港湾技術研究所報告 (REPORT OF P.H.R.I.)

目 次 (CONTENTS)

1. Oxygen Uptake by Resuspended Sediments

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Synopsis

An experimental study has been performed to examine the characteristics of oxygen uptake by resuspended silty sediment. Experiments were conducted on the sea bottom materials taken from the Tokyo Bay, the Osaka Bay, and the Hiroshima Bay. Those bays are famous for their entrophic condition. The effects of the resuspended sediments on the dissolved oxygen were investigated to various conditions of water temperature, concentration of the suspended sediments and the organic content in the sediments. After the basic tests of its property, a manometric type respirometer device was selected for this purpose.

The results demonstrate that the oxygen demand of the resuspended sediments is different from that of the quiescent sediment. The first stage uptake process by the resuspended sediments is formulated as a first order kinetics approximation. Through experimental studies, it is clarified that the oxygen uptake rate parameter changes remarkably with the changes of temperature, while the uptake potential parameter changes with the organic concentration of the sediments. The oxygen demand during resuspension is proportional to the mass of the suspended sediments.

Disturbances to the quiescent organic bottom sediments can make the oxygen uptake increase in rate.

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1. 再浮遊した海水の酸素消費実験

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要　旨

　波，流れ，浚渫等により，底泥が攪乱されて再浮遊すると，水質に対し影響があると言われている。そこで，東京湾，大阪湾，広島湾の底泥等を用いて，再浮遊時の酸素消費特性を室内実験により調べた。

　磁石式の攪拌子により絶えず攪拌し浮遊状態を維持しながら，浮遊けん濁液中での酸素消費量を水封したマノメーター内の減圧量として読みとった。水マノメータ式のこのレスピロメーターは，ワールブルグ検圧計と同様な原理で作動する。この装置を用いて，けん濁液の水温，けん濁濃度，底泥の泥質などの影響を検討した。

　その結果，次のことが明らかになった。

1) 浮遊けん濁時の酸素消費量は，一次反応式でほぼ近似でき，この式は再浮遊後数十時間の間成立する。一次反応式においては，酸素要求ポテンシャル（消費可能量）と反応速度との両者をパラメータとして消費特性が表示される。

2) 浮遊けん濁時の酸素消費量は，けん濁底泥量に比例して増加する。単位底泥量あたりの酸素消費ポテンシャルは，底泥の含有有機物濃度により左右され，底泥の COD の1～2割程度である。

3) 反応速度は，酸化分解のしやすさの程度を表わし，5～30°C の範囲では水温により指数関数的に大きく変化する。

　底泥の舞い上がりは，その直後に著しく大きな酸素消費を招く恐れがある。東京湾底泥の値などを用いて試算したところ，底泥の影響水深を底泥上1mまでとすると，不攪乱底泥の酸素消費量に見合う消費は，300mg/l 程度のけん濁濃度時に起きることが予想された。

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CONTENTS

1. Introduction

Recently, the water quality of inner bays in Japan has been polluted by organics and nutrient contaminations. In the bays under eutrophic condition, organics produced in a photic layer are likely to settle down to the bottom. Particulate organics loaded through rivers are also easy to coagulate at the mouth and settle down to the bottom. Such organics as accumulated on the bottom are gradually decomposed into inorganic components and consume the dissolved oxygen in the overlying water through degradation processes. Organic sediments release the nutrients such as nitrogen and phosphate into overlying water. Release rate grows higher as the overlying water becomes anaerobic. Nutrient release from sediments accelerates the biological reuse and organic production to make the water quality worse. Thus the organic bottom sediments may exert measurable influence upon the overlying water quality.

Among these interactions between sediments and water, oxygen consumption by the sediments is one of the most important problems. The dissolved oxygen is often used as an important index of water quality. When the oxygen supply to the bottom water is obstructed by a thermocline in summer, bottom water might lose most of the dissolved oxygen through the activities of oxygen consumption by sediments. The biologic systems present in waters are quite sensitive to dissolved oxygen concentrations. It is said that condition becomes anaerobic at the concentration less than $1mg/l$. Anaerobic or oxygen deficit waters destroy the biological activity in the bottom layer.

The strong turbulences due to the waves, currents and intensive dredgings can sometimes make the bottom sediment released and resuspended into the overling water. Resuspension of the organic silty sediments may have a greater influence upon the oxygen consumption than undisturbed quiescent sediments.

But no accurate and reliable predictive methods which can quantify the oxygen consumption process during the resuspension have been developed. The paucity of reports on the oxygen uptake by the resuspended sediments prompted us to investigate it.

The purpose of this investigation is to examine the oxygen uptake equation and to estimate its parameters.

2. Previous Background of Survey

2.1 Theory of Oxygen Budget

Concentration of the dissolved oxygen (D.O.) in water is determined by the balance between supply rate and consumption rate. The classical theory of the time rate change of the concentration of D.O. in the water body is named Streeter-Phelps' equation:

$$\frac{\partial C}{\partial t} = k_2(C_s - C) - k_1 \cdot L \tag{1}$$

where

C : concentration of D.O. (mg/l)

t : time (h)

C_s : saturated concentration of D.O. (mg/l)

L : organic concentration expressed in terms of BOD (mg/l)

k_1 : deoxygenation constant (1/h)

k_2 : reaeration constant (1/h).

The supply rate, the first term on the right hand side of the Eq. (1), is influenced by the diffusion and transport process of oxygen from the atmosphere into the solution. C_s means the concentration of dissolved oxygen when solution is in equilibrium with air. Rate constant, k_2, is the index of the efficiency of the oxygen dissolution and is governed by hydraulic factors[1] such as current velocity and turbulence. On the other hand, the oxygen consumption rate, $k_1 \cdot L$, represents the oxidation rate of the organic compounds. Existing reduced substances, also, consume dissolved oxygen. The concentration of these oxygen consumption materials is expressed as the concentration of oxygen demand. Biodegradation, which is the degradation process of the organic compounds through microbial activity, is governed[1] by water temperature, pH, D.O., toxity or obstruction compounds. But chemical oxidation reactions, which is the oxidation process of the redox substances such as H_2S and CH_4, are very rapid in rate and governed by O.R.P. and the D.O. concentration.

In order to estimate the oxygen budget in a bottom water body overlying on the sediment, the reaction rate as well as the standing concentration of water quality indexes such as D.O. and COD, is greatly important and necessary.

2.2 Oxygen Consumption Process by Sediments

Both chemical and biological mechanisms govern the oxygen uptake process by the resuspended sediments. It contains the following processes ;

1) oxygen uptake by released redox substances through chemical reaction. These redox substances have been produced in the anaerobic sediment layer before resuspension.

2) oxygen uptake through microbial degradation of the organics particles, which are brought into the overlying water accompanied by the resuspended sediments.

3) oxygen uptake through biological utilization of the soluble organics, which are dissolved from the sediments into the water by the resuspension turbulence.

There are different opinions on the relative importance of biological versus chemical process, and soluble versus particulate organics.

After some experiments on river sediments, Murakami[2] reported that the

oxygen demand exerted by the fraction of the dissolved organics was only 10~20 per cent of the whole oxygen demand of the resuspended sediment. He concluded that the uptake rate in resuspended condition is much greater than in quiescent condition, because of the release of the easily degradable substances into the overlying water and their rapid consumption through chemical reactions.

Wang[3] compared biological demand with chemical demand of the lake sediment. After his experiments of the intensive fractionation of the sediment oxygen-demand, he reached the following conclusions. Regardless of the distinction of chemical or biological demand of oxygen, almost all demands are originated from biological metabolic activities. It is especially evident in entrophic waters. High temperature and low D.O. in bottom water will promote the anaerobic digestion and the formation of chemical oxygen demand in the sediments. The fraction of biological demand is estimated about 20~30 per cent of all the demand of the quiscent sediment in lake, and the fraction of chemical one is about 70~80 per cent. Among reduced inorganic constituents which contribute chemical oxygen uptake, sulfide is most dominant. The components and constituents of organics in the sediment including interstitial water is more important than the mere concentration of organics.

2.3 Kinetics of Oxidation Process

To the kinetics of the biological decomposition of the organic materials, the following equation is commonly applied,[1,4]

$$\frac{\partial L}{\partial t} = -k_1 L \qquad (2)$$

where

L : organic concentration (mg/l).

This equation was originally modelled for unimolecular chemical reactions such as ferrous iron Fe (II) oxidates to ferric iron Fe (III). When the variable L of the organic concentration is expressed in terms of the biological oxygen demand (BOD), Eq. (2) is quite the same as the second term on the right hand side of Eq. (1). Eq. (2) is called the equation of the first order reaction. When the rate at which the concentration of a reactant (L) decreases is found to be proportional to the concentration of the reactant remaining, the reaction is identified as first order. The rate constant k is very important in defining the rate at which a reaction takes place. This equation seems to be of use also for the oxidation process, which is including both biological and chemical mechanisms.

But there are few reports[5,6] which have discussed the oxygen uptake by resuspended sediments as a first order process. After an extensive literature survey, Fukunaga[7] showed that in many studies on the oxygen uptake by the sediments the consumption process was considered to be zero-order kinetics.

In zero-order reactions, the rate at which the concentration of the reactant decreases is constant and is independent of the reactant concentration. In case that k and t become smaller, Eq. (2) can be expressed as zero-order equation;

$$\frac{\partial L}{\partial t} = -k \tag{3}$$

where

k : rate constant (1/h).

Eq. (2) and Eq. (3) can be easily solved:

first-order-kinetics

$$L = L_0 \cdot \exp(-kt) \tag{4}$$

zero-order-kinetics

$$L = L_0 - kt \tag{5}$$

where

L : organic concentration (mg/l)

L_0 : ultimate organic concentration at $t=0$ (mg/l).

And the mass of the consumed oxygen (Y) by the organics is:

first-order-kinetics

$$Y = L_0(1 - \exp(-kt)) \tag{6}$$

zero-order-kinetics

$$Y = kt \tag{7}$$

where

Y : consumed oxygen concentration (mg/l)

L_0 : ultimate organics in terms of BOD (mg/l).

L_0 and k characterize the consumption process. L_0 means the overall oxygen demand and is influenced by the organic contents and the reduced substances which are easily oxidized. L_0 expresses oxygen consumption potential of the sediments. Rate constant k means the activity of oxidization and is influenced by temperature, D.O., agitation strength, pH, salinity and other water quality indexes which may obstruct or promote the biological activity. Of course, k has a dependence on the organic contents. Sediments which contain easily degradable organics show larger value of k than those which contains only non-degradable organics.

An object of this paper is to examine the influence of waves or dredging in the bays. In the bays and coastal waters, the variation of salinity is usually within 35~25‰ and the variation of pH is normally within 8.0~8.6. Then the effect of the variations of salinity and pH is usually negligible. The resuspended sediments in overlying water is agitated strongly enough to keep resuspension. Then the effect of the turbulence and the agitation strength in overlying

water is negligible in resuspension compared with in nondisturbed quiescence. The presence of light is not reported[5] a significant factor in initial oxygen uptake. Baity[8] concluded that the rate of the oxygen consumption was independent of the oxygen concentration as long as any residual oxygen remain. But some other researchers reported[6] a dependence on D.O. in the range below 4mg/l. The oxygen diffusion to the oxidizable substances is important as a rate controlling process in oxygen deficit water. But in resuspension condition, the turbulence promotes the vertical mixing of the D.O. Thus, D.O. concentration is considered to have no significant effects on the consumption rate in resuspention.

The possible influences of concentration of the resuspended sediments, temperature and sediment quality on the oxygen uptake profile have been examined in this paper.

3. Equipment and Method

3.1 Principle

The equipment used for this investigation is a set of the water-manometric respirometer. This equipment is similar to the Warburg apparatus. Fig. 1 shows a set of bottle cell. The reaction bottle has a capacity of 200ml for a sample water and about 130ml for air space. Ten bottle cells with manometers are enclosed in a thermal control incubater during an experiment. This incubater is filled with temperature-controlled water, which flows in from a thermo-controller, circulates in this incubater and returns back to the controller apparatus through a weir. Temperature in the incubater can be set from low 5°C to high 30°C and held at the settled degree to plus or minus 0.5°C. The incubater box is sealed to maintain the dark condition. The circulating water is also used as the manometric fluid and is introduced into the manometric bullet. The magnetic stirrer chip in every bottle agitates the sample and produces suspended condition.

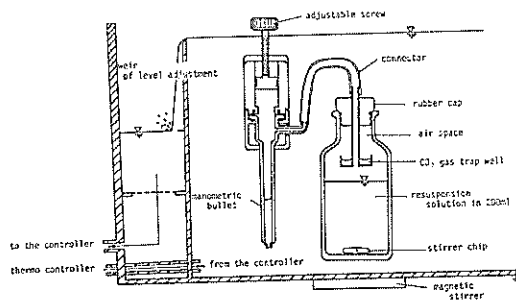In this system, oxygen removed from the sample water by consumption

Fig. 1 Schematic diagram of the test bottle

is replenished from the air space above the sample water. Oxygen can easily dissolved into the agitated sample water through the water surface. On the contrary, carbon dioxide (CO_2) produced in the sample water by oxidation is released into the air space, and absorbed by sodium hydro-oxygen (NaOH) in the center well. The 130ml air in the bottle contains 1.16m mol oxygen, which is 37mg in weight. The pressure decrement by the oxygen consumption is measured on the manometer in terms of water volume introduced into the graduated bullet. Mass of the oxygen can be calculated by the gas equation:

$$y = \frac{p \cdot v}{R \cdot T} \cdot M \qquad (8)$$

where

y : mass of the consumed oxygen (mg)
p : pressure (atm)
v : volume readings on the manometer (ml)
R : gas constant (0.082 atm・l/mol/°K)
T : absolute temperature(°K)
M : molecular weight of oxygen (32g/mol).

When the manometer reaches full scale deflection (10ml), the system may be re-equilibrated for the following measurement by adjusting the screw manually on the top of the manometer. The minimum division of the scale is 0.2ml. The water volume can be read to 0.05ml.

The dilution seawater itself may contain a little organics and oxygen demand materials. It is of requisite to distinguish the real oxygen demand of the resuspended sediment from that of the dilution water. So dilution seawater without any sediments must be incubated at the same time to measure the oxygen-uptake as a blank test. We also have to take it into consideration that the daily fluctuation of the air pressure is caused by the atmospheric phenomena. Air-pressure variation must also be compensated by subtracting the readings of the blank bottles from those of the sample bottles. The details of the compensation method is shown in appendix.

3.2 Characteristics of Equipment

Experiments must be performed to determine whether the readings on the manometer exactly show the oxygen uptake rate. It is an important factor of the respirometer as well as the stability of the environmental condition such as temperature and strength of agitation.

In this equipment, oxygen is transported through the chain of the following 5 processes as shown in Fig. 2.

1) oxygen uptake by organics in the sample water,
2) oxygen diffusion in the sample water,
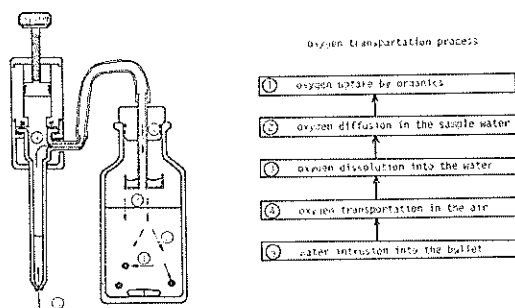3) oxygen dissolution from the air space into the sample water,

Fig. 2 Oxygen transportation process

   4) oxygen diffusion in the air space,
   5) water intrusion into the manometer bullet.
Among these processes, the slowest process of the whole chain of the system determines the overall transportation rate. The oxygen uptake process should be the slowest in rate, so that it may control the whole process of the system. If there is any slower process than the oxygen uptake, the readings on the manometer do not show the exact uptake rate. As the sample water is agitated continuously in this equipment, the diffusion process takes place fast. Then the oxygen dissolved process is the slowest of all the other four except the uptake process. The rate of the dissolved process should be sufficiently faster than that of the uptake process.

   The dissolution rate, which is expressed as the first term of Eq. (1), is influenced by concentration of D.O., temperature of the water and strength of agitation. Magnetic stirrer of this equipment is rotated at the speed of 540 r.p.m. The length of the stirrer chip for normal use is 2.5cm and that of the larger chip is 3.8cm.

   Sodium sulfite (Na_2SO_3), which consumes the dissolved oxygen immediately and changes into Na_2SO_4, was used as a reagent with copper ion as a catalyst. Added 10mg Na_2SO_3 consumes about 1.3mg dissolved oxygen. Na_2SO_3 first consumes the dissolved oxygen, then the residual Na_2SO_3 consumes the fresh oxygen transported into the water. Due to its rapid consumption, consumption rate means dissolution rate. As the saturation concentration of the sea water at 20°C is 7.4mg/l, 200ml sea water solution contains no more than 1.5mg oxygen. Then more than 12mg Na_2SO_3 should be dissolved in 200ml solution to maintain the D.O. in solution zero. The sea water solution of sodium sulfite was filled in the test bottle up to 200ml. The oxygen dissolution rate from the air space into the sampled water solution was calculated by the readings on the manometer bullet with time.

   The test cases were chosen as follows:
   1) two cases for the agitation strength, by using two types of the stirrer chips—normal chips and large chips,

2) two cases for the initial concentrations of Na_2SO_3, by using about 200mg Na_2SO_3 in 200ml solution, which makes strongly reducing condition, and about 20mg Na_2SO_3 in 200ml solution. 20mg Na_2SO_3 is equivalent to about 2.5mg oxygen demand.

3) four cases for the water temperature, by using 8°C, 18°C, 20°C and 28°C for test condition.

Fig. 3 represents one of the typical oxygen consumption curves at 18°C. As long as the residual Na_2SO_3 exists enough in the sample solution and keeps the concentration of D.O. zero, the dissolution quantity of the oxygen increases linearly at a constant rate as shown by the solid line in **Fig. 3**. But when the reducing reagent is fully oxidized and D.O. is recovering above zero, oxygen dissolution gradually decreases in rate. And the concenration of D.O. ultimately reaches up to the saturation concentration to which the partial pressure of oxygen gas in the air space is equilibrated, and oxygen dissolution into the water terminates. The oxygen dissolution curve of the case L_0=2mg is shown by the broken line in **Fig. 3**. L_0 is rapidly oxidized by the oxygen dissolved from air space and the quantity of the dissolved oxygen reaches the equilibrium in a few hours.
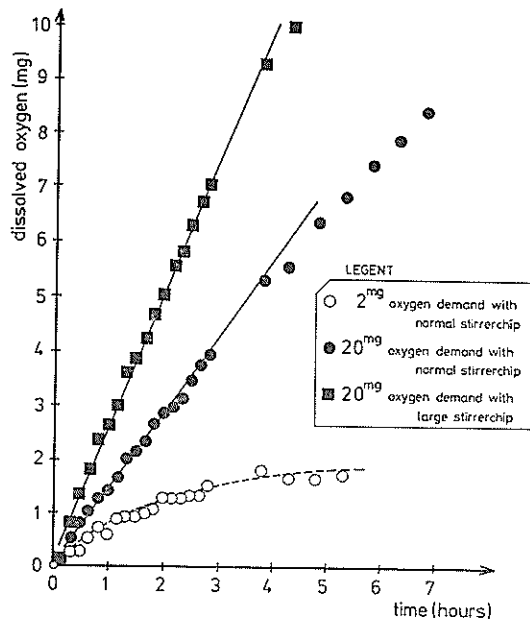

Fig. 3 Oxygen dissolution curve at 18°C
Oxygen demand of the sample solution is
controled as an initial Na_2SO_3 concentration

Using the data of the 200mg Na_2SO_3 additional solution, both the dissolution rate (mg/h) and k_2 (1/h) are calculated. The reaeration coefficient (k_2) is defined

Table 1 Dissolution rate and reaeration coefficient (k_2)

temperature		8°C			18°C			20°C			28°C		
stirre chip size	bottle No.	rate	(r)	k_2	rate	(r)	k_2	rate	(r)	k_2	rate	(r)	k_2
normal chips	♯ 1	0.757	(0.987)	0.398	1.381	(0.998)	0.874	2.104	(0.999)	1.377	2.406	(0.997)	1.807
	♯ 2	0.875	(0.994)	0.460	1.192	(0.994)	0.754	1.740	(0.998)	1.139	2.348	(0.997)	1.763
($L=25$mm)	mean	0.816		0.429	1.287		0.814	1.922		1.258	2.377		1.785
large chips	♯ 1	2.408	(0.879)	1.266	2.514	(0.999)	1.591	3.005	(0.998)	1.967	3.324	(0.997)	2.495
	♯ 2	2.601	(0.956)	1.368	2.755	(0.998)	1.744	4.082	(0.998)	2.671	3.389	(0.997)	2.544
($L=38$mm)	mean	2.505		1.317	2.635		1.668	3.544		2.319	3.357		2.520
temperature measured		8.8°C			18.5°C			20.2°C			29.5°C		

in the Eq. (1). The results are shown in **Table 1**. The dissolution rate at D.O.
$=0$mg/l varies between low 0.8mg/h for 8°C and high 2.4mg/h for 28°C. The
dissolution rate is plotted against the temperature in **Fig. 4**.
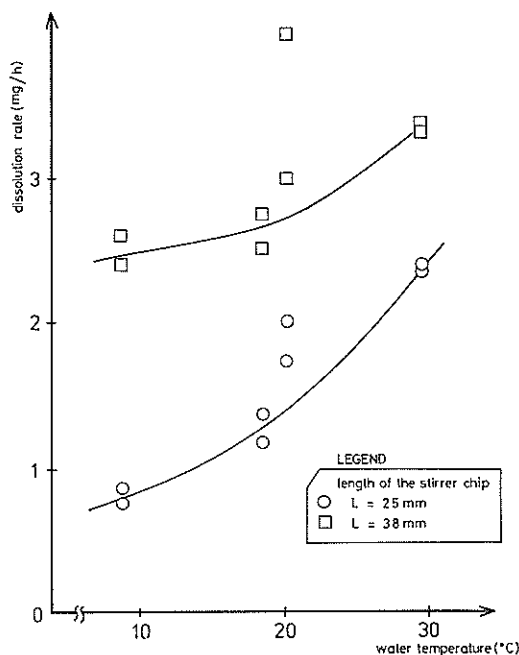

Fig. 4 Relations between the dissolution rate *vs* the water
temperature, and the strength of agitation

This figure shows that the dissolution rate becomes faster for higher
temperature and stronger agitation. The temperature dependence of the reae-
ration coeficient is generally expressed as :

$$k_2 = A\Theta^{(T-20)} \tag{9}$$

where

    A : constant of proportionality, representing the value of k_2 at 20°C (1/h)

    Θ :·temperature coefficient

    T : water temperature (°C).

The value of Θ is calculated at 1.055 using the data in **Table 1**. comparing with the values of 1.016 by Streeter and Phelps and 1.024 by Churchill[9] et. al., the value of 1.055 is enough reasonable. The confirmation that the dissolution rate is much faster than the consumption rate in this equipment, is left alone until the consumption rate of resuspended sediments is measured.

3.3 Experimental Procedure

For measuring the oxygen consumption by resuspended sediment, following operations are done:

    （1） Weigh the sample sediment into a test bottle,

    （2） fill the sea water to 200m*l* in volume in the test bottle

    （3） connect the manometric bullet to the test bottle and place this cell set in the thermo-controlled chamber,

    （4） wait for a while to allow the temperature of the sample water equilibrate to the test condition,

    （5） start the agitation and adjust the initial readings on the manometer,

    （6） read the manometer and temperature at appropriate time intervals and record the readings,

    （7） calculate the oxygen weight from the readings on manometer.

The organic content (COD) and the moisture content of the sediment should be examined soon.

4.　Oxygen Uptake by Resuspended Sediments

4.1　Equation of Oxygen Consumption

Silty and fine bottom sediments consume oxygen rapidly in suspended condition. **Fig. 5** shows the typical oxygen consumption curve at 20°C. For this experiment, sediment materials collected from the Osaka Bay were used. Suspention concentration was 2.8g dry weight of the sediment in 200m*l* sea water, that is, 14,000mg/*l*. At the beginning of the resuspension, the uptake rate $(\partial L/\partial t)$ was as fast as 0.5mg/h, and the rate gradually decrease to approach to a constant rate 0.015mg/h. Even the fastest rate, 0.5mg/h, is much lower than oxygen dissolution rate, 1.7~2.1mg/h (20°C), shown in **Table 1**. Thus, it is confirmed that this equipment is suitable for measuring oxygen uptake rate by resuspended sediments.

Fig. 5 also shows clearly that the uptake rate has a functional relationship with the resuspension time. We can separate the uptake process into two phases. The first part of the process in which the rate decreases gradually
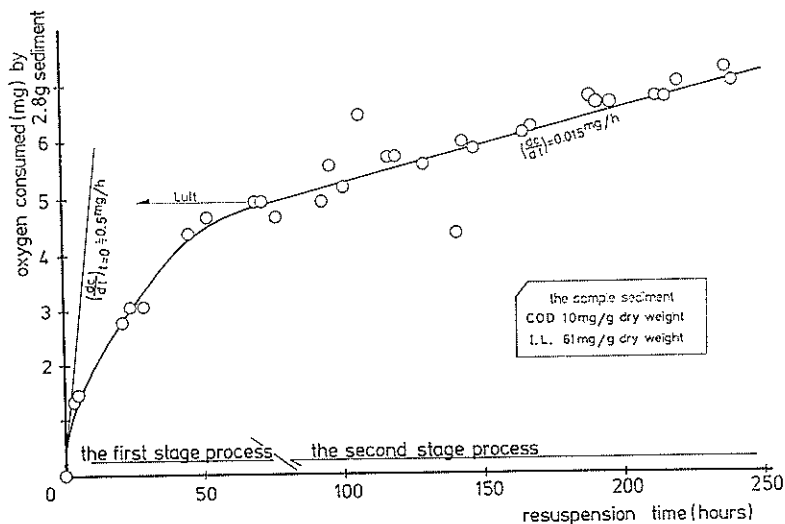
Fig. 5 Oxygen uptake curve of the bottom sediment

with time, is called the first stage oxygen uptake process. The next part of the process in which the rate maintains constant at a low level, is called the second stage oxygen uptake process. The first stage process has carried on for about 70 hours. After this process, much slower reaction takes place.

The first stage process is considered as an oxidation process of easily degradable organics. We may well call the overall oxygen demand of this degradable organics the ultimate first stage oxygen demand. For this sample in Fig. 5, the ultimate first stage oxygen demand was 5mg in 2.8g dry weight, that is, 1.8mg/g. As the COD of this sediment was 10mg/g, the ultimate first stage oxygen demand is calculated 18% of COD. This process is considered approximately as a first order reaction shown in Eq. (2). Because of its slow rate and large organics contents remaining, the second stage process is approximated as a zero order kinetics. The second process is considered as an oxidation process of difficultly degradable organics. Then, the following equations can be applied to the uptake process:

$$\frac{\partial L}{\partial t} = -kL \quad \text{for} \quad L \leq L_1 \tag{10}$$

$$\frac{\partial L}{\partial t} = -m \quad \text{for} \quad L > L_1 \tag{11}$$

where
     L : concentration of organics in terms of oxygen demand (mg/l)
     t : time (h)
     k : rate constant of the first stage process (1/h)

— 17 —

L_1 : ultimate oxygen demand of the first stage process (mg/l)

m : rate constant of the second stage process (1/h).

The decrease of the organics (L) in terms of oxygen demand means the increase of the oxygen consumption total mass (Y).

The solutions of the Eqs. (10) and (11) are:

$$Y = L_{ult}\{1 - \exp(-kt)\} \quad \text{for} \quad t \leq t_1 \tag{12}$$

$$Y = L_{ult} + m(t - t_1) \quad \text{for} \quad t > t_1 \tag{13}$$

where

L_{ult} : ultimate first stage oxygen demand (mg/l)

t_1 : elapsed time at which the first stage process is over (h)

Y : oxygen consumed during elapsed time t (mg/l)

k : oxydation constant for the first stage process (1/h)

t : time (h)

m : oxidation constant for the second stage process (1/h).

It takes about 30~300 hours for the first stage process to be finished. Duration (t_1) listed in **Table 2** was observed from experiments using the some bottom sediments of the Tokyo and the Osaka bays at the suspension concentration of 1~3mg dryweight per 200ml sea water. On the other hand, in the field, most of the sediment solids suspended by currents and dredgings are expected to settle down onto the bottom within some ten hours. Dominant diameter of the resuspended bottom sediments is 10~15μm. Its settling velocity calculated by the Stokes' law is about 0.01cm/s. It takes no more than 30 hours for these particles to settle down completely through 10m-depth quiescence water column. So, when to deal with the oxygen uptake process of the resuspended sediments by dredgings, it is reasonable to consider that the first stage uptake process is predominant.

Table 2 Duration of the first stage process

water temperature (°C)	5	8	10	18	20	28
duration (h)	250~300	100	80~100	30~50	30~50	38

L_{ult} in Eq. (12) shows the concentration of the easily degradable organics, and corresponds to the oxygen demand potential of the first stage process. And k represents the uptake rate which corresponds to degradability of L_{ult}. These two parameters, both L_{ult} and k, can be estimated from the data of manometric readings. The Thomas method[10] and the Least Square method were applied to this purpose. The outline of the methods is shown in **appendix B**.

4.2 Influence Factors on Parameters

There are some factors which influence the oxygen consumption by resuspended sediments. The possible influences of the following factors on the

uptake profile have been examined:

1) the concentration of the resuspended sediment solids,
2) the water temperature,
3) the organic components of sediments.

a) effect of the concentration of the resuspended sediment solids

Bottom sediments collected in the Tokyo Bay and the Osaka Bay were examined. Experiments were conducted at the condition of a few different concentrations. 3g~11g bottom sediments, that weigh 0.5g~4g in dry condition, were placed in the test bottles and the fresh sea water were poured up to 200ml. Then the tests started at 20°C. The results are shown in **Table 3**.

Table 3 Effect of the resuspension concentration

site	station	dry weight / wet weight	dry weight in test solution	k	$\bar{k}$*	S.D.**/$\bar{k}$	L_{ult}	unit L_{ult}	unit* L_{ult}	S.D.**/ u.L_{ult}
		g/g	g/200ml	1/h	1/h	%	mg/200ml	mg/g	mg/g	%
Tokyo Bay	T—16	0.235	0.729	0.0866			2.413	3.31		
			1.763	0.0885	0.0850	4.3	5.526	3.14	3.19	2.7
			2.491	0.0800			7.769	3.12		
	T—10	0.174	0.539	0.0940			3.362	6.23		
			1.235	0.0755	0.0847	11.0	6.917	5.60	5.92	5.3
Osaka Bay	O—126	0.289	1.097	0.0776			3.936	3.59		
			1.617	0.0343	0.0560	39.0	6.931	4.29	3.94	8.9
	O—129	0.717	2.798	0.1833			0.728	0.26		
			3.954	0.0680	0.1257	46.0	1.378	0.35	0.30	14.8
	O— 3	0.345	1.484	0.0372			4.062	2.74		
			3.278	0.0367	0.0369	0.7	10.018	3.06	2.90	5.5
	O— 11	0.395	2.252	0.0534			4.217	1.87		
			3.990	0.0478	0.0506	5.5	8.075	2.02	1.95	3.9

* $\bar{A}$ represents an arithmetric mean of A_i $\left(\dfrac{1}{N}\sum\limits_{i=1}^{N}A_i\right)$

** S.D. represents standard deviation

Table 3 shows that the values of k for the same sample varies little. The coefficient of variation (standard deviation divided by the mean value) of k for the same sediment is less than eleven per cent except two samples, O–126 and O–129. This indicates that k changes only slightly with the changes of the resuspension concentration within above range. So long as L_{ult} is concerned, it seems to be proportional to the weight of the sediment sample. L_{ult} per unit dry weight of the sample sediment (unit L_{ult}) is clearly changed little for the same sample as shown in the column next to L_{ult} in **Table 3**. The coefficient

of variation of unit L_{ult} is less than ten per cent with one exception, O-129. Because the degradable organics constitutions are the same among the sampled portions of the same sediment, both unit L_{ult} and k should be constact and independant of the resuspension concentrations.

Unit L_{ult} and k of the sample O-129 vary significantly. The uptake profiles of this sample and T-16 are plotted for resuspension concentration as a parameter in Fig. 6. O-129 consumes little oxygen. Because of the low resolving power of the manometer, the parameters k and unit L_{ult} tend to vary when the sample shows small quantity of oxygen consumption. For more accurate analysis, experiments should be made with higher resuspension concentration and stronger agitation.
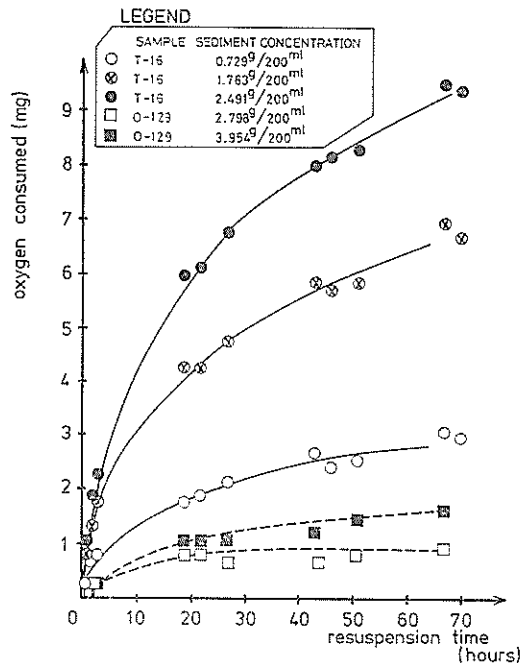
Fig. 6 Oxygen consumption curve in various resuspension concentrations

The concentration of the resuspended solid (mg dry weight per litter) were 2,500~20,000mg/l. But prototype concentration observed in the vicinity of a dredging area is expected much less. When the proportional relationship between L_{ult} and sediment weight is established, we can model the process and estimate parameters easily. Examined equation and parameters can be applied directly to the lower concentration of resuspension. The oxygen uptake process can be formulated as :

$$Y = \text{unit } L_{ult} \cdot S \cdot (1 - \exp(-kt)) \tag{14}$$

where

unitL_{ult} : first stage oxygen demand per unit dry weight of the sediment
(mg/g)

S : concentratinn of the dry weight of solids in resuspension
solution (g/l).

b) variation of the parameters

The variation of the parameters may be caused as a sum of individual errors in the experimental technique. Sampling error and reading error will be the main factors. Prior to an experiment, any large animals or particle contaminants (fibers and rocks) in the sediment should be removed. If the sediment portions which are sampled into the test bottle contain these contaminations, the variation of the parameters will become large. In order to reduce the contamination ratio, we had better weigh much sample into the test bottle. The variation of the parameters was examined for various concentrations of the resuspended sediments. Reading error is related to the resolving power of the apparatus. The use of a lot of sample makes the accuracy higher.

Sediment sample taken from the Osaka Bay, St. O-P, was used. Temperature was set at 10°C, 15°C and 20°C. Suspension concentration was chosen at 0.27g/200ml, 0.80g/200ml, 1.6g/200ml and 2.4g/200ml of dryweight. Two bottles of the same testing condition were examined simultaneously. The results are shown in **Table 4**. The difference of the values of parameters between the pair of two bottles is about 10 per cent with some exceptions. Even at the maximum (15°C, #5 and #6), the difference of these exceptional samples is only 15 per cent of the mean value. Effects of the resuspension concentration on the variation of the parameters is not clear within the range of this examination. But the experiments of the low resuspension concentration tend to give a little larger value of unit L_{ult}.

To make a comparison between the variation of unit L_{ult} and that of k, the mean value of the eight data, the standard deviation (S.D.) and the coefficient of variation (S.D./mean) are listed for each temperature case. The coefficient of variation of unit L_{ult} is 9.4~27.8 per cent, while that of k is 7.3 ~15.8 per cent. These variations indicate the difference of the sampled sediment in every test bottle. **Table 4** shows that the difference of the sampled sediment influences more sensitively on unit L_{ult} than on k.

The parameter unit L_{ult} can be determined to an accuracy of the order of 0.1mg/g, and k to the order of 0.001/h. To maintain this accuracy, it is needed that L_{ult} in the test bottle is more than 2mg/200ml.

According to **Table 4**, both unit L_{ult} and k have similar values even if the suspended concentration changes remarkably. Furthermore, unit L_{ult} changes only slightly even if the temperature changes over the range of 10°C to 20°C.

c) effect of temperature

Table 4 shows that the water temperature affects the value of k. It becomes

Table 4 Oxygen consumption parameters at various concentrations and temperatures

No.	concentration	10°C dry weight in 200ml (g)	10°C L_{ult} (mg/200ml)	10°C unit L_{ult} (mg/g)	10°C k (1/h)	15°C d.w. in 200ml (g)	15°C L_{ult} (mg/200ml)	15°C unit L_{ult} (mg/g)	15°C k (1/h)	20°C d.w. in 200ml (g)	20°C L_{ult} (mg/200ml)	20°C unit L_{ult} (mg/g)	20°C k (1/h)
1	0.27g/200ml	0.266	1.147	4.316	0.06846	0.266	1.326	4.988	0.08519	0.266	0.880	3.310	0.09284
2		0.292	1.426	4.878	0.07041	0.266	1.260	4.740	0.09898	0.266	0.944	3.550	0.12878
3	0.8 g/200ml	0.797	2.919	3.661	0.05745	0.797	2.362	2.962	0.08064	0.797	2.803	3.515	0.09530
4		0.877	2.990	3.408	0.05869	0.797	3.175	3.982	0.08558	0.797	2.307	2.893	0.12148
5	1.6 g/200ml	1.595	5.918	3.711	0.07004	1.595	4.078	2.557	0.05997	1.595	4.836	3.032	0.08666
6		1.754	6.134	3.497	0.06099	(1.595)	2.990	(1.875)	0.06378	1.595	6.159	3.862	0.09234
7	2.4 g/200ml	2.392	8.546	3.573	0.06522	2.392	8.756	3.660	0.08044	2.392	8.192	3.424	0.08189
8		2.419	8.630	3.568	0.06522	2.392	9.306	3.890	0.09083	2.392	9.170	3.833	0.09311
mean ($n=8$) ($n=7$)		—	—	3.826	0.06456	—	—	3.582 (3.826)	0.08068	—	—	3.427	0.09905
standard deviation		—	—	0.475	0.00472	—	—	0.995 (0.810)	0.01223	—	—	0.323	0.01568
variation (S.D./mean)		—	—	0.124	0.073	—	—	0.278	0.152	—	—	0.094	0.158
observed water temperature		10.8°C				15.0°C				20.0°C			
experimental duration		0~51hours				0~45hours				0~44hours			

sample sediment; 0.266g dry weight/g wet weight, I.L. 9.62%, taken from St. O-P in the Osaka Bay

larger as the temperature becomes higher. This tendency appears because the microbial oxidation activity increases due to the rise of the temperature in the range of 10°C to 20°C. Chemical oxidation process progresses rapidly and the rate of this process is influenced by the absolute temperature. Then, chemical oxidation process is less sensitive to the variations of the temperature than the process of the biological oxidation. Consequently, the first stage process is primarily the biological degradation of organics.

The dependence upon temperature of the biological activity is generally expresses by the equation:

$$k = A \cdot \Theta^{(T-20)} \tag{15}$$

where

k : biological activity, in this case, oxidation rate (1/h)

A : constant of proportionality. This constant means the value of k at 20°C (1/h)

Θ : temperature coefficient

T : temperature (°C).

This equation is the same form as Eq. (9) on k_2. When temperature changes

Table 5 Effect of the temperature on rate parameter (k)

sample (site & station)	temperature range	data $T(°C)$	$k(1/h)$			lregression equations, (r) application of Eq. (15), and Eq. (16)
detrital material (Osaka Bay St. O-P)	7.5~27°C	7.5°C	0.0388,	0.0244,	0.0148	$k = -0.0082 + 0.0047 \times T$ (0.985)
		8.5°C	0.0317,	0.0342,	0.0344	
		18.5°C	0.0884,	0.0727,	0.0707	$k = 0.0750 \times (1.082)^{(T-20)}$ (0.935)
		27.0°C	0.1175,	0.1211,	0.1191	
detrital material (Hiroshima Bay St. H-P)	7.5~27°C	7.5°C	0.0226,	0.0165,	0.0168	$k = 0.0111 + 0.0013 \times T$ (0.825)
		18.5°C	0.0504			
		27.0°C	0.0469,	0.0496,	0.0333	$k = 0.0342 \times (1.045)^{(T-20)}$ (0.857)
bottom sediment (Osaka Bay St. 9)	4.8~20°C	4.8°C	0.0032,	0.0063,	0.0108	$k = -0.0006 + 0.0035 \times T$ (0.849)
		8.9°C	0.0456,	0.0427,	0.0421	
		19.5°C	0.0781			$k = 0.0882 \times (1.148)^{(T-20)}$ (0.747)
		20.0°C	0.0471			
bottom sediment* (Osaka Bay St. O-P)	10.8~20°C	10.8°C	0.0685,	0.0704,	0.0575	
			0.0587,	0.0700,	0.0610	
			0.0652,	0.0652		
		15.0°C	0.0852,	0.0990,	0.0806	$k = 0.0242 + 0.0037 \times T$ (0.767)
			0.0856,	0.0600,	0.0638	
			0.0804,	0.0908		$k = 0.0985 \times (1.046)^{(T-20)}$ (0.788)
		20.0°C	0.0928,	0.1288,	0.0953	
			0.1215,	0.0867,	0.0923	
			0.0819,	0.0931		

*) same data as shown in Table 4

slightly, Eq. (16) can be applied:

$$k = a + bT \tag{16}$$

where

   a, b : constant.

Table 5 shows the values of k for various temperature. Fresh materials settled on the bottom surface as well as the bottom sediment were used as test solids. Thin layer of freshly settled fine materials usually covers the bottom sediment in the sea. This layer consists of the organic detritus, the fine deposits of resuspended sediments and the particulate materials carried through rivers. In order to examine freshly settled materials, the divers have collected fine materials of thin layer before the sampling of the bottom sediment. This silty materials were tested as a sample of the detrital material. In this tablet, the parameters A, Θ of Eq. (15) and a, b of Eq. (16) calculated by the least square method were listed with the correlation coefficient (r). Θ is in the range of 1.04 to 1.15 and b is between 0.0013 and 0.0047. When the temperature becomes lower than 8°C, k has decreased rapidly. This tendency is shown in Fig. 7. In Table 6, Θ is compared with the values measured by other researchers. It is well reasonable to adopt 1.05 or 1.08 as the value of Θ over the range from 8°C to 28°C.
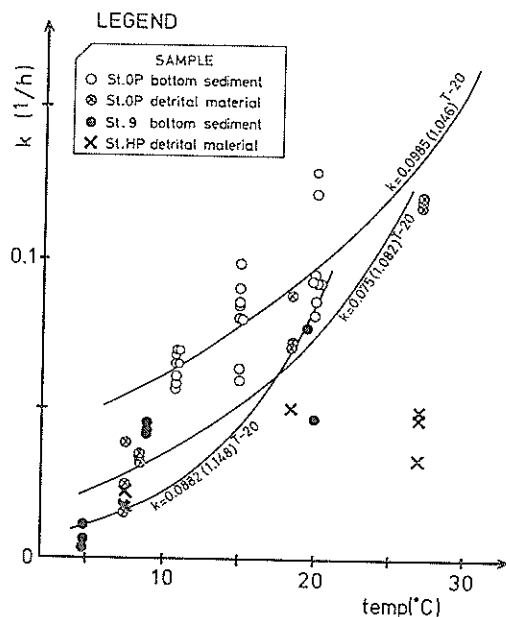

Fig. 7 Effect of temperature on k

d) effect of the organic contents of the sediment

Table 3 shows that unit L_{ult} varies widely between 0.3 and 3.9mg/g, even if the test sediments are taken from the same bay on the same day. The

Table 6 Comparison of temperature coefficient $\Theta(k=A\cdot\Theta^{(T-20)})$

condition	researcher	year	sample examined	temperature range	Θ
aerobic					
	Streeter & Phelps	1925	house swage, river water	8 ~38°C	1.047
	Theriault	1927	river water	9 ~30°C	1.049
					1.053
	Moor	1941	house swage	0.5~20°C	1.065
					1.145
			river water	0.5~20°C	1.026
	Gotaas	1948	house swage	5 ~15°C	1.109
				15 ~30°C	1.042
				30 ~40°C	0.967
	Zanoni	1964, 1967	house swage	2 ~15°C	1.126
				15 ~32°C	1.047
				32 ~40°C	0.985
anaerobic					
	Fair	1941	swage sludge	15 ~30°C	1.073
bottom sidiment					
	Baity	1938	swage sludge	22.3, 28.7°C	1.08
	Fair	1941	river sediment	10 ~25°C	1.07
	Edward et. al.	1965	river sediment	10, 20°C	1.07
	authors		sea bottom sediment in suspension	5 ~20°C	1.148
				10 ~20°C	1.046
			detrital materials in suspension	8 ~27°C	1.045
					1.082

experiment was conducted to examine the relationship between unit L_{ult} and sediment organic contents. Samples from the Osaka Bay and the Tokyo Bay were used. The results are shown in **Table 7**. Usually organic concentration in sediments has been represented by I.L. (ignition loss, volatile weight per unit dry weight) and COD (chemical oxygen demand per unit dry weight). The value of the ratio, dry weight/wet weight, of sand materials is high, while the value of the silt is low owing to its interstitial water.

As is evident from **Table 7**, unit L_{ult} is very sensitive to the organic content in the sediment. Unit L_{ult} is 10~17 per cent of COD of the sediment. The ratio of unit L_{ult} (mg/g) at 20°C to I.L. (%) of the sediment varies over a range from 0.24 to 0.61 with two exceptions. One of the exceptions is the value 0.12 of the sandy material O-129, another is the value 0.98 of the strongly polluted sample O-9. I.L. of the silty materials varies from 4.7 to 10.2%, which does not show the oxygen demand directly but shows the weight of the volatile organic matter at 600°C. Then the correlation between unit L_{ult} and COD is much higher than that between L_{ult} and I.L. **Fig. 8** shows the variation of unit L_{ult} and k against I.L. using the sediments from the Tokyo Bay. Unit L_{ult}

Yasushi Hosokawa · Eiichi Miyoshi · Takeshi Horie

Table 7 Relationb etween unit L_{ult} and sediment organic contents

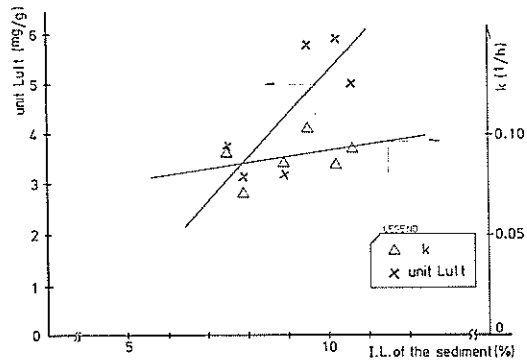| sample	experimental condition		unit L_{ult}		sediment contents					ratio	
site and station	temp.	number of bottles	(MEAN±S.D.)		dry/wet	I.L.	COD	T-N	T-P	unit L_{ult}/COD	unit L_{ult}/I.L.
			mg/g	mg/g	g/g	%	mg/g	g/kg	g/kg		
Osaka Bay											
O—3	9°C	$n=2$	1.72	±0.40	0.35	8.1	20.9	0.9	0.3	0.08	0.21
O—9		$n=3$	5.53	±0.09	0.29	9.4	—	—	—	—	0.59
O—11		$n=3$	1.90	±0.38	0.40	6.91	9.1	1.6	0.3	0.10	0.28
O—3	20°C	$n=2$	2.90	±0.16	0.35	8.1	20.9	0.9	0.3	0.14	0.36
O—9		$n=2$	9.24	±0.48	0.29	9.4	—	—	—	—	0.98
O—11		$n=2$	1.95	±0.08	0.40	6.9	19.1	1.6	0.3	0.10	0.28
O—113		$n=2$	1.13	±0.16	0.53	4.7	10	0.9	0.4	0.11	0.24
O—126		$n=2$	3.27	±0.21	0.29	8.2	19	2.1	0.6	0.17	0.40
O—129		$n=2$	0.28	±0.02	0.72	2.3	6.7	0.6	0.3	0.04	0.12
Tokyo Bay											
T—2	20°C	$n=1$	5.8		0.19	9.5	—	3.2	0.8	—	0.61
T—4		$n=1$	3.8		0.33	7.5	—	2.2	10.8	—	0.51
T—6		$n=1$	5.0		0.17	10.6	—	3.7	16.8	—	0.47
T—10		$n=2$	5.92	±0.32	0.17	10.2	—	4.1	8.8	—	0.58
T—16		$n=3$	3.19	±0.09	0.24	8.9	—	—	7.2	—	0.36
T—19		$n=1$	3.1		0.24	7.9	—	2.1	15.0	—	0.39

Fig. 8 Relation between I.L. *vs* unit L_{ult} and k

becomes large as I.L. becomes large. As long as the test temperature is same, however, k varies little with I.L.

A comparison is made between bottom sediment and other materials such as detrital material and mud. **Table 4** shows the parameters of the bottom sediment. The parameters of the detrial material taken from the same station are shown in **Table 8**. The value of I.L. in **Table 8** is 9.93%, which is similar to 9.62% of the bottom sediment in **Table 4**. Therefore, organic content of the two seems to be similar. Unit L_{ult} of the detrital matter is slightly higher and k is slightly lower than those of the bottom sediment. The history of the aerobic degradation along settling affects the organic constitution of the detrital matter. Organics which can be degraded most easily, have been already degraded rapidly during settling. Though any clear conclusion cannot be drawn due to an insufficient number of experimental samples, it is likely that organics in the detrital matter contains slightly higher oxygen demand and shows slightly lower degradability than those in the sediment.

Table 8 Oxygen consumption and contents of the fresh detrital materials

	oxygen consumption parameters			sample contents	
temp.	number of test bottle	unit L_{ult}	k	dry weight/wet weight	I.L.
		mg/g	1/h	g/g	%
18.5°C	$n=3$	5.47±0.38	0.0772±0.00079	0.174	9.93

The mud samples were collected from the land surface, on the mountain near the Osaka Bay where the materials for reclamations had been taken. Silty fraction was collected after screening by 0.047mm mesh sieve. The oxygen uptake test was conducted using this silt fraction of the reclamation materials. Results are shown in **Table 9**. Because of the small values of unit L_{ult}, oxygen consumption of the silt is observed negligible. Sands and rocks of the land surface will soon settle down without any consumption of D.O. in the sea.

Table 9 Oxygen consumpt on of the mud taken from the land surface

sample	oxygen consumption parameters			organic contents	
	temp	unit L_{ult}	k	I. L.	COD
		mg/g	1/h	%	mg/g
mud T		0.089	0.09	3.3	<1
mud A	20°C	0.038	0.08	3.5	<1
mud M		0.063	0.02	5.1	16.2

e) distribution of unit L_{ult}

As mentioned above in section d), unit L_{ult} is deeply related to the organic content of the sediment. The geographical distribution of unit L_{ult} is similar to the distribution of I.L. and COD of the sediment. **Fig. 9** shows the distribution at the Tokyo Bay and the Osaka Bay of unit L_{ult}, the values of which is Listed in **Table 7**. At the mouth of the main rivers, the Tama River to the Tokyo Bay and the Yodo River to the Osaka Bay, high values are plotted. Organic pollutants and nutrients are loaded mainly from these rivers. The value of unit L_{ult} decreases gradually as the distance from the shore line increases.
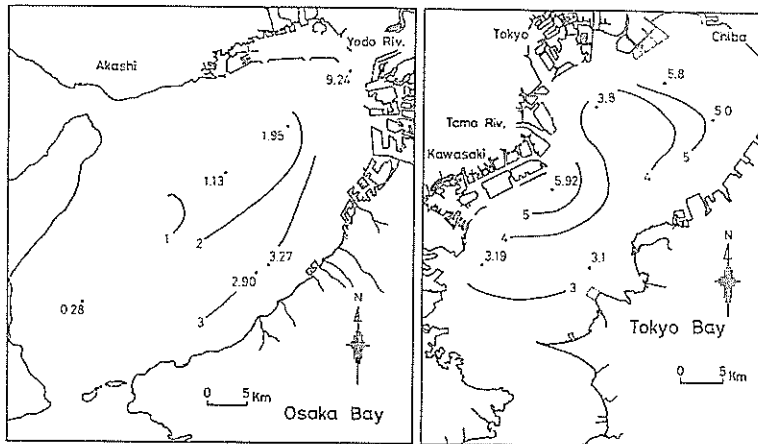

Fig. 9 Distribution of unit L_{ult} in the Tokyo Bay and the Osaka Bay

Fig. 10 shows the distribution of D.O. consumption rate and nutrient release rate from the quiescent sediment. These rate were measured[11] in summer at the Tokyo Bay. Undisturbed sediment cores were taken from the bottom sediment. Cores were incubated in the dark in a batch mode under the fixed conditions of temperature in a sealed chamber. Nutrient and D.O. analysis on the overlying water were made daily. As shown in the figure, nutrient release rate shows small at the place where D.O. consumption rate is small. Consumption rate of the quiescent sediments rages from 0.5g to 2.0g of the oxygen per unit surface area (m²) per a day. Horizontal distribution of the consum-
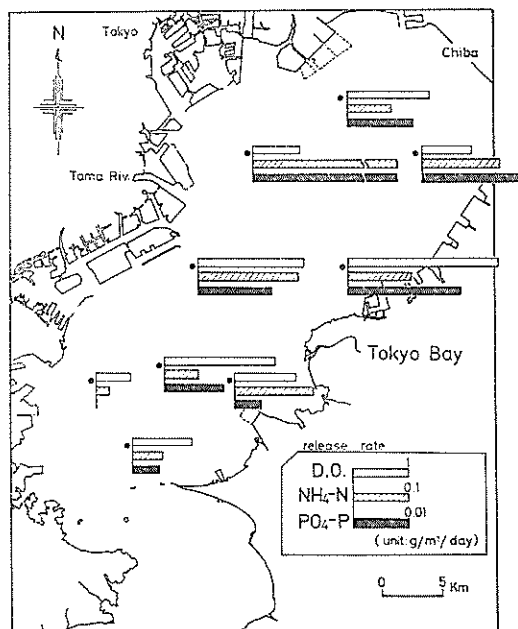
Fig. 10 Distribution of D.O. consumption rate and nutrient
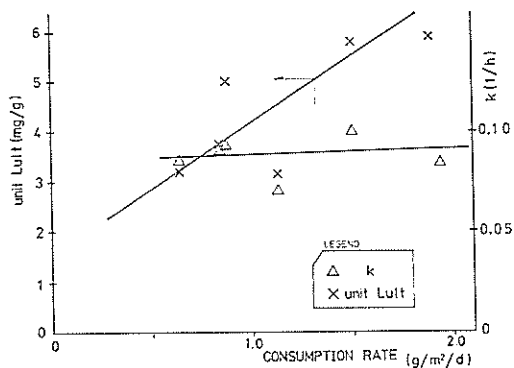release rate from quiescence sediment in the Tokyo Bay

Fig. 11 Relationship between the consumption rate in quiescence
and that in resuspension (Samples were taken from the
Tokyo Bay)

ption rate in the quiescent condition is similar to that of unit L_{ult} in resuspe-
nsion condition in Fig. 9. Fig. 11 shows the relationship between the oxygen
consumption rate in the quiescent condition and unit L_{ult} in the resuspension
condition. k is also plotted with the oxygen consumption rate in the quiescent
condition in Fig. 11. As the oxygen consumption rate increases along the X-axis,
unit L_{ult} clearly increases. But k changes little. Thus, the oxygen consumption
in resuspension of the sediment whose oxygen consumption even in quiescence
is large will be large.

4.3 Influence of Sediment Resuspension on Water Quality

Serious problems will happen if the deficit of D.O. in the bottom water destroys the ecological stability of the bottom biota. The decrease of D.O. resulted from the sediment resuspension can be calculated for various resuspension concentration using the Eq. (14). Relation between consumed D.O. and resuspension time is shown in **Fig. 12** plotted for SS (suspended solid) concentration as parameter. In **Fig. 12**, the values of unit L_{ult} and k are chosen 3.33mg/g and 0.08~0.12 1/h respectively. After 10 hours elapse, the oxygen of 0.6mg/l for SS 300mg/l and 5.5~7mg/l for SS 3,000mg/l has consumed. The consumption rate can be calculated by the following equation derived from Eq. (14):
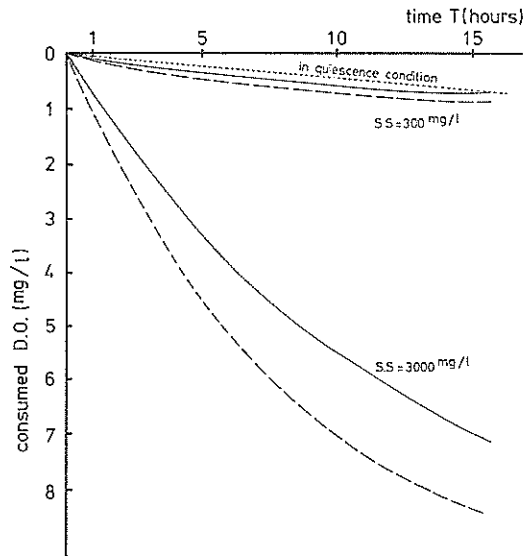

Fig. 12 Relation between consumed D.O. in resuspension
condition and resuspension time, SS concentration
asa parameter
solid line; unit L_{ult} 3.33 (mg/g), k 0.08(1/h)
dotted line; unit L_{ult} 3.33 (mg/g), k 0.12 (1/h)
broken line; uptake from quiescence sediments

$$\frac{dY}{dt} = \text{unit } L_{ult} \cdot S \cdot k \cdot \exp(-kt) \tag{17}$$

At the very beginning of the rsuspension ($t=0$), the rate is 0.08~0.12mg/l/h for SS 300mg/l.

Assuming that the effective height of the bottom water is 1m above the bottom surface. and the D.O. consumption rate of quiescent sediment surface is 1g/m^2/d, then the decrease rate of D.O. in bottom water will be 0.042mg/l/h. This consumption rate is shown as a straight broken line in **Fig. 12**. This rate

is much smaller than the rate in resuspension condition. But after 15 hours, the value of consumed D.O. mass sums up to 0.63mg/l, which is similar to the mass of the consumed D.O. by 300mg/l resuspended sediment in 15 hours. The resuspended sediment influences on the water quality rapidly and strongly. If either waves, bottom current or the dredging activity gives the turbulence impacts on bottom sediments frequently enough, fresh sediment whose consumption rate is high, will suspend successively. Then the oxygen uptake by respended sediment will become very large. An appropriate frequency of the dredging work will be decided from the settling time of the resuspended sediments. Of course, the standing D.O. concentration should be calculated using Eq. (1).

5. Conclusions

At the present stage of this investigation, some points have not been solved. The dynamics of the sulfur cycle in the sediment is one of the most important problems to estimate the oxygen demand of the sea bottom sediment. Fortunately, most of the sediment samples treated in this work contained little free-sulfides, which would act as strong redox materials.

From a practical point of view, the authors' aproach using respirometer is successful. In order to get higher accuracy, the authors will continue to try to clarify the oxygen consumption in detail.

The important conclusions in this investigation are:

(1) Consumed oxygen by resuspended sediment can be approximated by the first order kinetics. The mass of consumed oxygen can be calculated if the ultimate oxygen demand (unit L_{ult}) and the consumption rate (k) are given. The consumption rate is not constant but decreasing with time. So the elapsed time after resuspension is very important.

(2) Unit L_{ult} represents the potential of the D.O. consumption in resuspension. This parameter is affected by organic content of bottom sediments. Unit L_{ult} is in a range of 10~20 per cent of the COD of the bottom sediment.

(3) Parameter k represents the rate of the D.O. consumption. It is affected by the water temperature. The dependence on temperature is expressed by exponential function. Temperature coefficient (θ) is estimated to be 1.04 or 1.08 for bottom sediments.

(4) Detrital materials also consume D.O. at the similar rate to the sediment. However, mud taken from land surface consume D.O. very little.

(5) At the beginning of the resuspension, the highest is the consumption rate. If the resuspension of the sediment occurs very frequently and successively, the D.O. may decrease rapidly.

The present investigation was initiated by the stimulating discussions with the late Dr. Shoichi Nanbu, the fromer Director of the Dept. of the Sanitary

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Appendix A; List of Symbols

A : constant of proportionality in Eqs. (9), (15),
   representing the rate at 20°C (1/h)

a : constant in Eq. (16) (1/h)

b : constant in Eq. (16) (1/h/°C)

C : concentration of D.O. (mg/l)

C_s : saturated concentration of D.O. (mg/g)

k : rate constant in Eqs. (3)~(7)

  rate constant for the first stage process (1/h)

k_1 : deoxygenation constant (1/h)

k_2 : reaeration constant (1/h)

L : organic concentration expressed in terms of oxygen demand (mg/l)

L_0 : ultimate oxygen concentration in terms of oxygen demand (mg/l)

L_1 : ultimate oxygen demand of the first stage process in Eqs. (10) and (11)

L_{ult} : ultimate first stage oxygen demand (mg/l)

M : molecular weight of oxygen (32g/mol)

m : rate constant for the second stage process (1/h)

p : pressure (atm)

R : gas constant (0.082 atm·l/mol/°K)

S : concentration of the dry weight of solids in resuspension solution (g/l)

T : water temperature (°C)

T : absolute temperature (°K)

t : time (hours)

t_1 : elapsed time at which the first stage process is over (hours)

unit L_{ult} : first stage oxygen demand per unit dry weight of the sediment (mg/g)

v : volume readings on the manometer (ml)

Y : consumed oxygen concentration (mg/l)

y : mass of the consumed oxygen (mg) in Eq. (8)

θ : temperature coefficient (—)

Appendix B; the Thomes Method and the Least Square Method

In this investigation, two parameters L_{ult} and k were estimated from laboratory data with the two methods. First, using the Thomas Method the preliminary values of the parameters are calculated. Next, with the Least Square Method, the final values are derived from the preliminary values. The out line of the two method is as follows:

1) the Thomas Method[10]

This method is based on the similarity of the two expression,

$$1-\exp(-kt)=kt\left[1-\frac{kt}{2}+\frac{(kt)^2}{6}-\frac{(kt)^3}{24}+\cdots\cdots\right] \qquad \text{(B-1)}$$

and

$$kt\left(1+\frac{kt}{6}\right)^{-3}=kt\left[1-\frac{kt}{2}+\frac{(kt)^2}{6}-\frac{(kt)^3}{21.6}+\cdots\cdots\right] \qquad \text{(B-2)}.$$

Therefore, Eq., (12) can be approximated by

— 33 —

$$Y=L_{\text{ult}} \cdot kt\left(1+\frac{k \cdot t}{6}\right)^{-3} \tag{B-3}$$

which can be re-arranged into a straight-line form:

$$\left(\frac{t}{Y}\right)^{1/3}=(kL)^{-1/3}+\frac{(k)^{2/3}}{6(L)^{1/3}} \cdot t \tag{B-4}.$$

From the data of (t, Y), the intercept $(kL)^{-1/3}$ and the slope $(k^{2/3}/6L^{1/3})$ are easily estimated. Then, the two parameters k and L can be calculated.

2) the Least Square Method[10]

As the values of k and L calculated with the Thomas Method are used as initial values, the Least Square Method can be applyed.

Assuming that k is the true value, k' is the initial value calculated with the Those Method, and h is error, then k is expressed as:

$$k=k'+h \tag{B-5}.$$

Then let Eq.(12) rewrite as follows:

$$Y=L(1-\exp(-(k'+h) \cdot t))=L(1-\exp(-k't-h \cdot t)) \tag{B-6}$$

Taylor's expansion gives:

$$e^z=1+\frac{X}{1!}+\frac{X^2}{2!}+ \qquad .$$

Then Eq. (B-6) is approximated as:

$$Y=L\left(1-e^{-k't} \cdot \left(1-ht+\frac{(ht)^2}{2}-\frac{(ht)^3}{6}+\cdots\cdots\right)\right)$$

$$\doteqdot L(1-\exp(-k't) \cdot (1-ht))$$

$$=L(1-\exp(-k't))+Lh(t \cdot \exp(-k't)) \tag{B-7}.$$

Set

$$a =L$$

$$b =L \cdot h$$

$$f1=1-\exp(-k't)$$

$$f2=t \cdot \exp(-k't)$$

then

$$Y=a \cdot f1+b \cdot f2 \tag{B-8}.$$

Let R be defined as:

$$R=\sum(y-a \cdot f1-b \cdot f2)^2 \tag{B-9}.$$

By the application of the least square technique to Eq. (B-8) yield the following equations:

$$\begin{cases} \dfrac{\partial R}{\partial a}=0 \\[2mm] \dfrac{\partial R}{\partial b}=0 \end{cases}$$

(B–10).

Rewrite the Eq. (B–10), we get:

$$\begin{pmatrix} \Sigma f1^2, & \Sigma f1f2 \\ \Sigma f1f2, & \Sigma f2^2 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \Sigma f1y \\ \Sigma f2y \end{pmatrix}$$

(B–11).

Using Eq. (B–11),we can calculate L and k. This is an outline of the Least Square Method.

Appendix C; Compensation for the Fluctuation of Temperature and Air Pressure

Assuming that the readings on the manometers of all the test bottles set the same value (V_0) at the biginning of the experiment, then each bottle including the blank test one has the same volume of the air space. Call this volume v_0. And temperature is T, atmospheric pressure is p.

Atmospheric condition changes later, and temperature and pressure become T' and p' respectively. Let the readings on the manometer of the sample bottle and the blank bottle V_1' and V_b' respectively at this time. And let the volume of the air space of the sample bottle and blank bottle v_1' and v_b'. Call
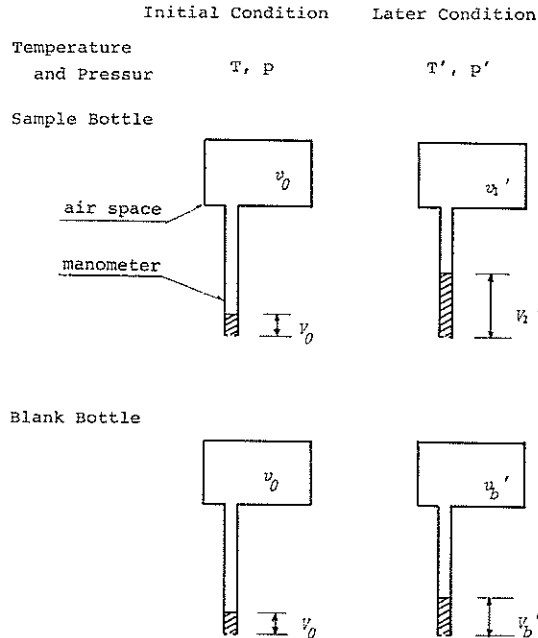

Fig. C1 Schematic diagram of the readings on the manometer

the true readings on the manometer $\overline{V}$ which is the value converted under the initial condition of the temperature T and the pressure p.

Using the gas equation

$$\frac{pv_0}{T} = \frac{p'v_b'}{T'} = \frac{p'(v_0 - (V_b' - V_0))}{T'} \tag{C-1},$$

we can get the expression of the decrease in the true readings,

$$\overline{V} - V_0 = v_0 - \frac{T}{T'} \cdot \frac{p'}{p} \cdot v_1'$$

$$= v_0 - \frac{v_0}{v_b'} \cdot v_1'$$

$$= v_0 - \left(\frac{1}{1 - \dfrac{(V_b' - V_0)}{v_0}} \right) \cdot v_1'$$

$$= v_0 - \left(\frac{1}{1 - \dfrac{(V_b' - V_0)}{v_0}} \right) \cdot (v_0 - (V_1' - V_0))$$

$$= \frac{V_1' - V_b'}{1 - \dfrac{(V_b' - V_0)}{v_0}} \tag{C-2}.$$

The value of v_0 is over 100ml, and the value of V_0, V_b', V_1', is less than 10ml as mentioned in 3.1 of the main text. Then,

$$\frac{V_b' - V_0}{v_0} \ll 1 \tag{C-3}.$$

The equation (C-1) consequently reduce to

$$\overline{V} - V_0 = V_1' - V_b' \tag{C-4}.$$

This equation (C-3) means that the true value of the decrease in readings can be calculated by subtracting the readings of the blank bottle from the readings of the sample bottle. The variation of the readings by the fluctuation of T, p can be compensated in this way.