, 1978) and about 10-40% of that of Shesapeake Bay (Boynton

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and Kemp, 1985). Polak and Haffner (1978) had studied on the oxygen depletion of Hamilton Habour and reported that the sediment consumed oxygen about 18 % of the oxygen entering the habour. In extreme anoxic conditions, fish kills and noxious smells may result and the transport of reduced substances from the sediments may be enhanced.

Up to date, many studies on benthal oxygen uptake have been carried out with different types of aquatic sediments. However, attempts to determine the effects of various environment factors on the rate of oxygen utilization by benthal sediments have resulted in a variety of conclusions. As it seems that the rate of oxygen uptake from overlying water is a rapid and sensitive index of benthal community metabolism (Edberg and Hofsten, 1973 ; Hargrave, 1978), this study has been made with an objective to define the relative effects of which factors such as oxygen concentration in the overlying water, chemical/biochemical properties of sediments, and character of biological community have on the oxygen uptake regime of benthal sediments.

In this study, the method which has been used for measuring the oxygen fluxes of the sediment-water interface consisted in transferring undisturbed sediment cores to the laboratory and measuring oxygen depletion in the overlying water. The results on the oxygen uptake of sediments reported here have been obtained totally by means of laboratory measurements. *In situ* experiment has not been extended.

MATERIALS AND METHODS

Sampling of sediment cores

The sediment cores for laboratory treatment were taken from Shido Bay (outer part), Yashima Bay, Nishihama Fishing Port, and Kozai Fishing Port, in the Seto Inland Sea, Japan (Figure 1). A diver was required in all cases to ensure that plexiglass corer apparatus was placed properly with minimum distortion of the sediment surface. Care was taken in removing samples and transporting them to the laboratory so as to make the least possible disturbance of the sediment.

Setting of the apparatus

The top and bottom ends of the tube containing water that originally overlaid the

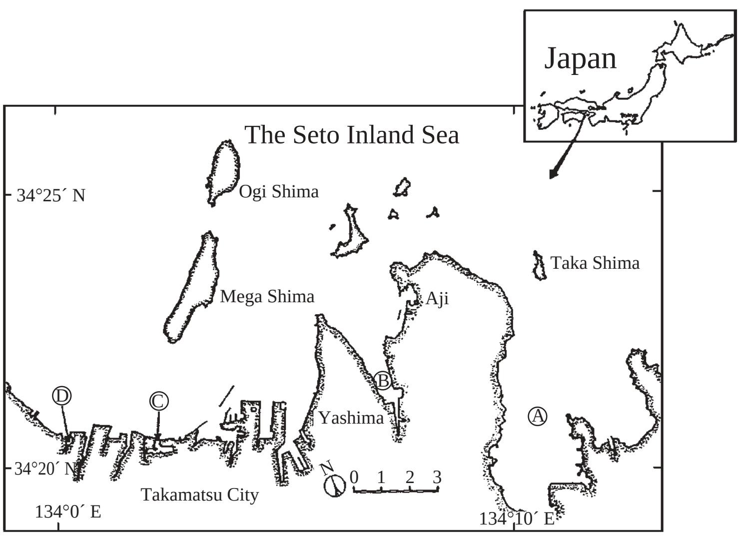

Figure 1 Sampling location in the Seto Inland Sea, Japan: (A); Shido Bay, (B); Yashima Bay, (C); Nishihama Fishing Port, and (D); Kozai Fishing Port.

sediment core were sealed with rubber stoppers. Before testing, the collected core samples were acclimated at a study temperature. The water overlying the sediment was then replaced, without disturbance of the sediment surface, by filtered (Millipore, HA 0.45 µm), well-aerated sea water which had been sterilized under 120 C at 1 kg/cm^2 for 20 minutes and kept in a dark at room temperature for a few days prior to replacement.

On the top rubber stopper, an oxygen probe was carefully fitted. Constant mixing and homogeneous conditions were provided in the water overlying the sediment using the vibrator that was connected to the oxygen sensor. Changes in oxygen concentrations of overlying water were continuously monitored by the stirring oxygen probe (YSI, Model 5739) that connected to dissolved oxygen meter (YSI, Model 57) and read off directly on a recorder (YEW, Model 3087) which coupled to it.

Experimental apparatus

Character of the plexiglass core (45 cm in length and 6.9 cm in diameter) in which sediments were sampled was shown in Figure 2. Laboratory experiments were directly carried out in the core. For setting of the experiment, the core containing *ca* 30 cm of water, overlying a sediment column with a depth of 8-15 cm was placed in a temperature-controlled water incubation tank. Since the change of dissolved oxygen was suggested to be able to affect the sediment oxygen uptake (Fillos and Molof, 1972), all experiments were thus performed in dark in order to inhibit possible production of oxygen by algae.

The oxygen measurements were performed until the oxygen concentration in the testing core was lower than 0.5 mg/l or until one week has elapsed. After measurement, the incubation tank was opened and the oxygen probe was then smoothly taken off, thereafter the water volume in the core was measured correctly. Temperatures of the sediment samples collected varied from 21-27 C. However, no attempt to introduce temperature compensation was made since it may add only little

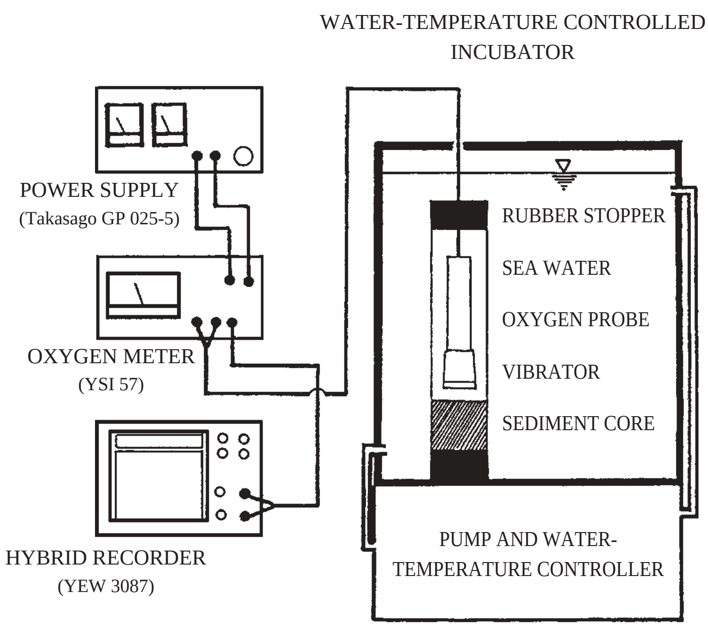

Figure 2 Diagram showing the setting of experimental apparatus for measuring the changes in amounts of dissolved oxygen over the collected sediment core.

variation to the results. Most samples were incubated at 20 C to cancel the effect of temperature on the oxygen uptake. The oxygen uptake of overlying water (blank) was measured in the same kind of plexiglass tube - but without sediment.

Calculation of the oxygen fluxes

Knowing the incubation time of the experiment, the enclosed mass of water, and the area of the sediment surface, changes in amounts of dissolved oxygen over sediment cores can be calculated as oxygen fluxes, and expressed as mgO_2 $m^{-2}hr^{-1}$. The quantity of oxygen reduced by oxygen electrode was negligible even when measurements were carried out continuously over a period of several days. The current consumed by the electrode was stated by the makers to be 19 A at 30 C in air.

MODEL EVOLUTION

Basic assumption and formulation of the model

It is a common practice to describe the problems related to chemical and biological processes in aquatic areas through determistic differential equations. A number of models have been proposed in recent years that treated water quality processes as stochastic. However, there was always some uncertainty, both in the evaluation of field data and in the use of the mathematical models to predict the outcome of the natural processes, since the processes were still not completely understood and the full representation was usually too complicated and too costly to implement. All these sources of uncertainty may be represented as input forcing terms in the balance equations.

Diffusive flux have revealed to obey Fick's First Law and was controlled by the concentration gradient between the overlying water and the interstitial water near the surface sediment (Glass and Poldoski, 1975 and Kasper *et al*., 1985). One dimentional (z-direction) diffusion of dissolved oxygen in the sediment has been described (Inoue, 1987) by the equation;

$$M = -\phi \frac{D}{\theta^2}\frac{\partial C}{\partial z} \qquad (1)$$

$$\frac{\partial(\phi C)}{\partial t} = \frac{\partial}{\partial z}\left(\phi \frac{D}{\theta^2}\frac{\partial C}{\partial z}\right) - S \qquad (2)$$

where

C = the concentration of dissolved oxygen per unit volume of pore water,
z = the depth in the sediment measured positively downward from sediment-water interface,
ϕ = the porosity,
D = Fick's Law diffusion coefficient,
θ = tortuosity (dl/dz) where "dl" is length of the actual sinous diffusion path over a depth interval "dz",
S = the uptake rate of dissolved oxygen per unit volume of sediment,
M = the diffusion flux in mass per unit area per unit time,
t = the time.

By these equations, the difference from the study of Bouldin (1968) was expressed. Here there was a progressive reduction in the values of the diffusion coefficient (D). A daily rate of change of D was observed to be very gradual with the average of less than 10.5 mg l^{-1} day^{-1}. Hence, the computation of D based on the assumption that it had a constant value within the period of a day was justified.

Benthal decomposition of sludge bottoms involves both aerobic and anaerobic processes. Aerobic activities are restricted to the mud surface comprising no more than a few millimeters of sludge depth. Anaerobic decomposition is active within the remainer of the sludge depth (Fillos and Molof, 1972). Inoue (1978) assumed that total oxygen uptake would include such processes as (i) chemical oxygen uptake, (ii) microbial oxygen uptake, and (iii) algae and macroinvertebrate oxygen uptake. Accordingly, the following conditions necessary for our model evolution were stated out.

(1) Steady-state condition exists: because

of the fact that when a sedimentary system was at steady-state with respect to solute diffusion and reaction, the sum of all reactions in the sediment must be balanced by transport across the sediment-water interface.

(2) ϕ and θ were constant values.

(3) $S = \phi B$: the microbial oxygen consumption rate in the sediment, B, was assumed to be constant per unit volume of pore water per unit time and did not change with depth. Bacteria, microflora, and protozoa would account for such an oxygen consumption.

(4) $C = C_0$ at $z = z_0$: C_0 was the constant concentration of oxygen at the sediment-water interface.

(5) $C = 0$ and $\phi \frac{D}{\theta^2} \frac{\partial C}{\partial t} \Big|_{z=z_0} = L$ at $z = z_0$: oxygen was required to react with the reducing substances which diffused toward the plane ($z = z_0$) separating the reduced from the oxidized zone. At the plane, chemical uptake was L and constant per unit area per unit time.

Under these conditions, the following equations of which oxygen was uptaken by the microbial and the chemical reactions, can describe the concentration of oxygen as a function of distance from the sediment-water interface.

$$C = \frac{B}{2(D/\theta^2)} z^2 - \frac{1}{\phi(D/\theta^2)} \sqrt{L^2 + 2\phi^2 (D/\theta^2) B C_0}\; z + C_0 \quad (3)$$

$$M_{z=0} = \sqrt{L^2 + 2\phi^2 (D/\theta^2) B C_0} \quad (4)$$

where L is the chemical oxygen uptake rate and $\sqrt{2\phi^2 (D/\theta^2) B C_0}$ is the microbial (e.g. bacteria, microflora, and protozoa) oxygen uptake rate.

Derivation of the model

Assuming that the conditions of (1), (2), and (3) explained in the paragraph above exist, thus Eq. (2) may be written as follows;

$$0 = \phi \frac{D}{\theta^2} \frac{d^2C}{dz^2} - \phi B \quad (1')$$

$$\frac{d^2C}{dz^2} = \frac{\theta^2 B}{D} \quad (2')$$

Integrating Eq. (2´), we get

$$\frac{dC}{dz} = \frac{\theta^2}{D} B z + E' \quad (3')$$

where E´ is an integrating constant.

As it had been stated that at $z = z_0$, $-\phi \frac{D}{\theta^2} \frac{dC}{dz} = L$, we can determine E´ as follows;

$$-\frac{\theta^2 L}{\phi D} = \frac{\theta^2}{D} B z_0 + E'$$

$$E' = -\frac{\theta^2}{\phi D} L - \frac{\theta^2}{D} B z_0 \quad (4')$$

Accordingly, we get Eq. (5´)

$$\frac{dC}{dz} = \frac{\theta^2}{D} B z - \frac{\theta^2}{\phi D} L - \frac{\theta^2}{D} B z_0 \quad (5')$$

Integrating Eq. (5´) again, thus Eq. (6´) will be derived.

$$C = \frac{1}{2} \frac{\theta^2}{D} B z - \frac{\theta^2}{\phi D} L z - \frac{\theta^2}{D} B z_0 z + E'' \quad (6')$$

where E´´ is an integration constant.

By using the condition (4), E´´ may be determined as $E'' = C_0$. Accordingly, the following equation which describe the DO concentration as a function of distance from the sediment-water interface will be derived from Eq. (6´).

$$C = \frac{1}{2} \frac{\theta^2}{D} B z - \frac{\theta^2}{\phi D} L z - \frac{\theta^2}{D} B z_0 z + C_0 \quad (7')$$

In order to eliminate z_0, we use the condition $C = 0$ at $z = z_0$.

$$0 = \frac{1}{2}\frac{\theta^2}{D} B z_0 - \frac{\theta^2}{\phi D} L z_0 - \frac{\theta^2}{D} B z_0^2 + C_0$$

$$z_0 = -\frac{1}{\phi D} L + \frac{1}{\phi B}\sqrt{L^2 + 2\phi^2 \frac{D}{\phi^2} B C_0} \quad (8')$$

Substituting Eq. (8′) into Eq. (7′) and arranging, we will obtain Eq. (3) as follows;

$$C = \frac{B}{2(D/\theta^2)} z^2 - \frac{1}{\phi (D/\theta^2)}\sqrt{L^2 + 2\phi^2 (D/\theta^2) B C_0}\, z + C_0 \quad (3)$$

The flux of DO across the interface; Eq. (4), would be estimated using Eq. (1).

$$M_{z=0} = -\phi \frac{D}{\theta^2}\frac{dC}{dz}\Big|_{z=0}$$

$$= -\phi \frac{D}{\theta^2}\left[-\frac{1}{\phi (D/\theta^2)}\sqrt{L^2 + 2(D/\theta^2) B C_0}\right]$$

$$= \sqrt{L^2 + 2\phi^2 (D/\theta^2) B C_0} \quad (4)$$

For the dependence of oxygen uptake rate of macroinvertebrate population on oxygen concentration, the following model was proposed.

$$F = F_m [1 - \exp(-k(C_0 - C'))] \quad (5)$$

Where

- F = the oxygen uptake rate of macroinvertebrate per unit area ($mgO_2\ m^{-2}\ hr^{-1}$),
- F_m = the maximum oxygen uptake rate of macroinvertebrate population in sufficient oxygen concentration,
- C_0 = the oxygen concentration of water over the sediment,
- k = the constant,
- C′ = the critical level of oxygen concentration below which no measurable oxygen uptake of macroinvertebrate population exists.

Consequently, it was assumed that the oxygen uptake by macroinvertebrate population had no relation to the chemical and the microbial uptakes and operated independently. Therefore, it is possible to predict a mathematical kinetic model for approximation of total benthic oxygen uptake (BOU) that can be accordingly expressed as the sum of Eq. (4) and Eq. (5) as;

$$BOU = F + M_{z=0}$$

$$= F + \sqrt{L^2 + 2\phi^2 (D/\theta^2) B C_0} \quad (6)$$

RESULTS AND DISCUSSION

Results from several runs were plotted in Figures 3-8, compared with proposed approximation using Eq. (6). For the benthal sediments containing a little macroinvertebrate (F = 0), when the squares of benthal oxygen uptake rate (BOU^2) were plotted against the oxygen concentrations (DO), linear relationships can be obtained as seen in Figure 3 (Shido Bay sediment) and Figure 4 (Yashima Bay sediment). The linear relationships have been predicted from Eq. (6) by putting F = 0. Slopes and intercept constants of the regression lines corresponded to $2\phi^2(D/\theta^2)B$ and L^2, respectively.

Importance of L^2

It seems that differences in slopes and intercept constants of such the regression lines indicate the differences in relative importance of microbial and inorganic oxidation reactions which may varied seasonally and in sediments from different areas. In well aerated benthal sediments, most of the oxygen consumed by sediments is the result of microbial respiration. In the areas where an oxidized zone is present, the diffusion of reduced compounds from below was slow enough that little inorganic oxidation occurs; that is, the intercept constant (L^2) approached zero (Figure 4).

On the other hand, sediment core taken from Shido Bay showed a relative high value of L^2 (Figure 3). In both sediments, however, the regression lines had nearly the same slopes. This meant that the microbial uptake rates corrected for temperature were nearly similar. There were many other benthal sediments, such as those in polluted area, and, the inorganic oxidation in such environments becomes much more important. Thus, L^2 became very large, as shown in Figure 5.

Evidence for macroinvertebrate respiration

For the benthal sediments containing large populations of macroinvertebrates, the dependency of total oxygen uptake rate on oxygen concentration was readily apparent. When the squares of total oxygen uptake rates were plotted against the oxygen concentrations, the data laid on a straight line up to the oxygen concentration of about 2.5 to 3.5 mg/l. They departed most significantly at the greater oxygen concentrations (see Figure 6). It may be suggested that such changes in oxygen uptake rates were due to the respiration of macroinvertebrate within the sediments.

Typical examples were shown in Figure 7 (Nishihama Port sediment) and Figure 8 (Yashima Bay sediment). From these figures in which total oxygen uptake rates were plotted against oxygen concentrations, it can be noticed that the influence of macroinvertebrate populations on benthal oxygen uptake rates appeared clearly, showing bending point at the levels of oxygen concentrations of about 2.5 to 3.5 mg/l. In each case (Figure 7 and Figure 8, respectively), plots of BOU^2 against oxygen concentrations within the ranges of oxygen concentration less than 2.5 and 3.5 mg/l yielded straight lines, corresponding to Eq. (4). Then, by using the extrapolated regression line, the values of $M_{Z=0}$ at the oxygen concentrations greater than the bending point were calculated. The difference, BOU - $M_{Z=0}$, would be the rate of oxygen uptake by macroinvertebrate population, F. The values of F obtained were plotted against oxygen concentrations, together with the fitted curves using Eq. (5) for each figure. Then the data on total oxygen uptake rate observed were compared with those calculated by Eq. (6). The results depicted very closely, as seen in Figures 7 and 8.

General consideration

Sediment oxygen demand involves the transport of oxygen from overlying water through the sediment-water interface and pore water to the site of oxygen consumption (bacterial cells, meiofauna and macroinvertebrates, or chemical reactions with reduced cations). Turbulence or laminar flow may control transport in the overlying water while molecular diffusion may control the transport in sediments. Transport in the sediments may be larger than molecular due to mixing caused by currents or by benthic organisms (bioturbation). Present concepts which tend to accept that transport in sediments, as apposed to transport in the water column, is the rate limiting step for the flux of oxygen into the sediments.

In this study, the overall view indicated that the oxygen fluxes of sediment-water interface was dependent firstly upon oxygen concentration. Such a dependency was primarily because of the respiration of the active macroinvertebrate population present in the sediment. The sediment oxygen uptake rates were partly characterized by the inorganic (particularly, reduced substances) properties of the deposits themselves. Moreover, the results have revealed that the uptake which has been attributable to microbial respiration appeared to be dependent on the oxygen concentration due to the influence of diffusion resistance.

ACKNOWLEDGEMENT

Special recognition for his great advice is due Dr. Hiroo Inoue, Kagawa University, Japan, who has kindly suggested during the whole research work. The author would like to express appreciation to Dr. Tadashi Ochi and Dr. Takashi Sasaki for their helpful comments. Thanks are also due to Mr. Takashi Hamagaki, Mr. Vaiyapoch Kruesanae, and Mr. Tadashi Nibuno for their kind cooperation on sampling at the sea.

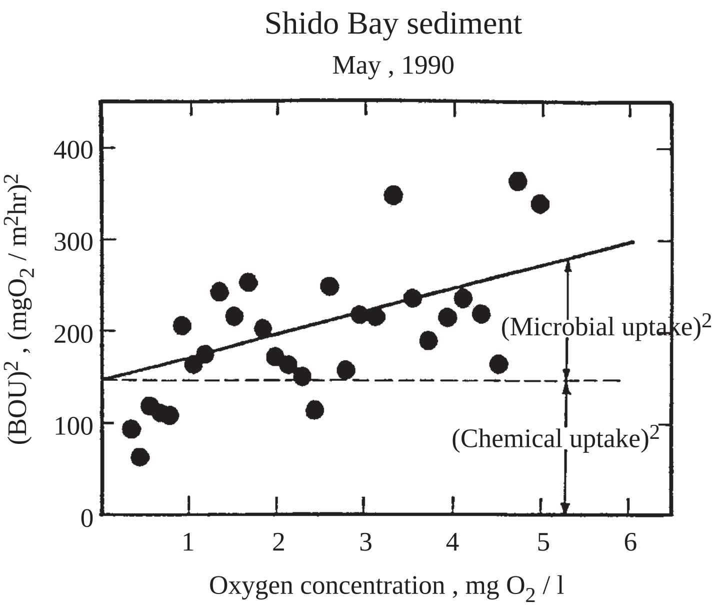

Figure 3 Linear relationship between the square of the benthal oxygen uptake rates (BOU^2) and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Shido Bay.

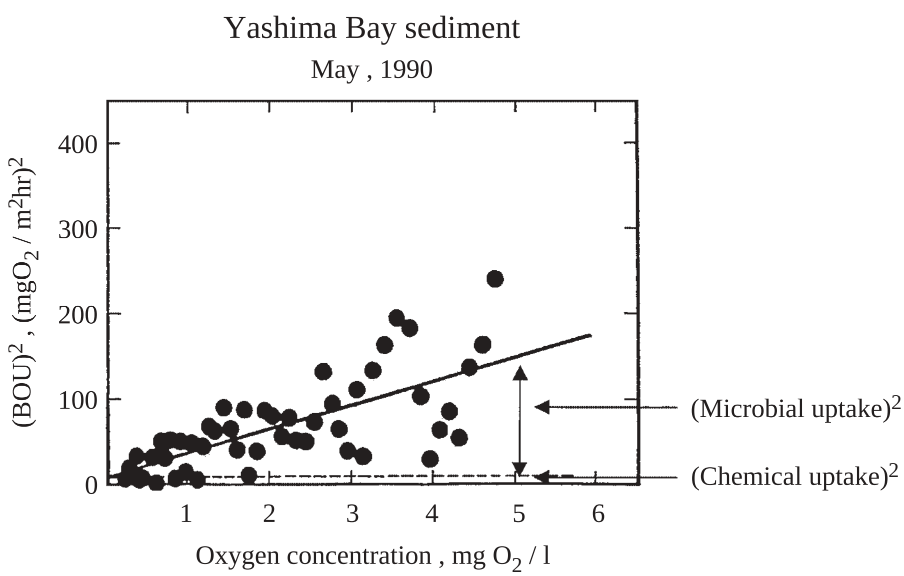

Figure 4 Linear relationship between the square of the benthal oxygen uptake rates (BOU^2) and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Yashima Bay.

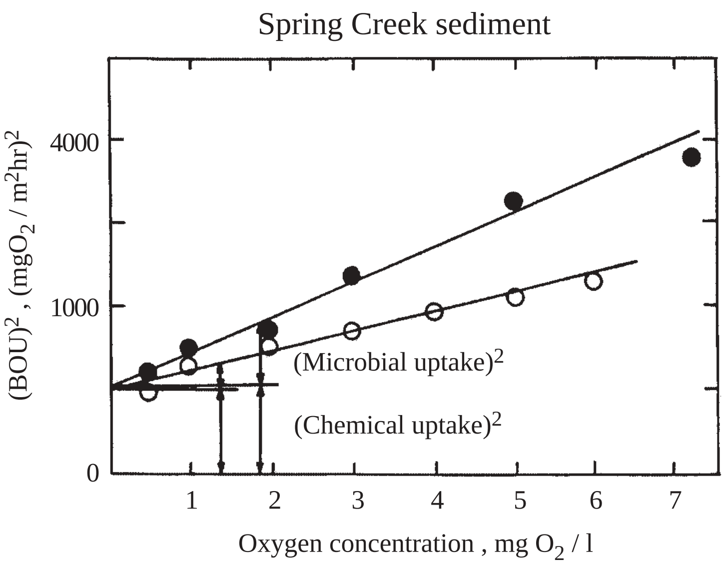

Figure 5 Linear relationship between the square of the benthal oxygen uptake rates (BOU^2) and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Spring Creek, Pensylvania; open and closed circles indicate winter and summer expressions, respectively. (Rearranged from the data of McDonnel-Hall, 1969)

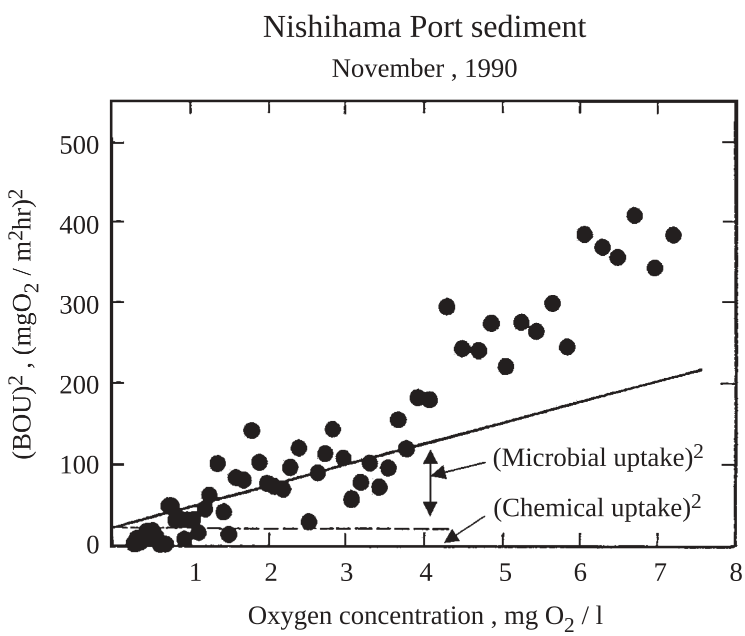

Figure 6 Linear relationship between the square of the benthal oxygen uptake rates (BOU^2) and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Nishihama Fishing Port.

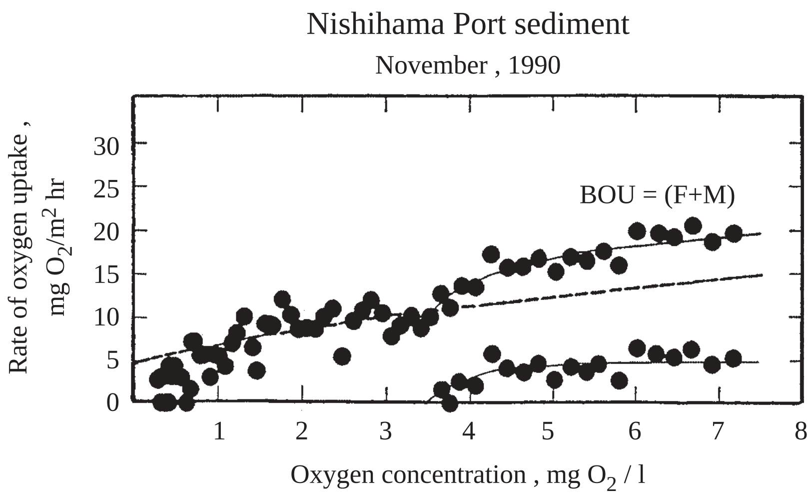

Figure 7 Plots between the measured rates of oxygen uptake and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Nishihama Fishing Port. Lines in the figure indicate the approximation by the kinetic models of Eq. (4) and (6).

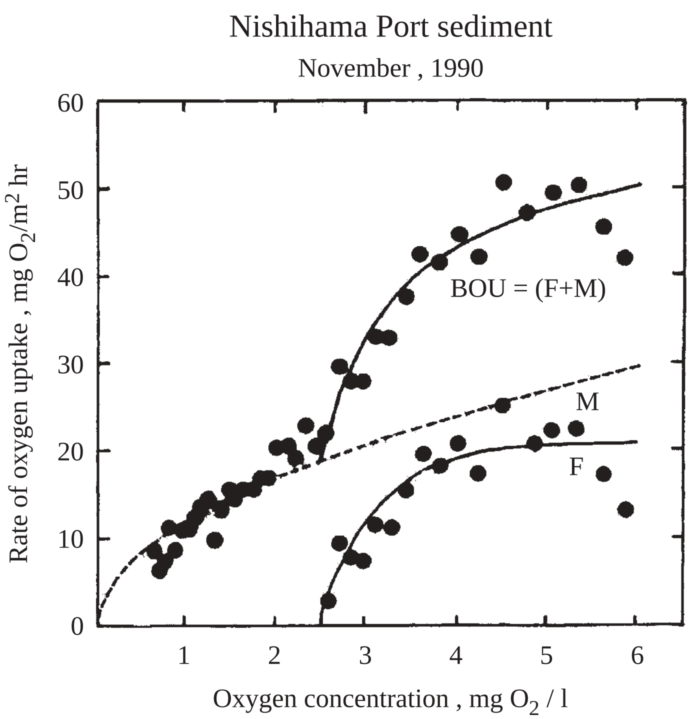

Figure 8 Plots between the measured rates of oxygen uptake and the dissolved oxygen concentrations of the water over the sediment surface (C_0), data obtained from the sediment core of Yashima Bay. Lines in the figure indicate the approximation by the kinetic models of Eq. (4) and (6).

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Received date : 02/10/00
Accepted date : 17/01/01