SEDIMENT OXYGEN UPTAKE: KINETIC MODEL EXPRESSIONS AND THEIR RELATIONS TO SEDIMENT QUALITY

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ABSTRACT

The oxygen uptake processes of suspended sediments (OUS) have been studied under laboratory conditions using an electrolytic BOD. The progressive exertion of OUS of given sediments generally increased with a tendency to taper off with time. Cumulative OUS curve showed a sharp initial increase of oxygen uptake, followed by relatively stable oxygen uptake rates that lasted until the fifth day of incubation. The expression of the curve was proposed to be accomplished by three distinct processes. The first; (A), a basic oxygen uptake phase in which organisms present in the sediments consumed oxygen biochemically with nearly constant rate. Mathematical equation, $L_m = \lambda t$, was proposed to explain its characteristic. The second; (B), the immediate chemical oxygen uptake phase in which end-products of anaerobic decomposition such as hydrogen sulfides reacted chemically with molecular oxygen in the suspended sediment solution and first-order kinetic model was proposed as $L_c = L_{c\infty}\{1-\exp[\phi(t-t_o)]\}$. The third; (C), the bacterial oxygen uptake phase in which specific labile organic matters were attached in significant amounts and bacterial respiration took place biochemically. Sigmoid characteristic of bacterial growth curve was fitted by the kinetic model $L_b = L_{b\infty} \exp\{(-\kappa/\xi) \exp[-\xi(t-t_o)]\}$. The approximated basic "λ" parameter showed significant relation to the levels of total organic carbon and total organic nitrogen of the sediments. The parameter "$L_{c\infty}$" in the chemical oxidation phase reflected the quantity of sediment total sulfides, whereas "ϕ" indicated the reaction rate that alternated as the change in sediment depths. The parameter "$L_{b\infty}$" of the bacterial respiration phase apparently related to sediment organic properties, and the parameters "κ" and "ξ" illustrated the shape expression of OUS during bacterial respiration phase and depended upon the depths of the deposits.

INTRODUCTION

The impact of organic bottom deposits on oxygen balance of overlying water has long been recognized. The removal of dissolved oxygen from the supernatant water is to satisfy the biochemical oxygen demand of the organic materials within the top, aerobic layer, and to satisfy the immediate chemical oxygen demand of end-products of anaerobic decomposition which diffuse to the aerobic zone from the deeper layers. The oxygen demand that was exerted by coastal bottom deposits had brought attention to the need for reliable predictive modelling of their impact of such bottom deposits on oxygen levels. Implementation of such models had required fundamental studies on aquatic oxygen demand, kinetics, and benthic oxygen uptake rate measurements in the water ways. Although it is known that bottom deposits play important roles and have effects on oxygen quality of the overlying water, it appears that the processes taking place in the benthal decomposition are not yet understood fully. The present paper, therefore, is an attempt to modify the earlier investigation of the biochemical oxygen demand of bottom sediments. The primary purpose of this study is to empirically establish kinetic models for approximation of the exertion of oxygen uptake by suspended sediments. Specifically, the following objectives were focused.

- To investigate general characteristics of the oxygen uptake processes of suspended sediments (OUS) that expressed by various sediment samples irrespectively with the kind of sediments.
- To define the appearance oxygen uptake into two compositions; the chemical and the biochemical oxygen uptakes.
- To evoluate the kinetic models in order to approximate the expressions of each composition.
- To examine whether model parameters could have some relations to the sediment quality.

Since the presence of reduced sulfur compound formed authigenically in sediments has typically been associated with a rather restricted range of sedimentary environment espectially in an aspect of the removal of oxygen (Boldhaber and Kaplan, 1974), one of the most interesting sediment chemical properties is ìsulfideî. Free sulfide and combined sulfide of various sediment samples have been investigated. Sediment organic properties (total organic carbon and total organic nitrogen) were also evidently suggested to have some quantitative relationships among the sediment oxygen demand and reduced sulfur, thus, careful investigations have been performed.

It was our purpose to apply the OUS kinetic modelling and their parameters as a tool for describing the extent to which the sediment oxygen uptake related with the sediment quality. This study should be completed to gain a better understanding of how the sediment oxygen uptake plays a role in benthic decomposition. However, since it was only the elementary evolution, the scope of changes in seasonal variation could not be extended.

MATERIALS AND METHODS

Study sites

The principle site used for this study was a mud flat area in the inner part of Shido Bay, a eutrophication water area in the Seto Inland Sea, Japan (Fig. 1). Sampling stations were setted out at a site 34° 19′ N, 134° 10′ E, nearly 5 m from the oyster culture zone in the inner of Shido Bay, and at 34° 20′ N, 134° 10′ E around the center of the mount of Shido Bay. Shido Bay was shosen mainly because it was a closed bay. Exchange characteristics of sea water were poor and its sediment pollution was pointed out that almost of organic-rich sediments had settled. The sediments were mostly muddy and homogeneous and that found in the inner part were somewhat more polluted than those in the mouth of the bay. Some of sediment samples were comparaviely collected from Yashima Bay (34° 21′ N, 134° 7′ E), Nishihama Fishing Port (34° 20′ N, 134° 2′ E), and Kozai Port (34° 20′ N, 134° 0′ E), the areas where received several factory and domestic waste runoffs. Another comparative investigation for the sediments of Thailand was also carried out. Here sediment samples were collected from Chao Praya River (near the river mouth and estuary), from the tidal flat and mangrove area in Samut Prakarn Province, and from Song Khla Lake in the southern part of Thailand.

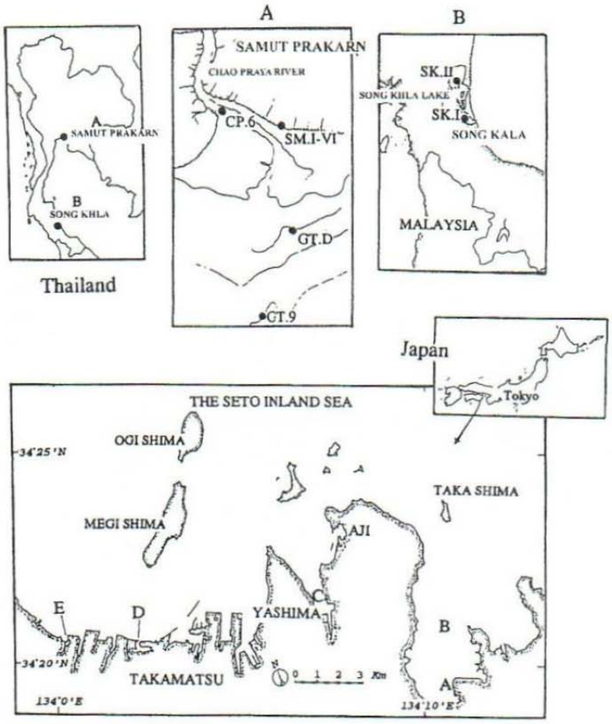


Fig. 1. Sampling location (Japan); A, Shido Bay (inner part) B, Shido Bay (outer part) C, Yashima Bay: D, Nishihama Fishing Port: E, Kozai Fishing Port. Sampling location (Thailand); CP.6, mouth of Chao Praya River: SM.I.-IV, mangrove area in Samut Prakarn Province GT.D & GT.9, Chao Praya Estuary: SK.I & SK.II, Song Khla Lake.

Collection of samples

Sediment samples were collected with a gravity core sampler equipped with a transparent plastic tube. Sedimentary cores about 17 cm long and 4.5 cm in inner diameter were taken in the tube (30 cm long) with minimum distortion of sediment surface (only cores with undisturbed stratification were used). The core sampler was slowly lower vertically until it touched the bottom and then allowed to sink strightly down by its own weight until the plastic tube had penetrated from about 14 to 17 cm into the mud. After the sampler was raised, a rubber stopper was placed over the bottom of the tube just when the tube reached the water surface. The mud holding tube was filled up carefully with the sea water from the sampling locality and then its top was closed by another rubber stopper. Great cares have been used to collect sediments. Every possible precaution was taken to obtain the representative sample. The sampled tube was then shrouded against light and placed at room temperature in the laboratory until OUS experiments started in the same day.

Experimental procedures

The study on chemical/biochemical oxygen uptake processes of suspended sediments has been carried out from May, 1989 to November, 1990. Three to five sedimental cores were collected for each sampling time. Bottom water above the sediment core was siphoned out, then the sediments was extruded toward the top of the core tube with a ramrod. Almost of the OUS runs were restricted to the upper 10 cm of the sediments. All experiments were conducted in a constant temperature incubator in which the temperature was maintained at 20 C. Sea water used for OUS tests was collected at 1 m of surface sea water. The water was equilibrated by stirring for 24 hr at 20 C after filtration (Millipore filter, HA 0.45 μm) and sterilization (120 C, 1 kg/cm^2 for 20 minutes). Fifty-six runs on OUS experiments were performed to study the nature of differences in locations, levels of depths, and chemical properties of bottom deposits on the oxygen uptake characteristics of suspended sediments. The runs on 16th February 1989 , 18th August 1989, 6th February 1990, and 8th August 1990 were performed in an attempt to verify the chemical oxygen consumption and biochemical (microorganism) oxygen consumption so that Mercuric Chloride and phenol were applied. The sediment samples of the runs of 6th September 1989 and 8th August 1990 were collected from Thailand, by using Ekman dredge and directly digging up with a spoon, respectively. They were kept in refrigerator for a few days before analysis.

Equipment and methodology

The OUS of given sediments were investigated by BOD meter (DKK, Model BOD-2). The principle of electrolytic BOD device is the maintenance of initial dissolved oxygen (DO) in the sample during oxygen demand progression by replacement from the gas phase. Oxygen equilibrium is maintained between the liquid and gas phase and oxygen activity in the gas phase is maintained by the electrolytic generation of oxygen. The oxygen demand of the liquid is then simply the amount of oxygen generated to maintain the initial gas phase composition. The obvious attraction of such an approach, in contrast to classical BOD determination by oxygen depletion in a fully aqueous system in the ease with which BOD progression can be followed. The bottles which contained the mixture of the well-aerated sterilized sea water and sediment samples were incubated at a constant temperature (air incubator, thermostatically controlled at 20 C) for at least 5 days. All of the light was excluded to prevent the formation of dissolved oxygen by algae in the sample. Reading values from recorder detected every 1 hr interval can be noted and calculated on the basis of dry weight (d) for chemical/biochemical oxygen uptake rate which expressed as mg O_2/hr g (d).

The core samples were divided into segments of 1 or 2 cm intervals. The sediments in each segment were mixed well. Some part of the sediment was dried at 110 C for 24 hrs to estimate percent of water content from the weight reduction. Dried sediments were then determined for total organic matter (mg O_2/g (d)) as loss on ignition at 450 C for 3 hrs. Levels of chemical oxygen demand and total sulfide of the sediments were by titrimetric methods. Dried sediment samples were also analysed for total organic carbon and total organic nitrogen (mg O_2/g (d)) by using a CN corder (Yanaco, Model MT-500) after removal of carbonate by treatment with 2N HCl.

RESULTS AND DISCUSSION

Calculation of the oxygen uptake rates of suspended sediments were performed on the basis of dry weight by reading the scale over 5 days (120 hrs) for every 1 hr interval after starting the experiments and expressed as mg O_2/g(d) hr. The OUS values (mg O_2/g(d)) were plotted against the incubation time (hr) and their characteristics were investigated thoroughly.

General characteristics of OUS

Figure 2 showed various accumulative OUS curves expressed by the sediments from bays and fishing ports, in the Seto Inland Sea, and from estuary and lake in Thailand. The overall view indicated the similar trend in which the cumulative OUS curves increased with a tendency to taper off with time. The results showed sharp initial increases of oxygen uptake, followed by relatively stable, lower oxygen uptake rates that lasted until the fifth day of incubation. Inflecting characters of cumulative OUS curve was apparently found in the data of Shido Bay and Yashima Bay and some data of Thailand. By visual observation on the expression of the rates of oxygen uptake during OUS progression, three distinct phases of oxygen uptake have been defined. Figure 3 depicted a diagram describing how different the characteristic of each phase is. Phase A was noticed to be a main, or a basic phase of oxygen uptake in which oxygen has been gradually consumed with a constant rate through out the fifth day of incubation. Phase B was noticed to consisted with high rates of oxygen uptakes that occurred only during the initial period of incubation. Thereafter, the rates immediately turned to be comparatively slower and then became constant during late period of incubation. Phase C clearly depicted a sigmoid characteristic of the oxygen uptake curves.

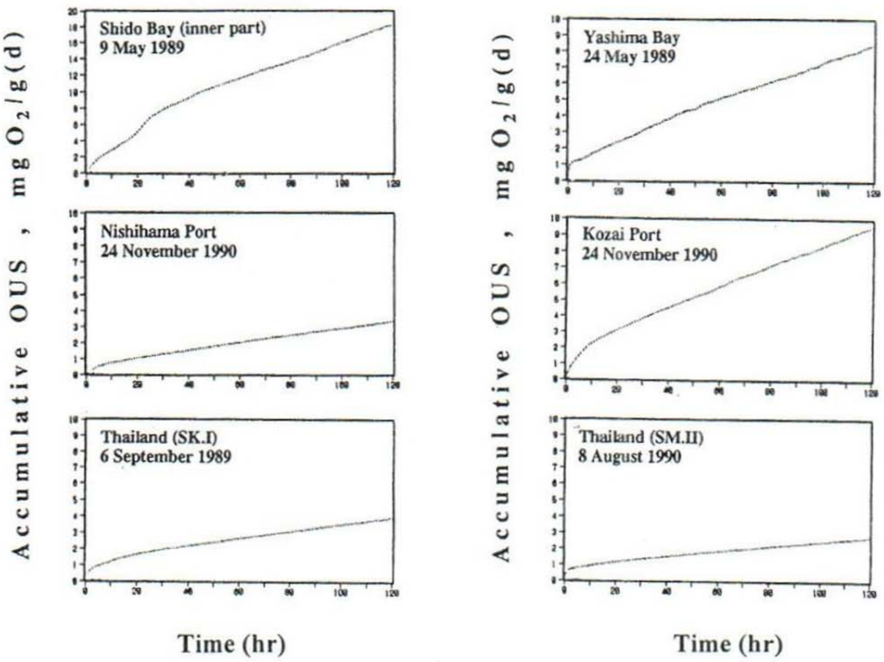


Fig. 2. General characteristics of various cumulative OUS curves expressed by the sediments from bays and fishing port in the Seto Inland Sea, Japan, and from estuary and lake in Thailand.

Non-biological oxygen uptake tests

In order to improve our understanding, the processes of oxygen uptakes should be separately defined into inorganic chemical oxidation (non-biological oxygen uptake) process and respiration (biochemical oxygen uptake) process of sediment-living organisms. For this purpose, Mercuric Chloride ($HgCl_2$) and phenol had been used as an attempt to eliminate all organism metabolisms in the OUS batch runs. The metabolisms in four sets of sediment samples (the samples of 16^{th} May 1989, 18^{th} August 1989, 6^{th} February 1990, and 8^{th} August 1990) were fixed by adding $HgCl_2$ and phenol in given concentrations (see Table 1). Afterthere, cumulative OUS curves were drawn against the incubation time. Results were depicted in dot lines, compared with those of the expectation in solid lines (Fig. 4). The effects of such treatments on the OUS characteristics were carefully considered. It was found that phase A, a basic rate of oxygen uptake, was decreased as the increase of treatment concentrations. This phase, therefore, should be the biochemical oxidation process performed by the activities of sediment-living organisms. Phase B could be the chemical oxidation process because it was not affected by the treatments of $HgCl_2$ or phenol at all. In addition, phase C was realized to be the biochemical oxygen uptake process due to the fact that the time onset of expected third-phase metabolism tended to delay as the increase of treatment concentrations. Moreover, the loss of apparent inflection character of the OUS curve was usually observed after the treatments.

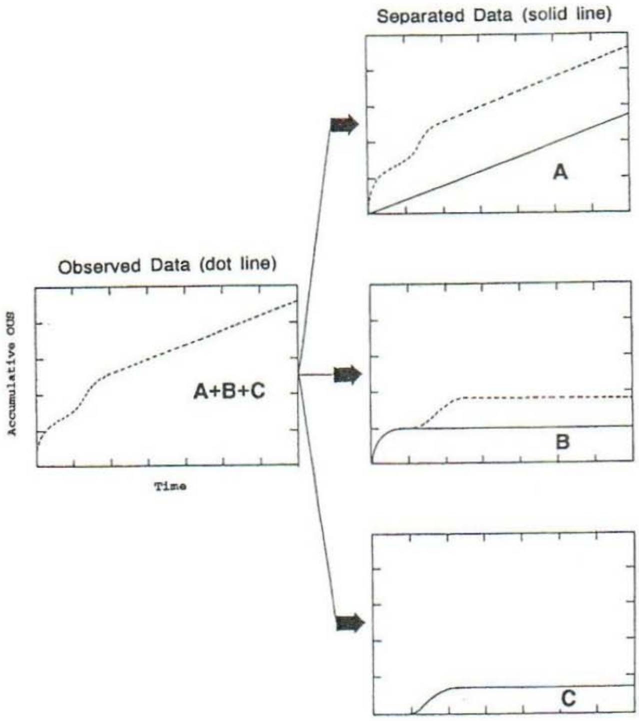


Fig. 3. The separation of three phases in the chemical/ biochemical oxygen uptake curves of suspended sediments.

Kinetic model expressions

Kinetics models of the three phases of oxygen uptake processes have been verified by the use of the metabolic inhibitors e.g. $HgCl_2$ and phenol. Results of these treatments have indicated remarkable influences on the phases A and C. However, no effect has been noticed for phase B (Fig. 4).

Although a conventional expression for the vitro sediment oxygen demand measurements is the weight of oxygen uptake per unit of time and surface area, i.e. g/day m^2, since this study was conducted with complex sediment mixing, the OUS experiment was thus expressed in oxygen uptake per unit mass of dry sediment (mg O_2/d). In an aspect of benthic oxygen consumption study, the respiratory activities of organisms concerned were considered not only to be composed of bacterial activities, but also the respiratory activities of some meiofauna and protozoa. The

Table 1. Non-biological oxygen uptake test; a comparison of various chemical/biochemical OUS approximated parameters with varying treatment concentrations and the sediment chemical properties.

Shido Bay (inner part)

Date	Depths & Treatments	BASE	Chemica oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	L_{c_∞}	delay time	L_{b_∞}	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
16.2.89	0-2 cm, no trt.	0.1102	0.380	1.11	1	4.87	0.320	0.082	3.90	0.062	27.18	3.56	7.64
	0-2 cm, 3.3% $HgCl_2$	0.0456	0.320	0.94	2	6.70	0.370	0.083	4.46	0.062	27.18	3.56	7.64
	0-2 cm, 6.7% $HgCl_2$	0.0080	0.370	1.00	1	4.82	0.320	0.076	4.21	0.062	27.18	3.56	7.64
18.8.89	0-3 cm, no trt.	0.0573	0.750	1.71	4	1.11	0.250	0.120	2.08	0.311	25.68	3.07	8.36
	0-3 cm, 1% phenol	0.0373	0.760	1.47	6	0.26	0.220	0.120	1.83	0.311	25.68	3.07	8.36
	0-3 cm, 5% phenol	0.0496	0.631	2.10	5	0.44	0.250	0.130	1.92	0.311	25.68	3.07	8.36
	7-10 cm, no trt.	0.0479	0.990	1.46	2	1.48	0.320	0.100	3.20	0.149	24.00	2.60	9.24
	7-10 cm, 1% phenol	0.0402	0.980	1.26	4	0.30	0.300	0.130	2.31	0.149	24.00	2.60	9.24
	7-10 cm, 5% phenol	0.0349	0.990	1.01	10	0.41	0.280	0.100	2.80	0.149	24.00	2.60	9.24
6.2.90	0-3 cm, no trt.	0.0792	-	-	8	2.18	0.219	0.072	3.04	0.183	26.63	3.06	8.72
	0-3 cm, 3% phenol	0.0366	-	-	26	0.66	0.228	0.090	2.55	0.183	26.63	3.06	8.72
	0-3 cm, 4% phenol	0.0258	-	-	49	0.06	0.210	0.097	2.16	0.183	26.63	3.06	8.72

Thailand (SM.V)

Date	Depths & Treatments	BASE	Chemica oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	L_{c_∞}	delay time	L_{b_∞}	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
8.8.90	0-5 cm, no trt.	0.0229	1.060	0.79	3	1.11	0.220	0.094	2.34	0.076	6.65	0.69	9.69
	0-5 cm, 3.3% $HgCl_2$	0.0084	1.070	0.72	5	0.09	0.500	0.210	2.38	0.076	6.65	0.69	9.69
	0-5 cm, 6.7% $HgCl_2$	0.0101	1.010	0.73	-	-	-	-	-	0.076	6.65	0.69	9.69

latter group were believed to play a major role on the oxygen uptake metabolisms of benthic deposits. On the whole, it caused us to realize that the basic metabolism of the suspended sediment that continued the constant rate of oxygen uptakes through out the OUS runs should be occurred by the latter group of organisms. In this phase, oxygen was consumed biochemical and constantly from the beginning period until the fifth day of the incubation.

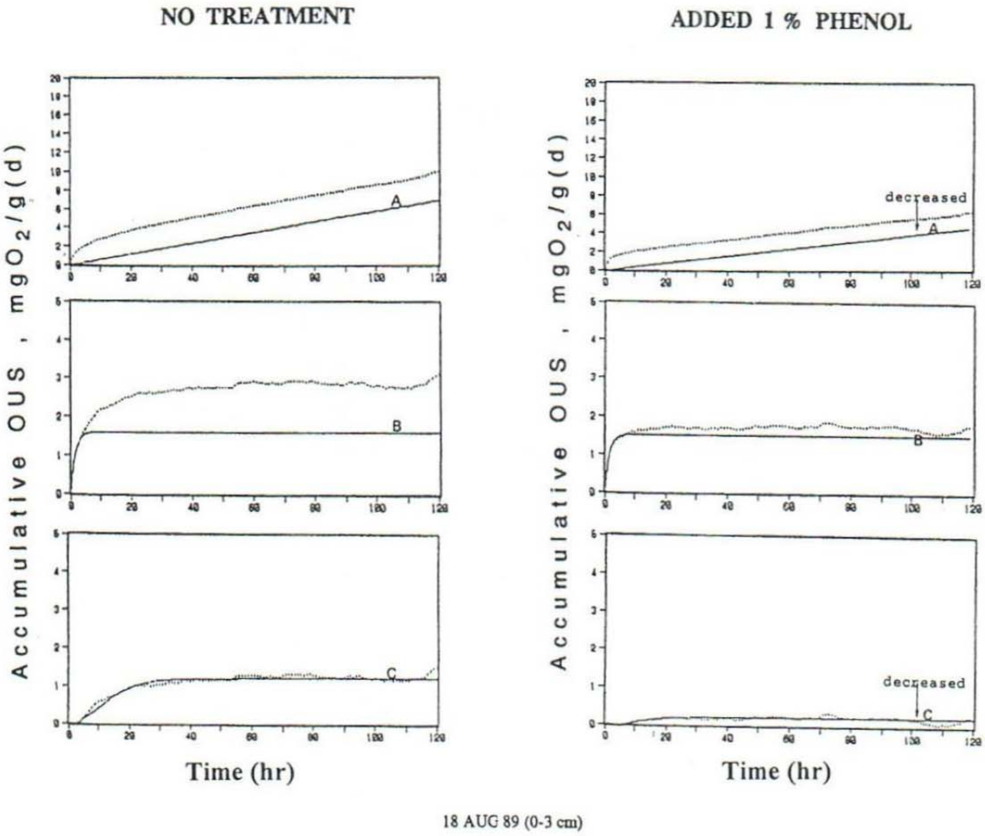


Fig. 4. Comparison of three phases in the chemical/biochemical oxygen uptake curves after treated with phenol (dot line: the observed OUS, solid line: the estimated OUS).

Mathematical expression for the basic oxygen uptake phase

Let "L" represent the cumulative OUS values, the rate of oxygen uptake can be written in the mathematical term as "dL/dt". The 120 values of dL/dt for each OUS curve were then computed in which appropriate values from the incubation period during the late 3 to 5 days were shosen and made an average. The value of oxygen uptake rate was set as the rate of basic metabolic phase, λ. By using λ value, oxygen uptake for the basic metabolic phase iL_m" was approximated as the equation,

$$L_m = \lambda t \tag{1}$$

In this aspect, Hayes (1964) had suggested that the steady state of oxygen uptake curve implied the measurement of supporting capacity of mud for microorganisms and related to various organic properties of sediments. However, there had no attempt to define the processes combined in those course of oxygen uptake and the chemical and bacterial demand were not separated in his study.

Model evolution for the chemical oxidation phase

In sediments, reduced compounds formed by reason of historical activities of anaerobic organisms will be oxidized spontaneously as aerobic conditions are provided. Under experimental condition, some easily oxidizable substances such as hydrogen sulfide in the mud-water suspension react quickly (Hayes, 1964). It was also said that the half life of hydrogen sulfide in the presence of oxygen was only about 1 hour. Thus, consideration on model expression could be made upon the fact that the chemical oxidation should apparently occur just in the initial period of OUS progression. The primary data on accumulative oxygen uptake (L) of several sediment samples that had been substracted with their basic oxygen uptake (L_m) were then considered.

During the initial period of OUS curve, increase in oxygen uptake along with the increase in incubation time was noted to have an initial steep slope with a tendency to taper off with time. Thus, changing rate of oxygen uptake in such a period has been suggested to be expressed by a convert exponential function. Let φ and ϕ be the deoxygenation rate coefficients, t be a time, and t_0 be the time onset of the chemical oxidation phase, then the kinetic expression for the chemical oxidation phase becomes

$$dL/dt = \varphi \exp\{-\phi (t-t_0)\} \quad (2)$$

From Eq. (2), the changes of cumulative chemical oxygen uptake depend on the coefficients, φ and ϕ. Integrating Eq. (2) with $L \rightarrow L_\infty$ at $t \rightarrow \infty$, we got

$$L = (\varphi/\phi)\{1-\exp[-\phi(t-t_0)]\} \quad (3)$$

The value of φ/ϕ represents the ultimate chemical oxygen uptake and will be termed as $L_{C\infty}$. Let L_C be the approximated chemical oxygen uptake, then

$$L_C = L_{C\infty}\{1-\exp[-\phi (t-t_0)]\} \quad (4)$$

This model was used to approximate the chemical oxygen uptake of given suspended sediment samples. The results agreed well with the observation data (Fig. 5b).

Most researchers depicted the oxidation kinetics of sediment oxygen demand in linear or semi-log plot with varying results (Hargrave and Connolly, 1978; Edberg and Hofsten, 1973; Martin and Bella, 1971). The important factor which play the role on the kinetics of sediment oxygen demand here was remarkably pointed out to be due to the oxidation reduction of ferrous iron. An interesting result of Wang (1981) was depicted by plotting oxygen uptakes against the log of time and fitting it by the first-order kinetic model composed of some inhibit effects of the oxidized product of ferrous iron (Fe^{2+}). It is important to emphasize that the measurement of Wang (1981) was conducted particularly in narrow period of the initial experimental run. Such a time was so short that it can give a more useful detail enough to explain the chemical oxidation kinetics that occurred in the second phase of OUS processes. Stumm and Lee (1961) had reported that the oxidation of Fe^{2+} in a water solution was a first-order reaction to the Fe^{2+} present. According to these supporting idea, even though such an oxidation have not been examined in this study, classifying of the chemical oxygen uptake in OUS progression to be best-fitted by the first-order kinetic model should be reasonably accepted.

Model evolution for bacterial respiration phase

The third-phase metabolism of OUS progression has been classified to characterize by the activities of microorganisms and stated as the ìbacterial respiration phase". In addition to bacterial, larger organisms e.g. meiofauna and diatom flora present also consume oxygen, although their contribution is generally less than that of bacteria (Pamatmat and Banse, 1969). Several species of protozoa also play a role in sediment oxygen demand. However, since the OUS progression in this study was performed only for 120-hours periods, the time was comparatively short so that only the endogeneous activity of meiofauna could affect on the process of oxygen uptake. For bacteria, the incubation time was long enough that bacterial cell propagation can apparently occur.

ESTIMAT ION OF THREE PHASES

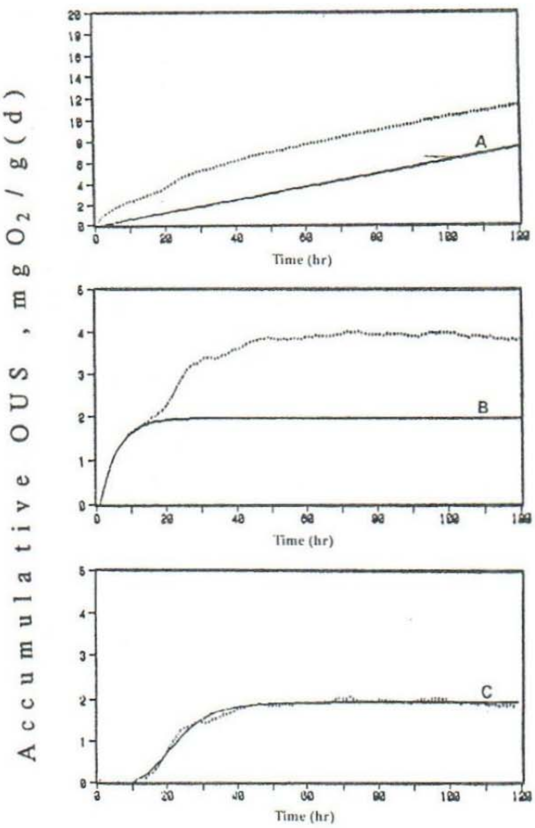


Fig. 5. The use of model expressions for three phases in the chemical/biochemical oxygen uptake curves; (A), the basic oxygen uptake phase: (B), the chemical oxidation phase: (C), the bacterial respiration phase (dot line: the observed OUS, solid line: the approximated OUS).

In nature, sediment bacteria seldom occur as single species. Usually, there are many different metabolic types present, both aerobes and anaerobes, and each group occupied a special ecological nitche which depends on substrate avialability and restrictions of the physical environment. When OUS runs started, the species that were best able to adapt to the new condition were then favoured and became dominant (Mechalas, 1974). This activity has lead to the uptake of oxygen from their solution circumstance. The remarkable inflection character of the cumulative OUS curve for this phase should, therefore, be the distinction of bacterial cell propagation. In addition, Parisod and Schroeder (1978) showed a net increase of microorganism population through measurement of weight increase. They reported similarly to our experiment that cell propagation occurred during a relative long period of measurement, in the range of 7-20 hours.

It was noted that the simple characteristic of bacterial growth curve in special circumstance behaved as sigmoid curve characteristic. Let "N" represent bacterial cell number and "t" be the incubation time (hr), the plot of the number against the incubation time depicted sigmoid characteristic of cumulative curve. In addition, bacteria, which has been noted to be the important decomposer in the ecological system, took organic substances as the energy sources for growth. Dissolved oxygen necessary utilized in this process was considered to be composed of two parts; (1) the oxygen utilized during cell propagation activity (in the course of rapid increasing of bacterial cell number, and (2) the oxygen utilized in the endogeneous respiration activity for the living of bacterial cells. With this in mind, the rate of oxygen uptake during cell propagation period should be proportional to the increasing rate of cell number, dN/dt, and the rate of oxygen uptake during the endogeneous respiration phase should be proportional to the number of cell, N, which maintained in the later period. When considered the overall view of the oxygen uptake process, the uptake rate "F" can be expressed by the following equation.

$$F = c_1 (dN/dt) + c_2 N \quad (c_1, c_2 > 0) \tag{5}$$

Generally, bacterial cell can propagate exponentially in the nutrient enriched media and the propagation rate of cell can be expressed by

$$dN/dt = \kappa N \tag{6}$$

Where κ is the propagation rate coefficient. Since the fact that energy source necessary for the microorganism growth in a cultures (e.g. in the OUS runs which were conducted in a closed system) was limited, the parameter κ was thus considered to decrease gradually as the time past. In our model expression, the propagation rate coefficient should be stated out by the term ì$\kappa \exp\{-\xi (t-t_0)\}$î in which κ was decreased exponentially upon the coefficient ξ. Equation (6) was then derived to be

$$(1/N)(dN/dt) = \kappa \exp\{-\xi (t-t_0)\} \tag{7}$$

or

$$\int d \ln N = \int \kappa \exp\{-\xi (t-t_0)\} dt \tag{8}$$

Let N be N_0 at the starting time, t_0, thus

$$\ln N = \ln N_0 + \kappa/\xi + \kappa/\xi \exp\{-\xi (t-t_0)\} \tag{9}$$

If the theoretical saturated value of cell number, N_s, was reached in the time $t-t_0 \rightarrow \infty$,

$$\ln N_s = \ln N_0 + \kappa/\xi \tag{10}$$

Substituing Eq. (8) and solving for N, we got

$$N = N_s \exp\{(-\kappa/\xi) \exp[-\xi (t-t_0)]\} \tag{11}$$

Attention to the dN/dt of Eq. (6), because it was expressed as differential pattern that characterized differently from the observed OUS curves, Eq. (6) was then integrated to be,

$$\int F\,dt = c_1 N \tag{12}$$

The integral term of the endogeneous respiration has been neglected because of the fact that it affected very little when compared with that of the cell propagation. Substituing N by Eq. (11), it became

$$\int F\,dt = c_1 N_s \exp\{(-\kappa/\xi) \exp[-\xi (t-t_0)]\} \tag{13}$$

The term ì$\int$ F dtî was stated earlier as the cumulative oxygen uptake, L. Then let $L_{b\infty}$ be the ultimate value of the bacterial respiration phase, the approximation of the bacterial oxygen uptake, L_b, will be

$$L_b = L_{b\infty} \exp\{-\kappa \exp[-\xi (t-t_0)]\} \tag{14}$$

Base on this relationship, the bacterial respiration phase in OUS progression was approximated and depicted in solid line comparing with its observed value drawn in dot line (Fig. 5c).

All of the approximated parameters were summarized in Table 2. The levels of total sulfide, total organic carbon, total organic nitrogen, and C/N ratio of the given samples were shown comparatively in the same table. Relationships between approximated parameters and various sediment properties will be discussed.

Table 2. The summerization of approximated OUS parameters for the three phases based upon Eq. (1), (4), and (14), respectively, comparing with their total organic carbon, total organic nitrogen, and total sulfide contents.

Shido Bay (inner part)

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ/ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
9.5.89	0-1 cm	0.0666	0.290	1.52	7	2.21	0.180	0.072	2.50	0.185	27.46	3.09	8.90
	1-2 cm	0.0905	0.240	2.08	3	4.29	0.450	0.120	3.75	0.543	27.21	3.07	8.87
	3-4 cm	0.1112	0.180	2.11	9	2.86	0.540	0.138	3.91	0.875	28.05	3.05	9.19
	4-5 cm	0.1116	0.110	2.00	15	1.25	0.580	0.185	3.14	0.509	25.27	2.71	9.32
	5-6 cm	0.0626	0.103	2.31	14	1.55	0.650	0.180	3.61	0.512	26.11	2.83	9.21
29.6.89	0-1 cm	0.0821	0.600	2.25	1	3.83	0.170	0.070	2.43	0.334	26.53	3.50	7.59
	0-1 cm	0.0983	0.550	2.18	1	2.18	0.144	0.072	2.00	0.334	26.53	3.50	7.59
	3-4 cm	0.0623	0.270	2.26	8	1.79	0.360	0.110	3.27	0.488	24.76	3.11	7.96
	3-4 cm	0.0544	0.280	2.46	6	-	0.400	0.115	3.48	0.488	24.76	3.11	7.96
31.7.89	0-1 cm	0.0701	0.700	1.13	3	1.90	0.210	0.070	3.00	0.034	26.62	3.00	8.55
	1-2 cm	0.0565	0.750	1.20	3	1.43	0.267	0.086	3.10	0.057	25.24	2.87	8.80
	2-3 cm	0.0715	0.280	1.30	11	1.98	0.350	0.115	3.04	0.148	25.59	2.84	9.02
	3-4 cm	0.0933	0.384	1.79	7	1.54	0.540	0.150	3.60	0.214	26.15	2.81	9.29
	5-6 cm	0.0516	0.240	1.42	14	1.64	0.550	0.150	3.67	-	23.84	2.51	9.49

Shido Bay (outer part)

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ/ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
24.5.90	0-2 cm	0.0297	1.950	0.65	1	1.49	0.270	0.063	4.29	0.033	8.39	1.06	7.89
	2-4 cm	0.0312	1.130	0.20	64	0.35	0.380	0.125	3.04	0.033	9.18	1.14	8.02
5.7.90	0-2 cm	0.0321	1.850	1.19	5	0.51	0.240	0.060	4.00	0.049	7.51	1.02	7.34
	2-4 cm	0.0272	2.200	1.36	4	0.36	0.300	0.100	3.00	0.050	7.44	1.00	7.44
24.8.90	0-2 cm	0.0519	1.450	1.01	5	0.56	0.200	0.060	3.33	0.036	8.67	1.17	7.41
	2-4 cm	0.0335	1.360	1.04	5	0.51	0.210	0.079	2.66	0.055	8.20	1.14	7.21

Table 2. (continued)

Yashima Bay

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
24.5.90	0-2 cm	0.0551	1.530	0.99	4	0.75	0.310	0.087	3.56	0.062	16.45	1.90	8.68
	2-4 cm	0.0449	1.200	1.04	2	0.78	0.410	0.120	3.42	0.150	15.93	1.88	8.48
5.7.90	0-2 cm	0.0466	1.860	1.52	5	0.41	0.190	0.085	2.24	0.127	15.42	1.84	8.38
	2-4 cm	0.0382	1.880	1.53	3	1.06	0.300	0.090	3.33	0.127	14.33	1.68	8.53
24.8.90	0-2 cm.	0.0374	1.010	1.38	5	0.62	0.210	0.078	2.69	0.210	13.75	1.54	8.91
	2-4 cm	0.0488	0.830	1.63	6	0.22	0.490	0.150	3.27	0.318	12.72	1.56	8.15

Nihama Port

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
24.11.90	0-2 cm	0.0255	0.410	0.11	30	0.11	0.200	0.105	1.90	0.101	5.01	0.67	7.44
	5-6 cm	0.0208	0.220	0.59	15	0.21	0.250	0.064	3.91	0.305	5.21	0.72	7.23

Kozai Port

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
24.11.90	0-2 cm	0.0748	0.400	0.18	34	0.37	0.220	0.080	2.75	0.179	14.09	1.64	8.58
	5-6 cm	0.0611	0.210	1.86	16	0.41	0.200	0.068	2.94	0.822	14.28	1.68	8.48

Thailand

Date	Depths	BASE	Chemical oxygen-uptake		Biochemical oxygen uptake				κ / ξ	Sediment chemical properties			
		λ	ϕ	$L_{c\infty}$	delay time	$L_{b\infty}$	κ	ξ		Total sulfide	Total organic carbon	Total organic nitrogen	C/N ratio
6.9.89	SK.I. 0-5 cm	0.0210	0.620	0.84	5	0.53	0.400	0.140	2.86	0.033	18.80	1.35	13.83
	SK.II. 0-5 cm	0.0201	1.630	0.44	8	0.13	0.160	0.110	1.45	0.000	10.04	0.70	14.32
	GT. D. 0-5 cm	0.0084	1.850	0.22	-	-	-	-	-	0.000	0.75	0.11	7.20
	GT. 9. 0-5 cm	0.0397	0.750	1.17	4	0.55	0.230	0.090	2.55	0.000	12.74	1.55	8.22
	CP. 6. 0-5 cm	0.0348	0.550	1.45	10	1.55	0.420	0.096	4.38	0.195	7.91	0.71	11.29
18.8.90	SM.I. 0-5 cm	0.0117	1.310	0.73	4	0.53	0.400	0.110	3.64	0.031	4.04	0.37	10.79
	SM.II. 0-5 cm	0.0150	1.110	0.70	4	0.23	0.220	0.100	2.20	0.021	4.29	0.37	11.76
	SM.III. 0-5 cm	0.0148	0.920	0.65	4	0.39	0.460	0.120	3.83	0.019	2.79	0.31	9.00
	SM.IV. 0-5 cm	0.0201	0.820	1.09	6	0.60	0.500	0.133	3.76	0.138	7.89	0.86	9.21
	SM.V. 0-5 cm	0.0229	1.060	0.79	3	1.11	0.220	0.094	2.34	0.076	6.65	0.69	9.69
	SM.VI. 0-5 cm	0.0288	0.650	1.69	5	2.81	0.390	0.103	3.79	0.467	16.55	1.50	11.01

Effects of sediment depths on the expression of cumulative OUS

Comparison of cumulative OUS curves of the upper-layer and the lower-layer sediments was depicted in Fig. 6. Remarkable differences of curve characteristics were not observed except for some alternation of the inflection period and the patern of bacterial respiration phase. For the upper-layer sediments, the inflection period of curves were very narrow and less apparent than those of the lower-layer sediments. When sediments were introduced to suspension condition in which the aerobic circumstance was provided, most of living aerobic bacteria present in the surface layer of sediments should be activated suddently. Therefore, the uptake of dissolved oxygen was increased consequently, by both the quantity and the quality of the bacteria present. Contrastingly, since aerobic bacteria were scarcely found in the deeper layer of sediments, the time that must be taken for acclimatization was comparatively longer. Thus, the occurrence of bacteria respiration phase should be slower than that of the upper-layer sediments.

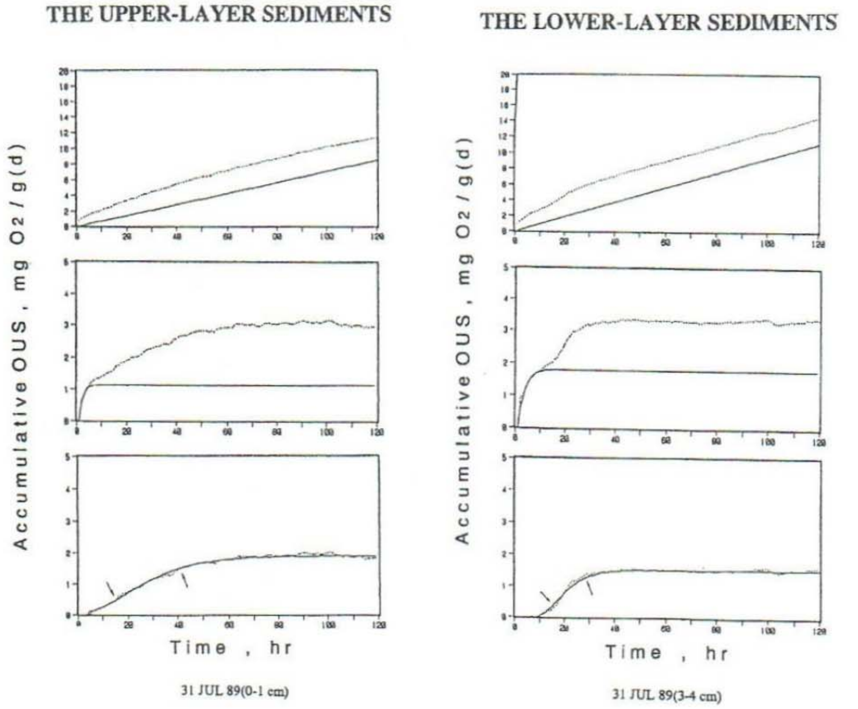


Fig. 6. Comparison of the approximated accumulative OUS curves (solid lines expressed by the upper-layer sediments and those by the lower-layer sediments.

Relations of model parameters (basic oxygen uptake phase) and sediment properties

Effects of sediment organic properties on λ

The plot between rate of oxygen uptake in the steady state basic metabolism (λ) and the sediment organic properties was depicted in Fig. 7. The approximated rate of oxygen uptake in this phase for all sediment samples ranged from 0.01 to 0.12 mg O_2/g (d) hr and total organic carbon (TOC) and total organic nitrogen (TON) ranged from 0 to 28 mg/g (d) and 0.0 to 3.8 mg/g (d), respectively. From the results, oxygen uptake rates were significantly relative to both TOC and TON with similar trend. A smaller in quantity of TOC and TON provided a smaller in value of oxygen uptake rate. Almost of the sediment samples from Thailand showed comparative low values of TOC and TON, so as to contribute some detail indicating the roles of the organic properties on the rates of oxygen uptake. Contrastingly, sediment samples from the inner part of Shido Bay that gave the highest values of TOC and TON provided highest rates of their oxygen uptakes. Such occurrences could be explained because of the fact that living organisms in sediments generally used organic carbon as the energy source and use particular organic nitrogen during cell division process. Simultaneously, their activities either during cell propagation or endogeneous respiration proportionally related to the uptake of dissolved oxygen in the solution.

However, the interrelation may not last so long because tolerance of living organisms in the organic-excess media was limited.

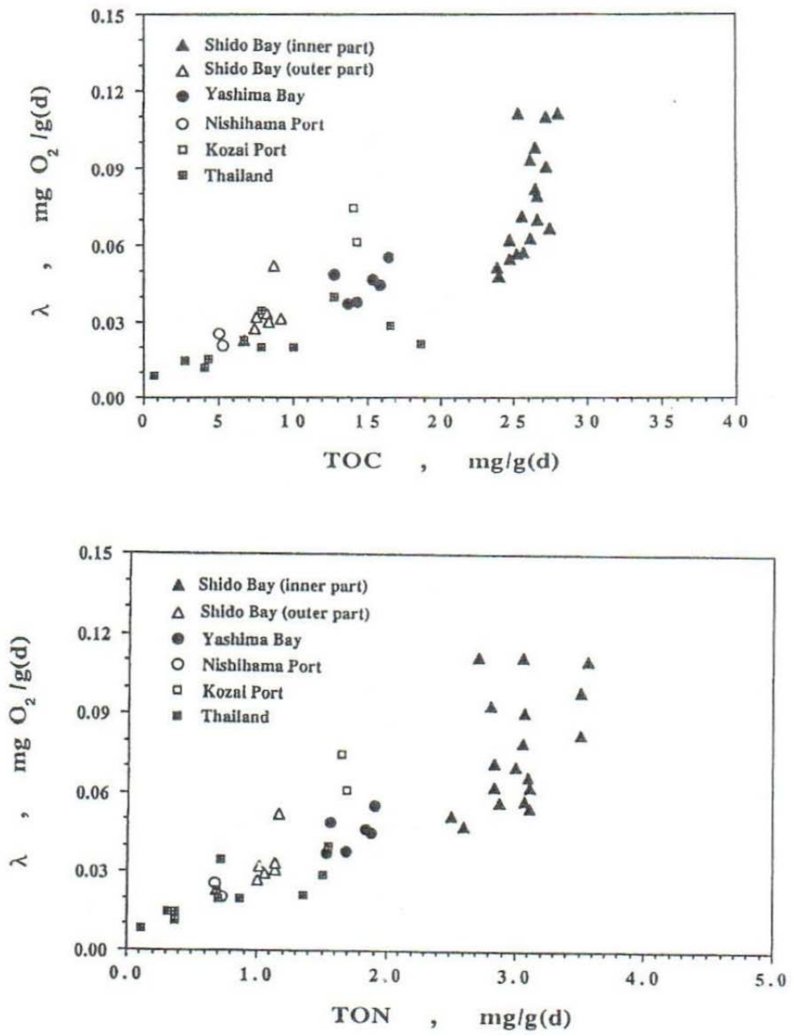


Fig. 7. The relation of the oxygen uptake rate in basic oxygen uptake phase, λ, and the sediment organic properties (total organic carbon and total organic nitrogen).

Vertical profile analysis

Figure 8 showed the vertical profile of the basic oxygen uptake rate, λ, comparing with those of TOC, TON, and C/N ratio. The λ tended to slightly decrease as the increase of the sediment depths. Vertical profiles of TOC and TON also depicted similar trend. The C/N ratio, oppositedly, gradually increased as the increase of depth since the decreasing rate of organic nitrogen was faster than that of organic carbon. The decrease λ as depth could be due to the decrease in number of aerobic organisms.

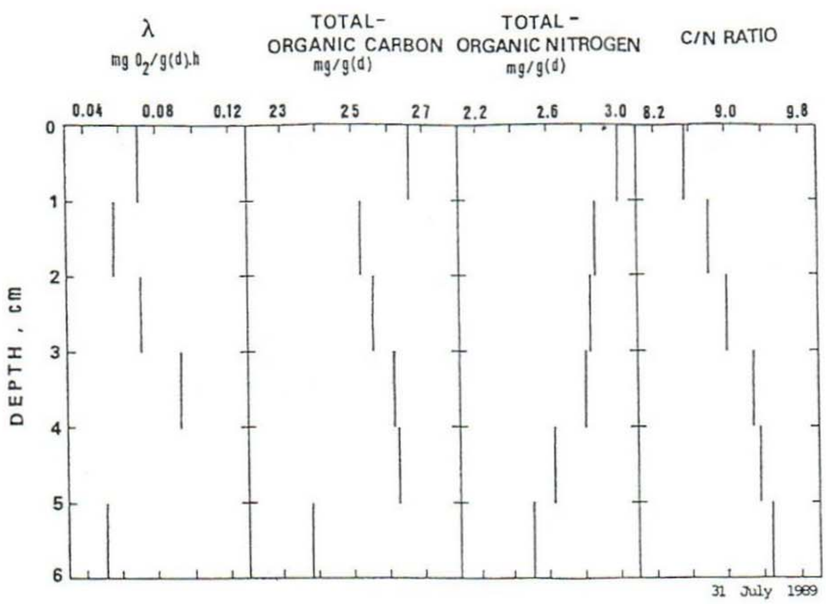


Fig. 8. Vertical profiles of the basic oxygen uptake rates comparing with those of total organic carbon , total organic nitrogen, and the C/N ratio for the given sediments.

Relation of model parameters (chemical oxygen uptake phase) and sediment properties

Effects of total sulfide on $L_{c\infty}$

Hydrogen sulfide has been expected to play an important role on fast reaction with molecular oxygen in the sediment-water solution. The ultimate chemical oxygen uptake calculated upon Eq. (4), $L_{c\infty}$, ranged from 0.1 to 2.5 mg O_2/g (d), whereas sediment total sulfide, TS, ranged from 0.0 to 0.9 mg/g (d). The maximum TS value was found in sediments from the inner part of Shido Bay but the minimum value was from Thai sediments. Considering on Fig. 9, when $L_{c\infty}$ were plotted agains TS, the increase in $L_{c\infty}$ values were found to response the increase of TS exponentially. These results supported well the hypothesis of which the present of hydrogen sulfide in sediments should significantly effect on the expression of chemical oxygen uptake.

Vertical profile analysis

Figure 10 showed the vertical profiles of water content (WC) and total sulfide (TS), comparing with the profiles of the chemical reaction rate constant (ϕ) and the ultimate chemical oxygen uptake ($L_{c\infty}$). The ϕ decreased remarkedly as the increase of sediment depths and the loss in sediment interstitial water (i.e. the decrease in WC). Such decreases was supposed to be influenced by the physical processes of diffusion and consolidation of the deposits. Contrastingly, the vertical profile of the $L_{c\infty}$ showed remarkedly increased as the depth increase. Since the profile of TS in sediment also depicted a similar trend, the $L_{c\infty}$ has clearly revealed to be influenced by the levels of sulfide in sediments.

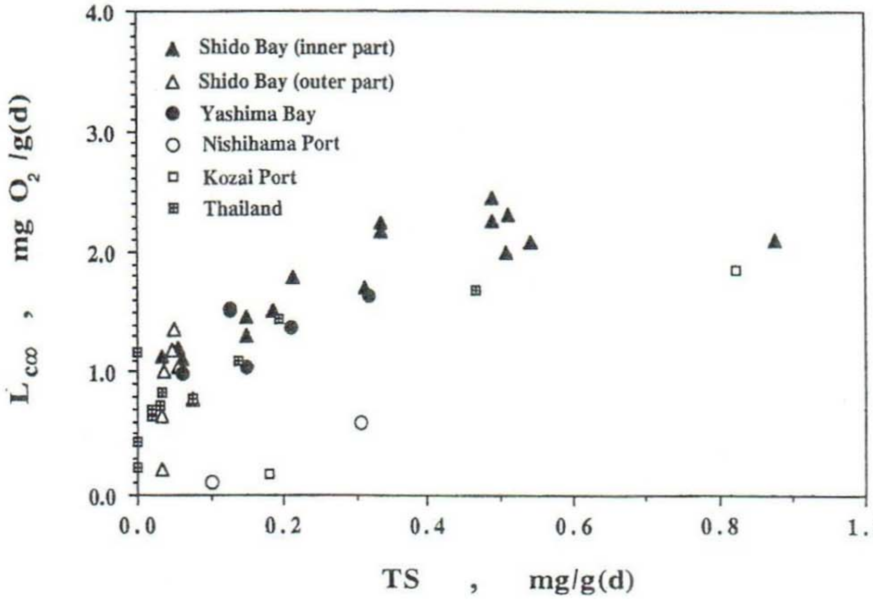


Fig. 9. The relation of the ultimate chemical oxygen uptake, $L_{c\infty}$, and the sediment total sulfides.

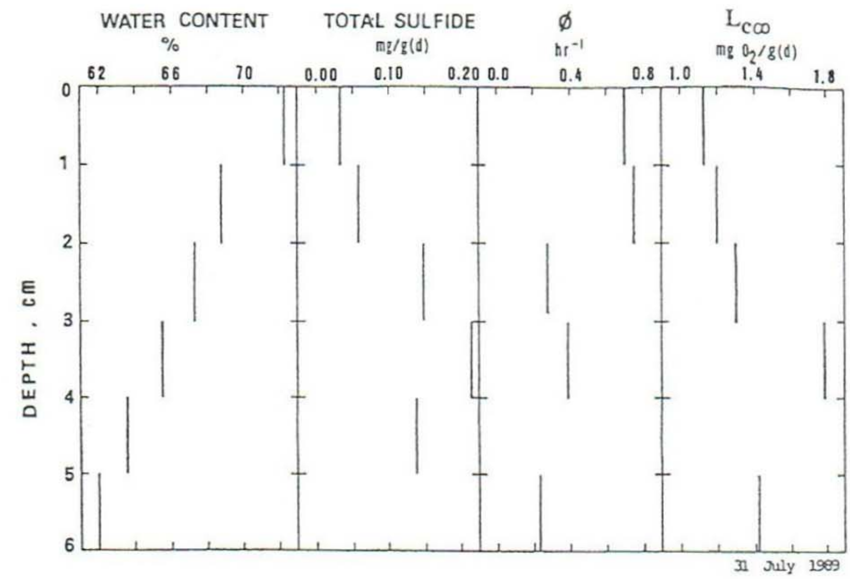
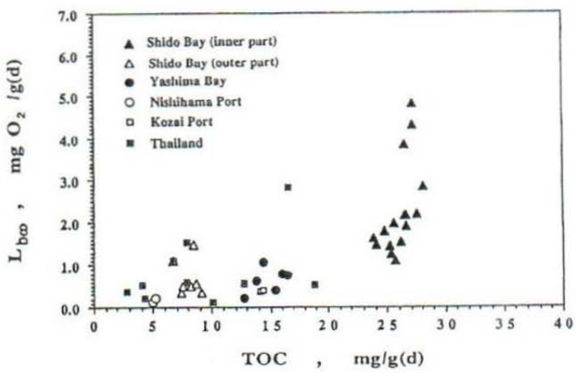


Fig. 10. Vertical profiles of the chemical reaction rate constant, ϕ, and the ultimate chemical oxygen uptake, $L_{c\infty}$ comparing with those of water content and total sulfide for the given sediment.

Relation of model parameters (bacterial oxygen uptake phase) and sediment properties

Effects of sediment organic properties on $L_{b\infty}$

Since bacteria decompose organic matter in sediments as an energy source for living and growth, relation of the ultimate oxygen uptake, $L_{b\infty}$, in the bacterial respiration phase and the sediment organic properties has been expected. The $L_{b\infty}$ calculated upon Eq. (14) ranged from 0.1 to 4.8 mg O_2/g (d). High values were obtained from the Shido Bay (inner part) sediments whereas slightly low values were obtained from almost of sediments from Thailand. By plotting $L_{b\infty}$ against TOC and TON, apparent relationships were obtained (Fig. 11). The results indicated the increase of $L_{b\infty}$ as the increases of TOC and TON of the sediments. Because the $L_{b\infty}$ value was depended on organic properties of the bottom sediments, such a value could be utilized as an indicator of organic strenght for particular benthic environments further.



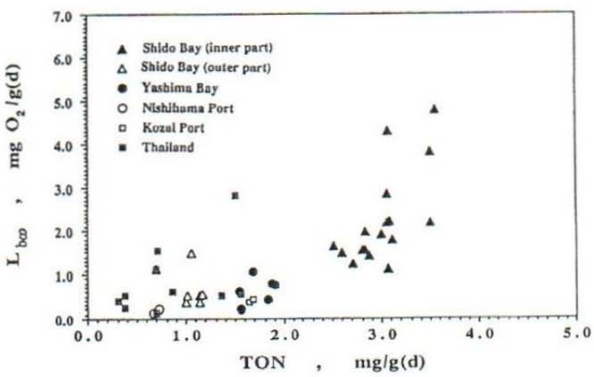


Fig. 11. The relation of the ultimate bacterial oxygen uptake, $L_{c\infty}$, and the sediment organic properties (total organic carbon and total organic nitrogen).

Effects of sediment organic properties on κ

The reaction rate constant, κ, in the bacterial respiration phase had been supposed to relate to the levels of TOC of the given sediments. However, no significant relation to the investigated organic carbon can be observed. Such occurence could be explained because when aerobic condition provides, bacteria in sediment-water suspension may activate and gradually consume oxygen for growth and for cell propagation. During their processes, only special (species specific) labile organic carbon could be appropriatelyde decomposed. Some parts of organic carbon may not be involved and thus still remained in the test bottle. These refractory fraction, unfortunately, were not defined in this study.

Effects of sediment organic properties on ξ

It is known that bacteria in sediment use organic carbon as an energy source for growth and, in the same time, organic nitrogen is necessary for the reproduction of bacterial cell material. Let C and N represent the quantities of total organic carbon and organic nitrogen really found in the given sediment samples, respectively, and let αC and αN represent the proportions of TOC and TON that really be used for the activity of dominant bacteria. Assumming that C be a constant and the value of N gradually decreases, the inhibition coefficient (ξ) should be increased consequently as the increase in C/N ratios of the sediments. Thus, the relation of ξ and the sediment organic properties can be expressed as $\xi = \gamma\,(\alpha C/\alpha N)\,(C/N)$, where γ is the correlation coefficient. All of the coefficients were gathered to be γ', then the equation above was derived to be $\xi = \gamma'\,(C/N)$. The log-log plot of ξ in the bacterial respiration phase against the C/N ratios of sediments was depicted in Fig. 12. According to Fig. 12, the inhibition coefficient ξ turned to increase linearly as the increase of the C/N ratios.

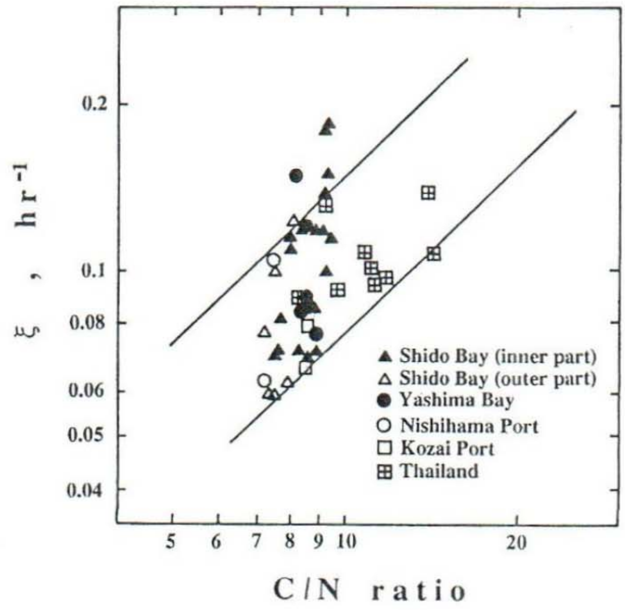


Fig. 12. The log-log plot of the inhibition coefficient in the bacterial respiration phase, ξ, against the C/N ratio.

Vertical profile analysis

Vertical profiles of the ultimate bacterial oxygen uptake ($L_{b\alpha}$), the biochemical reaction rate constant (κ), the inhibition coefficient (ξ) and the profile of $\xi/(C/N)$ were depicted in Fig. 13. The $L_{b\alpha}$ slightly decreased as the increase of sediment depths. Such trend has been extrapolated because of the decrease in levels of organic materials and also the changes in quality and quantity of sediment bacteria that acclimatized to the new condition. However, the vertical profiles of κ and ξ showed remarkedly increases as the increase of depths. Both κ and ξ appeared to play important roles on controlling the OUS curve characteristic during the bacterial respiration phase. The value of κ reflected the expression of oxygen uptake rate during the initial period of bacterial uptake, whereas, the value of ξ reflected the depletion of oxygen uptake rate during late bacterial respiration process. Such occurrences can be seen in Fig. 6, in which the OUS expressions for the upper-layer and the lower-layer samples were compared. Similarly to the vertical profiles of κ and ξ, the profile of ξ/(C/N) also gradually increased as the increase of sediment depths.

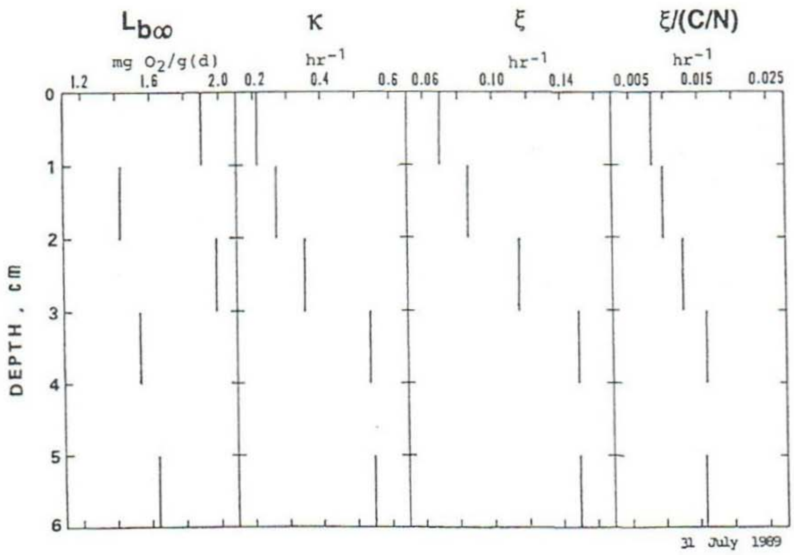


Fig. 13. Vertical profiles, of the ultimate bacterial oxygen uptake, $L_{c\infty}$, the biochemical raction rate constant, κ, the inhibition coefficient, ξ, and the ξ/(C/N) ratio for the given sediments

GENERAL CONSIDERATIONS

Suspension of bottom sediments in streams, lakes, estuaries, or coastal areas have effects on the qualities of the overlying water. The principal effect is to exert oxygen demand on the water. The progression of aerobic decomposition and hence of stabilization of organic matter in sediment can be reflected by a gradual withdrawal of oxygen or a gradual satisfaction of OUS.

From the overall views, it is possible to apply the knowledge of OUS kinetic models and their parameters obtained as a tool for describing the extent to which the sediment oxygen uptake correlated with the sediment quality. In this study, moreover, the importance of clarification of the oxygen uptake processes into three phases (the basic biochemical oxygen uptake, the chemical oxygen uptake, and the bacterial oxygen uptake) has been emphasized. Without such a clarification procedure, interpretation of sediment oxygen demand may provide somewhat misunderstanding of benthic environmental conditions.

We beleive that these results represent a significant advance in understanding of the pattern of sediment oxygen uptake processes at least under laboratory conditions. The approximated parameters could illustrate both the rapidity of chemical changes in the sourrounding waters and also the necessity of careful monitoring of aquatic environments. To develop the models, further study should deserve more depth evaluations on typical expression of infauna oxygen uptake and roles of labile and refractory components of sedimentary orgnic material on the OUS expression.

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