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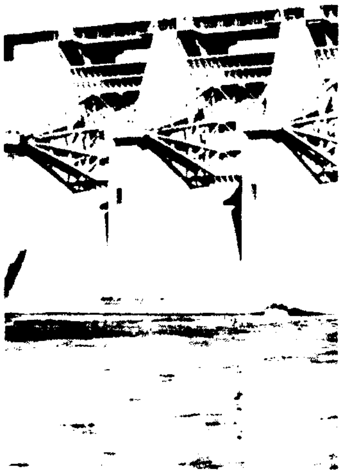

WATER QUALITY RESEARCH PROGRAM

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PROCEEDINGS, US ARMY CORPS OF ENGINEERS WORKSHOP ON SEDIMENT OXYGEN DEMAND; PROVIDENCE, RHODE ISLAND 21-22 AUGUST 1990

by

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13. ABSTRACT *(Maximum 200 words)*

Sediment oxygen demand (SOD) and related processes control many water quality conditions. An understanding of SOD processes and their quantification is needed to assess the effects of US Army Corps of Engineers (CE) projects on sediment-water interactions and water quality. The US Army Engineer Waterways Experiment Station (WES) is presently developing methods to quantify SOD and determine its effect on water quality. A literature review and other papers presented at a WES workshop give an understanding of current techniques used to measure SOD and nutrient flux and determine the current state of the art of SOD research. Three major areas are examined by the papers: (1) the physical, chemical, and biological processes critical to SOD; (2) a predictive model for SOD; and (3) the techniques presently available to monitor and measure SOD. A panel discussion following the presentations identified the present strengths and weaknesses in the understanding of SOD processes and determined important areas for future investigation.

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Prediction
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SOD measurements
Winter kill

PREFACE

This report presents the papers given and the subsequent panel discussion held at the US Army Corps of Engineers Workshop on Sediment Oxygen Demand convened at Providence, Rhode Island, on 21 and 22 August 1990. The information developed is integrated with the objectives of the work unit and summarized in terms of the sediment oxygen demand (SOD) measurement techniques, the modeling of SOD, and the relationship between measurement and modeling.

The work reported herein was conducted as part of the Water Quality Research Program (WQRP), Work Unit Number 32694, "Sediment Oxygen Demand (SOD) and Water Quality." The WQRP is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE), and is assigned to the US Army Engineer Waterways Experiment Station (WES) under the purview of the Environmental Laboratory (EL). Funding was provided under Department of the Army Appropriation No. 96X3121, General Investigation. The WQRP is managed under the Environmental Resources Research and Assistance Programs (ERRAP), Mr. J. L. Decell, Manager. Mr. Robert C. Gunkel was Assistant Manager, ERRAP, for the WQRP. Technical Monitors during this study were Messrs. Pete Juhle and James Gottesman and Dr. John Bushman, HQUSACE.

The study was conducted by Dr. Carl Cerco of the Water Quality Modeling Group (WQMG) and Dr. Douglas Gunnison of the Aquatic Processes and Effects Group (APEG), Environmental Research and Simulation Division (ERSD), Environmental Laboratory (EL), WES. Ms. Cynthia B. Price of the APEG assisted with preparation of the report.

The study was conducted under the direct supervision of Dr. Richard E. Price, Acting Chief, APEG, and under the general supervision of Mr. Donald L. Robey, Chief, ERSD, and Dr. John Harrison, Chief, EL. The report was reviewed by Dr. Judith C. Pennington and Dr. James M. Brannon, APEG.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander and Deputy Director was COL Leonard G. Hassell, EN.

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CONVERSION FACTORS, NON-SI TO SI (METRIC) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
fathoms	1.828804	metres
inches	0.02540	metres
pounds (mass)	0.4535924	kilograms
revolutions per minute	0.1047198	radians per second

PROCEEDINGS, US ARMY CORPS OF ENGINEERS WORKSHOP ON SEDIMENT OXYGEN DEMAND; PROVIDENCE, RHODE ISLAND, 21-22 AUGUST 1990

PART I: INTRODUCTION

Background

Interactions between bottom sediments and overlying water are often dominant factors contributing to poor quality of surface waters. A primary sediment-water interaction that affects water quality is sediment oxygen demand (SOD). SOD is a key contributor to low dissolved oxygen levels in the water column (Hargrave 1972; Giga and Uchrin 1990). SOD is the rate of oxygen removal from the overlying water column due to the decomposition of settled organic matter and is dependent upon the microbial and chemical oxidation activity in the sediment. SOD encompasses: (1) oxygen consumption through biological activity in sediments and (2) oxygen consumption resulting from the chemical oxidation of reduced chemical species (Wang 1981).

Many nutrients and heavy metals have a high affinity for sediment. Movement of these materials from the sediment to the overlying water is related to SOD processes occurring at the sediment-water interface (Brannon et al. 1983; Gunnison, Chen, and Brannon 1983). Microbial degradation of organic matter in the sediment surface layer results in a depletion of dissolved oxygen and the release of nutrients and metals, such as nitrogen, phosphorus, iron, and manganese, into the overlying water column. The development of anoxic conditions combined with the release of nutrients and metals into the water column can lead to severe water quality problems (Gunnison, Chen, and Brannon 1983).

SOD is not exerted until oxygen in the overlying water column comes into contact with the oxygen-consuming constituents of the sediment. Contact occurs by diffusion of oxygen down to the sediment and/or by the movement of oxygen-consuming species in the sediment up into the oxygenated water column as a result of diffusion and physical mixing at the sediment-water interface.

Predicting the effects of US Army Corps of Engineers (CE) water resource projects on water quality has been difficult due to lack of methods to accurately quantify SOD and related processes. Standard procedures and equipment for measuring SOD have not been developed. An understanding of SOD processes and their quantification is needed to assess the effects of CE projects on sediment-water interactions and, ultimately, on water quality. However, the lack of an integrated, universally applicable method for determining SOD necessitates development of a procedure with CE-wide application to analyze SOD in riverine, lacustrine, and estuarine environments.

Objective

The US Army Engineer Waterways Experiment Station (WES) is currently developing research techniques to accurately measure, evaluate, and predict SOD for CE water resource projects. Three major objectives of WES are to: (1) Document our current understanding of SOD and processes related to it, identify weaknesses in our knowledge, and design investigations to supply the needed information; (2) Develop a model to predict the releases of chemical species to the water column as controlled by SOD processes; and (3) Develop a standard technique to measure SOD that can be implemented CE-wide.

Approach

Initial efforts to accomplish these objectives consisted of conducting a literature review and hosting a workshop to determine state of the art of SOD research. This report includes the literature review and presentations and panel discussion from the workshop. The literature review provided an understanding of current techniques used to measure SOD and nutrient fluxes. The presentations illustrated two major areas of SOD research: sampling and measurement of SOD, and modeling of SOD. Based on the information provided, the panel participants discussed the present strengths and weaknesses in our understanding of SOD processes and identified areas in which further investigation is needed.

PART II: PRESENTED PAPERS

Literature Review of Sediment Oxygen Demand and Nutrient Flux Measurement Techniques

by

Heidi Vigil[1]

Introduction

The transfer of solutes across the sediment-water interface is an important factor in describing a marine or freshwater system (Froelich *et al*. 1979) (Figure 1). Sediment oxygen demand (SOD) and nutrient fluxes have received a great deal of attention in the last several years as the increase in pollutants has become a major problem.

Most of the chemical reactions taking place in the sediments are associated with the decomposition of organic matter by microbes, as well as $CaCO_3$ and SiO_2-nH_2O (Berner 1976). The reaction rate is highly dependent on the microbial activity of the sediment and, therefore, also dependent on temperature. The order and extent of the oxidation-reduction reactions are dependent on the concentrations of the reactants and the free energy available. The geochemical reaction in the sediments affects the pH and oxidation-reduction potential and can deplete or increase the reactants or products in both the fluid and solid phases of a deposit (e.g. Ben-Yaakov 1973; Goldhaber and Kaplan 1974). Representations of organic matter decomposition pathways are listed in Table 1.

In addition to the chemical forces present, there are several important physical processes that affect the oxygen and/or nutrient fluxes. The major processes are:

<u>Sediment resuspension</u>. An increase in sediment resuspension increases sediment surface area and, in turn, increases the uptake of oxygen (up to a factor of ten) (Hargrave 1969; Lucas and Thomas 1971; Butts 1974).

<u>Photosynthesis</u>. The potential effect of photosynthesis and respiration is enormous. Large plankton blooms, which occur when there is an increase in the nitrogen species (e.g. from sewage effluent or an increase in river discharge and ground water), are a big problem for shallow water bodies. (The

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[1] Marine Sciences Research Center, State University of New York, Stony Brook.

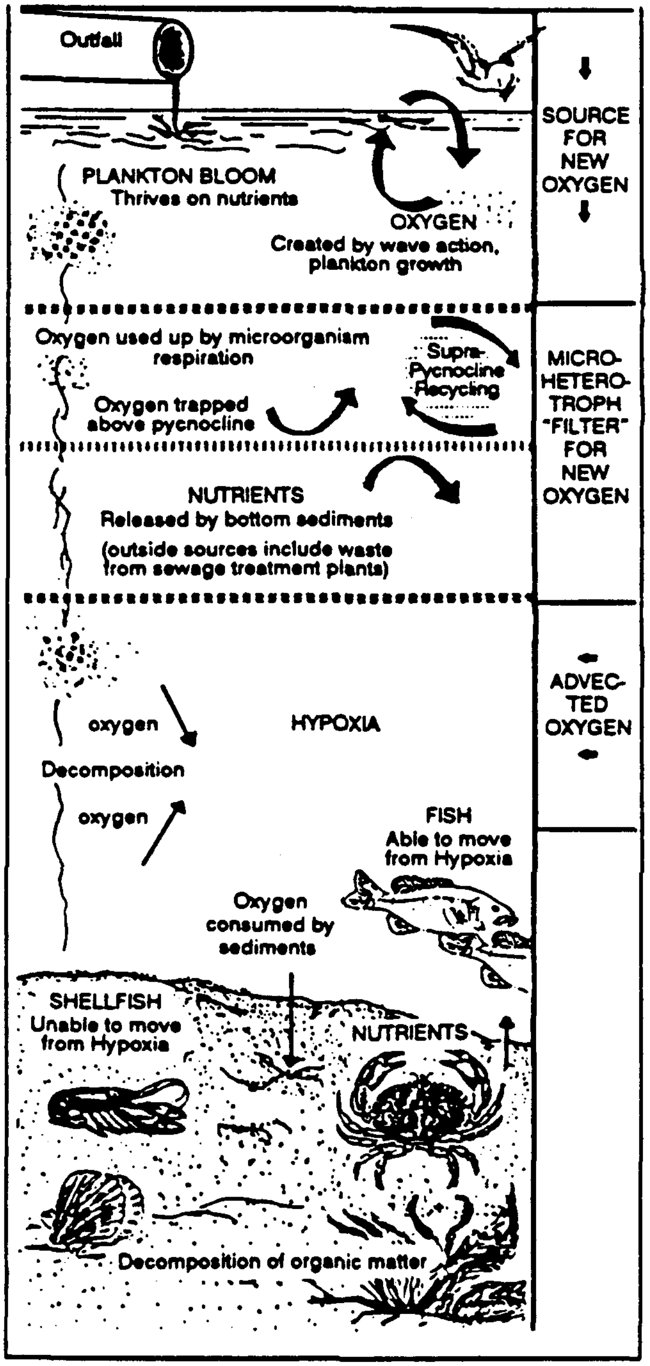


Figure 1. Schematic of the solute dynamics in shallow-water systems (Froelich et al. 1979)

Table 1

Pathways of Organic Matter Decomposition and Oxygen Consumption in Sediments

---

Aerobic Respiration

$$CH_2O + O_2 = CO_2 + H_2O$$

Nitrification and Denitrification

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+$$

$$4NO_3^- + 5CH_2O + 4H^+ = 5CO_2 + 2N_2 + 7H_2O$$

Manganese Oxidation and Reduction

$$2Mn^{++} + O_2 + 2H_2O = 2MnO_2 + 4H^+$$

$$MnO_2 + CH_2O + 4H^+ = CO_2 + 2Mn^{++} + 3H_2O$$

Iron Oxidation and Reduction

$$4Fe^{++} + O_2 + 6H_2O = 4FeOOH + 8H^+$$

$$4FeOOH + CH_2O + 8H^+ = CO_2 + 4Fe^{++} + 7H_2O$$

Sulfide Oxidation and Sulfate Reduction

$$H_2S + 2O_2 = SO_4^{=} + 2H^+$$

$$SO_4^{=} + 2CH_2O + 2H^+ = 2CO_2 + H_2S + 2H_2O$$

(Modified from Richards 1965; Stumm and Morgan 1970; and Froelich et al. 1979).

effluent problem is greater if the area surrounding a shallow body of water is densely populated.) As the plankton die and fall to the floor they decompose. The decomposition, in part, is responsible for the redox reactions.

Macrofaunal activity. There is still great debate as to if, and how much, macrofaunae may play a role in oxygen fluxes in shallow water systems (Figure 2). Generally, oxygen penetrates nearshore sediment on the order of millimetres. Macrofaunae (especially polychaetes) which are longer than a few millimetres may not affect the oxygen flux (e.g. Aller 1982; Mackin and Swider 1989). On the other hand, nonburrowing organisms that disturb the sediment-water interface can increase the oxygen flux by resuspending sediment. Aller (1982) showed that burrowing macrofaunae can have a significant effect on the concentration and flux of nutrients and can affect the zonation of electron acceptors in the sediment.

Temperature. An increase in temperature increases the metabolic rate of bacteria, increasing oxygen flux into the sediment and nutrient rates out of the sediment. For each increase of 10°C, McDonnell and Hall (1969) showed there was a doubling of biological processes.

SOD and Nutrient Flux Measurement Methods

There are four general techniques used today for measuring solute uptake in shallow water regions. The techniques are based on a concentration change with time or depth.

Nonaerated flux chamber

There are two different types of nonaerated flux chambers, one used in the laboratory (e.g. Mackin and Swider 1989) (usually a subsection from a box core or obtained by hand) and one placed *in situ* (e.g. Smith, Burns, and Teal 1972; Anderson et al. 1986; Snodgrass and Fay 1987). Both are sealed chambers (closed system) and have a known volume of overlying water and surface area of sediment. The overlying water is circulated in the chambers (e.g. stirred with a teflon-coated stir bar connected to a battery or motor) to simulate bottom conditions and to keep a chemical gradient from forming. Time series sampling is done, usually until the oxygen concentration is very near zero. Solute fluxes are measured as a difference in concentration in the overlying water with time and are calculated using

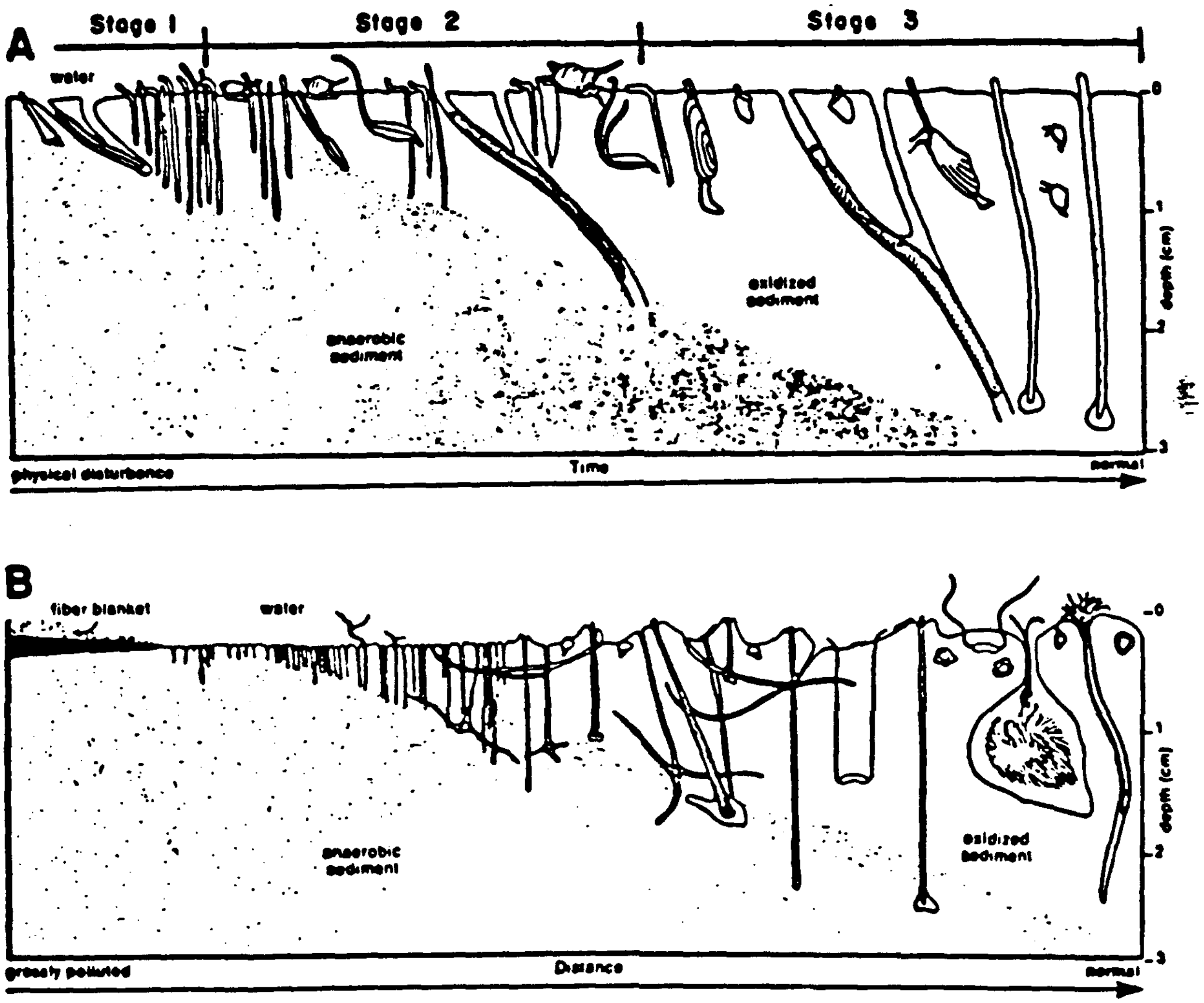


Figure 2. Stages of macrofaunal importance (from Rhodes and Germano 1982)

$$M_o = [C(t) - C_c(t-t)]V_o/A$$

where

$C(t)$ = the solute concentration at time t

$C_c(t-t)$ = the corrected solute concentration for the original solute concentration (done because the overlying water volume is constant at all times, removed sampled is replaced with water of known concentration, hence the correction)

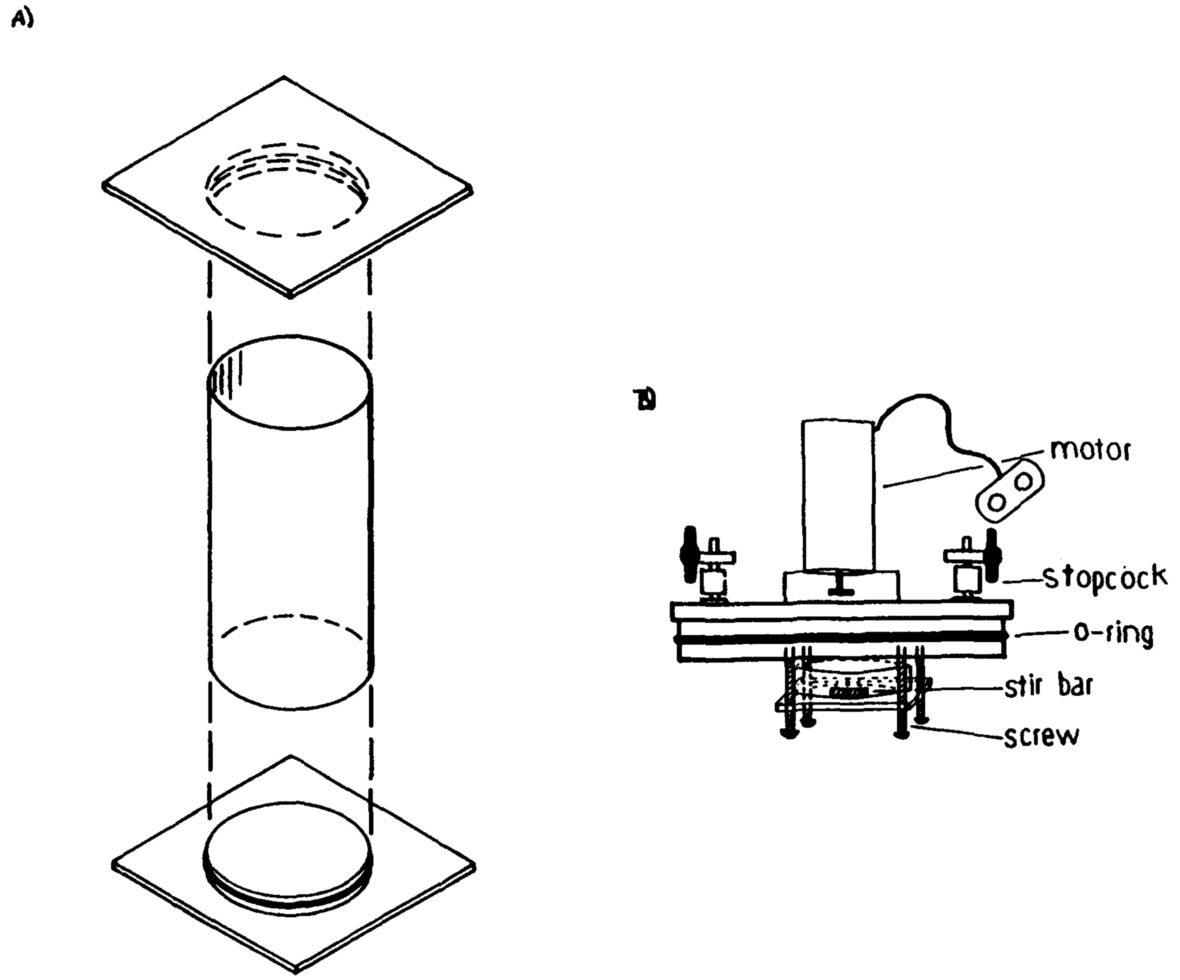
V_o = the volume of overlying water on the core

A = the cross-sectional area of the core

Although the closed systems are usually able to give accurate solute flux measurements, the systems may also produce artifacts under certain conditions. Because the nonaerated flux chambers are designed to simulate bottom conditions all parameters are thought to be taken into consideration. However, the chambers do not account for the stress placed on the macrofaunae. As there is a difference in the water flow and/or pressure, the macrofaunae may begin to adapt to the difference by changing their metabolism and, therefore, possibly affecting the solute exchange between the sediment and the overlying water. Also, the length of the experiment is dependent on the amount of oxygen available.

Laboratory nonaerated flux chambers (see example in Figure 3) require an undisturbed sediment core. The laboratory chambers are designed to make sampling easier and are kept in incubators in the dark (to inhibit photosynthesis) and at *in situ* temperatures (to help ensure correct reaction rates).

See Figure 4 for an example of an *in situ* nonaerated flux chamber. The idea is the same as that for the laboratory counterparts, but sampling is done by SCUBA or snorkeling. In place of a bottom, the chambers are open and placed to some depth in the sediment. A possible advantage of using *in situ* cores is that there may be a reduction in the amount of stress placed on the macrofaunae, leading to a more accurate reading of solute fluxes with time. Another advantage of the *in situ* cores is that the chambers can be a great deal larger and, therefore, a time series can continue for a longer period. However, the *in situ* cores are much more difficult to sample because of location.



Schematic of nonaerated flux core used for solute exchange sampling across the sediment-water interface. (A) Flux core assembly as subsampled from the box core. (B) Detail of the refitted top, which stirs the overlying water and is connected to either a 9-v battery or a d-c power supply

Figure 3. Example of laboratory flux chamber

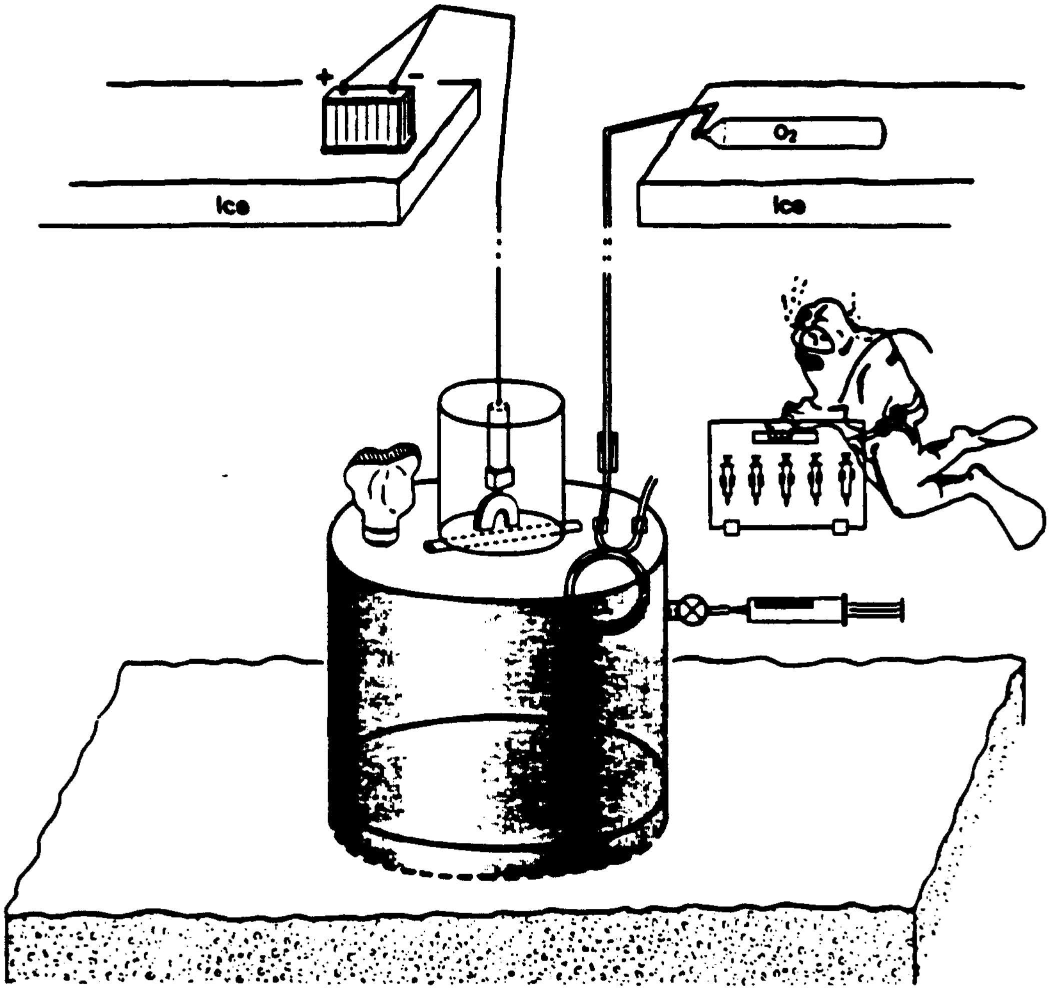


Figure 4. Example of *in situ* flux chamber (from Hall 1984)

Continuous flow chambers

Continuous flow chambers (see Figure 5) can be subsampled from a box core or obtained by SCUBA for undisturbed sediment. In addition, there have been a few experiments done *in situ*. Flow systems are open systems and have a known sediment area and a regulated continuous flow of water circulating over the sediments (e.g. Belanger 1981). Solutes are measured as the difference in solute concentration measured in the inflow water and outflow water and calculations are done. For the most part, flow chambers are used in long-term time series experiments. Many investigators prefer this system because they feel that it more closely simulates bottom and flowing stream conditions and, therefore, is easier to test different parameters under steady-state conditions. This system has also been used in determining the effect of macrofaunae on solute fluxes where intact sediment and sieved sediment have been compared. The calculation for the flow chambers, using oxygen as an example, is

$$D_r = [(DO_1 - DO_2/t) - BOD_t]V/A$$

where

D_r = net oxygen uptake rate
DO_1 = influent dissolved oxygen concentration
DO_2 = effluent dissolved oxygen concentration
t = time spent in the chambers
BOD_t = biological oxygen demand of the overlying water for a certain time t
V = volume of overlying water
A = surface area of the sediment

Again, the biggest problem is macrofaunal stress in addition to approximating bottom flow conditions.

Electrodes

Since 1980, there has been an increased use of electrodes. The electrodes are more sensitive (e.g. oxygen microelectrodes) (see example Figure 6) and can very accurately produce a high resolution profile with depth (e.g. Revsbech 1983; Andersen and Helder 1987). Electrodes determine the concentration of solutes by reducing the volume of the surrounding pore water and

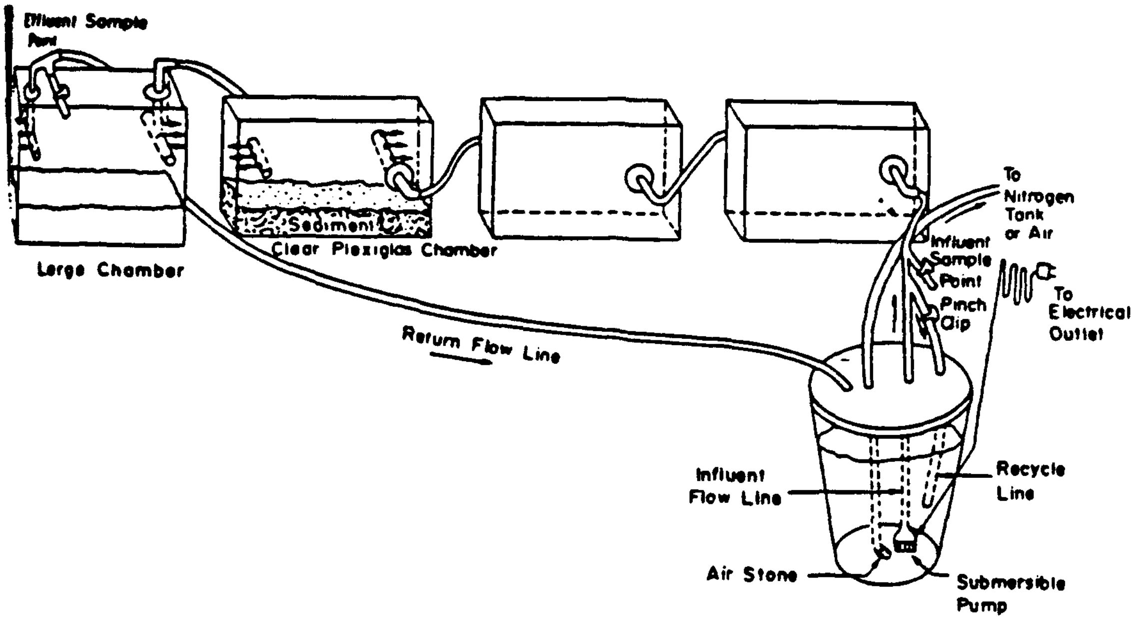


Figure 5. Example of continuous flow chamber (from Belanger 1981)

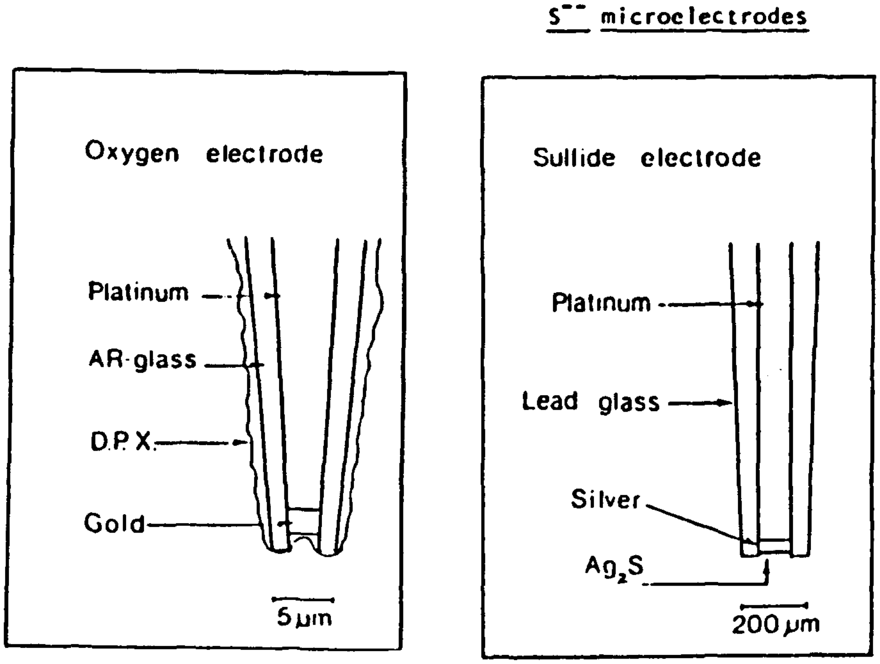


Figure 6. Example of microelectrodes (from Revsbech 1983)

measuring the voltage generated. Sedimentary solute profiles are used to calculate the flux into or out of the sediment using Fick's first law appropriately modified for sediments (Berner 1980).

$$J_{DP} = -\phi D_S(\delta C/\delta x)_{x=0}$$

where

J_{DP} = "diffusion-prediction" of the flux across the sediment-water interface

ϕ = porosity

D_S = whole sediment diffusion coefficient, calculated from
$D_s = \phi^2 D_0$ (D_0 = free solution diffusion coefficient; Ullman and Aller 1982)

C = solute concentration

x = depth below the sediment-water interface

The equation is a very good prediction of sediment-overlying water exchange when diffusion occurs by molecular motions and in the vertical dimension only. In turn, the biggest problem is that the electrodes are a measure of diffusion alone; physical processes are completely ignored. This, however, may also be an advantage because the difference can often be used to infer the extent of macrofaunal influence on a system. There seems to be a critical point when macrofaunal abundance significantly changes the flux; however, up to that point, a comparison of a time series to a diffusion predicted measurement should be statistically close. One of the major drawbacks to the electrodes is the fragility of the microelectrodes. Because the tips are between 4 and 10 microns in diameter, a small shell fragment can break the tip. Also, if the electrodes are poisoned (for example, an oxygen electrode poisoned with hydrogen sulfide) severe drifting can occur. However, once the tips have been poisoned, the electrodes seem to remain stable. Lastly, the larger electrodes (< 100 microns) are not as accurate because they tend to reduce a large portion of the pore water, not allowing for a high resolution core.

Sediment incubation techniques

There are three types of incubation techniques used, and production-reduction rates are calculated as the slope of the solute concentration versus incubation time, appropriately corrected for adsorption to sediment solids and converted to units of mass/time/total sediment volume using measured porosities. Samples are taken from a box core, retrieved by hand, or left *in situ*. In describing a system as a whole using the incubation methods, a nonsteady-state model is best. The biggest problem in using incubations is if there are large macrofaunae present. The decomposition of a polychaete, for example, makes the profile unusable. Therefore, an ideal incubation core should be as free as possible of large macrofaunae.

"Jar" or interval incubations are sediment core samples, which are sectioned into desirable intervals (e.g. 0-1, 1-2, 2-3, 3-5, 5-10 cm) (see Figure 7) and placed into centrifuge tubes (e.g. Martens and Klump 1984; Crill and Martens 1987). The tubes are then placed into a nitrogen atmosphere, at ambient temperatures, and each depth suite is sampled over a time period of weeks to months (one suite for the initial pore water profile).

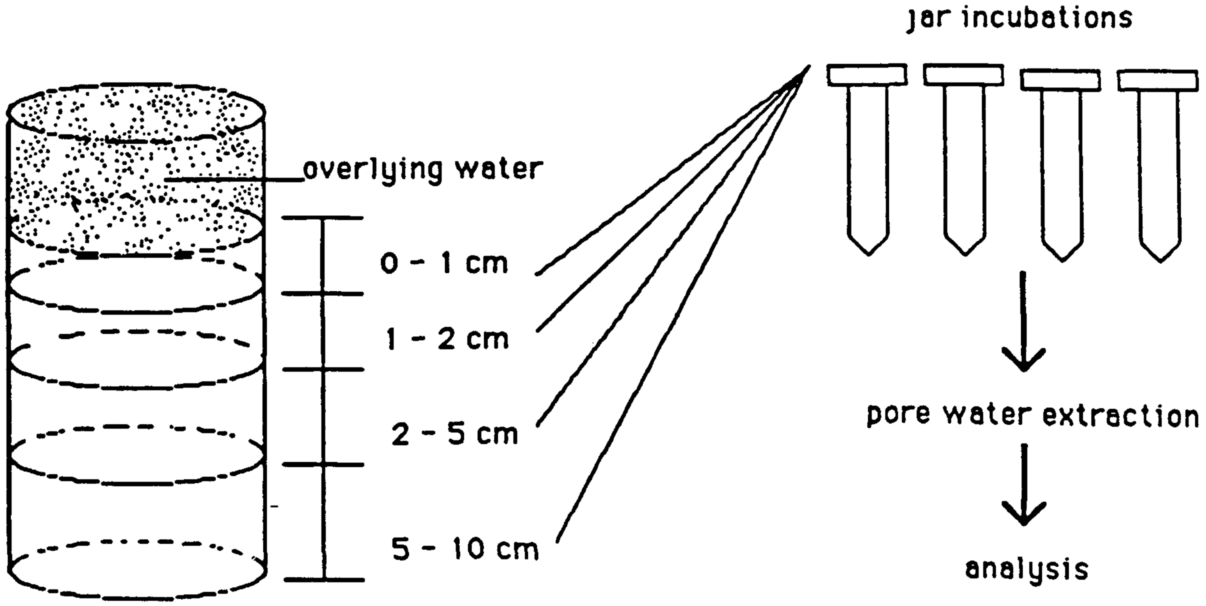


Figure 7. An anoxic "jar" incubation

"Whole core" incubations are also undisturbed sediment core samples (e.g. Aller and Mackin 1989). Once in the lab, the overlying water is removed and the ends of the core tube are sealed (using one core for the initial pore water profile) (Figure 8). The whole cores are then placed into a nitrogen atmosphere and are sampled at time periods of weeks to months. At the time of sampling, the cores are sectioned as above, centrifuged, and analyzed. The whole core method is very useful if incubation space is a limitation; there is also no time-consuming manipulation of many discrete depth intervals. Whole core incubations can also be done *in situ* or in large tank experiments. Using

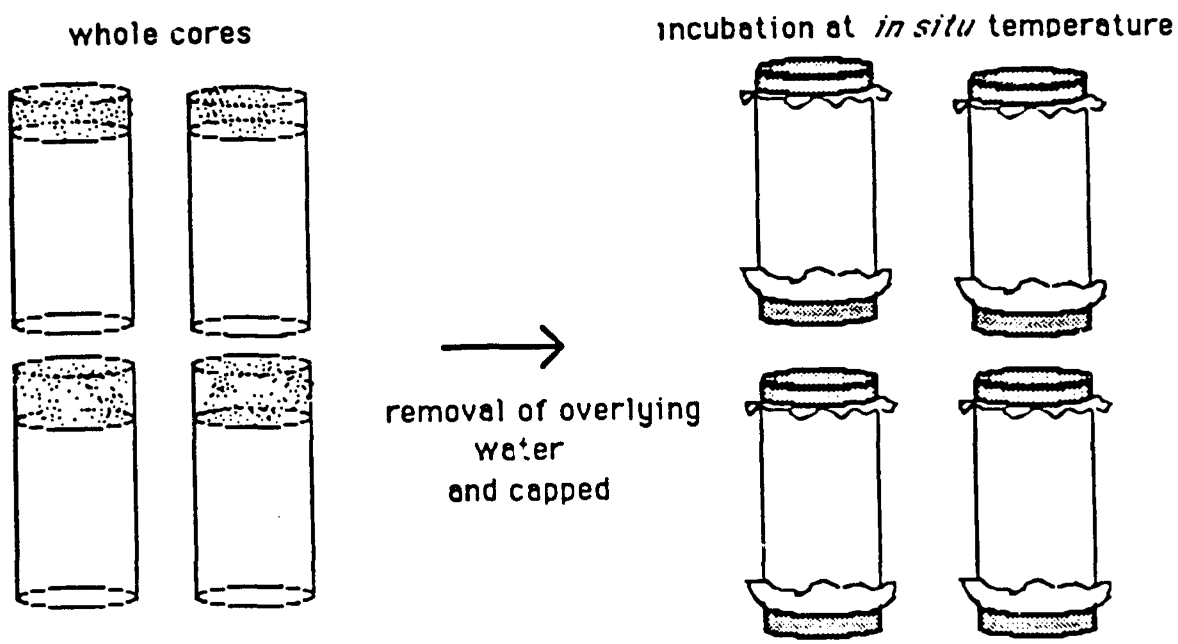
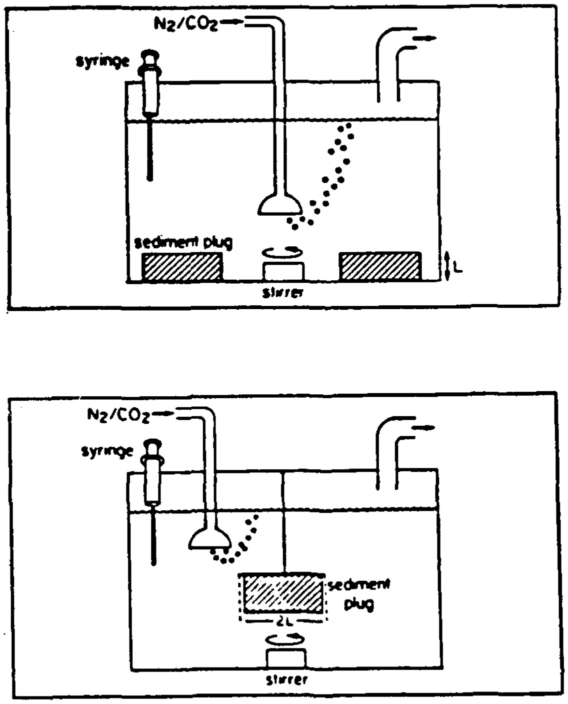


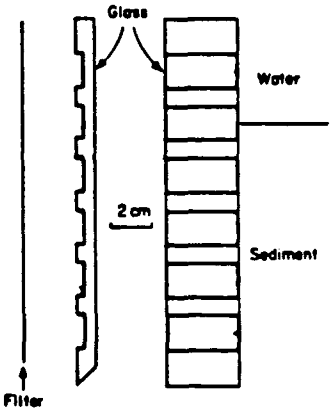
Figure 8. An anoxic "whole core" incubation

the whole core method, the depth (L) is allowed to become very large and the overlying water reservoir is virtually gone. For both methods, the change in the pore water solute profile with time allows a calculation of reaction functions. Results from the two methods are not significantly different from one another.

"Plug" incubations (Aller and Mackin 1989) expose the surface of a sediment slice of known thickness to a well-stirred water reservoir of known volume; the reservoir can either be oxic or anoxic (Figure 9a). An adaption of the plugs is the "peeper" (Figure 9b) (e.g. Mackin 1989); placed vertically in the sediment, a depth profile can be obtained. Here the two measurements are (a) the pore water solute concentration at any given time and (b) the flux of the solute into or out of the plug. Because the overlying water reservoir is stable and organic matter decomposition (a major reaction rate) changes with time, the solute concentrations will only approach steady-state. A major drawback of using the plugs is that they can be very labor intensive and the use of some membranes (which allow diffusion across the surface) may add artifacts.



a. An anoxic "plug" incubation (from Aller and Mackin 1989)



b. A "peeper" (from Mackin 1989)

Figure 9. "Plug" incubations

Early Diagenesis of Dissolved Organics

For the most part, the solute fluxes across the sediment-water interface are well understood and quantifiable. However, the entire area of organic geochemistry is still in its infancy and in need of understanding. Because little is known about the fate of dissolved organics (humic material) (Table 2) and their overall effect on the solute fluxes (especially oxygen) (Figure 10), a major effort should focus on the early diagenesis of dissolved organics.

Many of the organic compounds in marine waters are present in very small concentrations (Table 3), which are often difficult to directly identify or isolate. The rates of microbial growth and the overall use of organic matter are very dependent on the activities of enzymes and the mechanisms used to interrelate ecologically and coordinate physiologically (Jorgensen 1983; Westrich and Berner 1988).

During the past several years, different decomposition rates of organic matter have been noticed. Small dissolved molecules, such as acetate, have been noted to remineralize faster (Henrichs and Reeburgh 1987) than the biopolymers in algal detritus and, in turn, break down faster than refractory polymers such as lignins, and melanoidins (Nissenbaum and Kaplan 1972; Krom and Sholkovitz 1977; Yamamoto and Ishiwateri 1989). The specific compound classes, which have been measured in sediments (e.g. amino acids and carbohydrates, fatty acids, and hydrocarbons) (Farrington et al. 1988), often decompose as slowly as the total organic carbon (TOC) in the upper metre of coastal sediments (Meyer-Reil 1986; Sansone 1986; Henrichs and Doyle 1986).

In many sediments, a large portion of the organic matter deposited to the sediment surface is not remineralized during early diagenesis, and the preservation is mostly unknown. A major process appears to be the incorporation of organic compounds by refractory geopolymers or humic substances. However, for the most part, the composition, structure, and mechanisms for formation of the geopolymers is generally not understood (Henrichs, submitted).

A possible scheme of the early diagenesis includes the biopolymers being hydrolyzed to release soluble molecules such as free amino acids and sugars, which are, in turn, metabolized by sediment bacteria (Meyer-Reil 1986; Hatcher, Breger, and Mattingly 1980). Dissolved compounds are also adsorbed by sediment particles, and this step could be the first step in the

Table 2

Naturally Occurring Organic Substances (from Stumm and Morgan 1970)

Life Substances	Decomposition Intermediates	Intermediates and Products Typically Found in Nonpolluted Natural Waters
Proteins	$\text{Polypeptides} \rightarrow \underset{\text{amino acids}}{RCH(NH_2)COOH} \rightarrow \left\{\begin{array}{l} RCOOH \\ RCH_2OHCOOH \\ RCH_2OH \\ RCH_3 \\ RCH_2NH_2 \end{array}\right.$	NH_4^+, CO_2, HS^-, CH_4, HPO_4^{2-}, peptides, amino acids, urea, phenols, indole, fatty acids, mercaptans
Polynucleotides	Nucleotides → purine and pyrimidine bases	
Lipids		
$\left.\begin{array}{l} \text{Fats} \\ \text{Waxes} \\ \text{Oils} \end{array}\right\}$ Hydrocarbons	$\underset{\text{fatty acids}}{RCH_2CH_2COOH} + \underset{\text{glycerol}}{CH_2OHCHOHCH_2OH} \rightarrow \left\{\begin{array}{l} RCH_2OH \\ RCOOH \\ \text{shorter chain acids} \\ RCH_3 \\ RH \end{array}\right.$	CO_2, CH_4, aliphatic acids, acetic, lactic, citric, glycolic, malic, palmitic, stearic, oleic acids, carbohydrates, hydrocarbons
Carbohydrates		
$\left.\begin{array}{l} \text{Cellulose} \\ \text{Starch} \\ \text{Hemicellulose} \end{array}\right\}$	$C_x(H_2O)_y \rightarrow \left\{\begin{array}{l} \text{monosaccharides} \\ \text{oligosaccharides} \\ \text{chitin} \end{array}\right\} \rightarrow \left\{\begin{array}{l} \text{hexoses} \\ \text{pentoses} \\ \text{glucosamine} \end{array}\right\}$	HPO_4^{2-}, CO_2, CH_4, glucose, fructose, galactose, arabinose, ribose, xylose
Lignin	$(C_8H_2O)_x \rightarrow$ unsaturated aromatic alcohols → polyhydroxy carboxylic acids	
Porphyrins and Plant Pigments		
$\left.\begin{array}{l} \text{Chlorophyll} \\ \text{Hemin} \\ \text{Carotenes and} \\ \text{Xantophylls} \end{array}\right\}$	Chlorin → pheophytin → hydrocarbons	Phytane Pristane, carotenoids Isoprenoid, alcohols, ketones, acids Porphyrins
Complex Substances Formed from Breakdown Intermediates, e.g.,		
	Phenols + quinones + amino compounds →	Melanins, melanoidin, gelbstoffe
	Amino compounds + breakdown products of carbohydrates →	Humic acids, fulvic acids, "tannic" substances

Table 3

Average Concentrations of Organics in Seawater

(from Stumm and Morgan 1970)

Components	Concentration in Seawater (μg C liter^{-1})
Free amino acids	20
Combined amino acids	50 (to 100?)
Free sugars	20
Fatty acids	10
Phenols	2
Sterols	0.2
Vitamins	0.006
Ketones	10
Aldehydes	5
Hydrocarbons	5
Urea	20
Uronic acids	18
Approximate total	340 μg C liter^{-1}

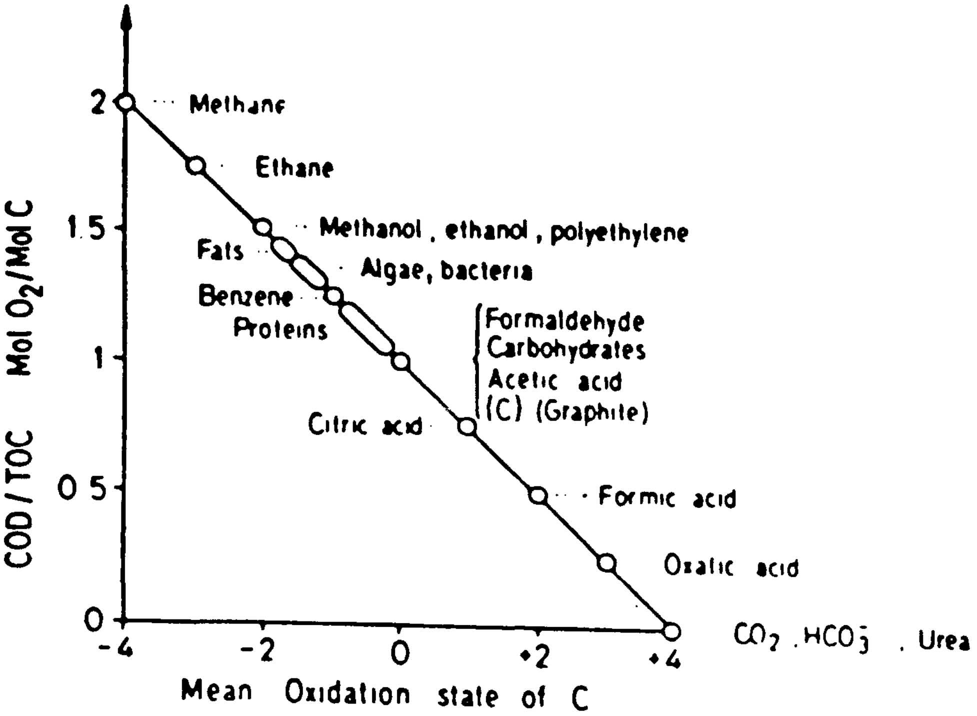


Figure 10. Oxygen demand and mean oxidation state of organic C (from Stumm and Morgan 1970)

incorporation by geopolymers (Ertel and Hedges 1983; Rubinsztain et al. 1984; Taguchi and Sampei 1986). Alternative pathways of geopolymerization could involve alteration of large molecules (e.g. proteins, polysaccharides, and triglycerides) (Hatcher, Breger, and Mattingly 1980; Hedges 1977; Gordon and Millero 1985).

Recommendations

Because of the many different factors involved in measuring the solute fluxes of a nearshore or freshwater system, a combination of techniques should be employed. For example, to obtain a good overall picture, combine a microelectrode profile with one of the other methods to give a comparison of the procedures and a better understanding of the system as a whole. Also, because most of the techniques are easy to use and relatively inexpensive (with the exception of the electrodes), a combination would only be to the advantage of the project.

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Sediment Oxygen Demand Model: Methane and Ammonia Oxidation[1]

by

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Abstract

A model of sediment oxygen demand is presented which determines the SOD from the extent of oxidation of methane and ammonia generated in the anaerobic zone of the sediment. The fluxes of dissolved methane, ammonia, methane, and nitrogen gas are also included in the model. The importance of methane and nitrogen gas fluxes and their quantitative relationship to SOD is established. This important relationship has implications both with respect to modeling SOD kinetics and for field data collection programs. Any field program that includes the measurement of SOD should also include the measurement of these gas fluxes. It is shown that the square root relationship that has been observed in experiments and in field data between SOD and sediment areal volatile solids and COD concentrations is the result of an increasing fraction of gaseous methane that escapes. The dissolved methane mass transfer coefficient and the two oxidation reaction rate parameters are estimated from laboratory and field data sets with simultaneous measurements of at least two of the modeled fluxes. The effect of overlying water, dissolved oxygen, and temperature is examined and found to conform to the model formulation. The model is limited to freshwater sediments since the oxidation of sulfides is not included. The contribution from the respiration of benthic macrofauna is also not incorporated.

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Introduction

The importance of sedimentary (or benthal) oxygen consumption in the oxygen balance of natural waters has been recognized since the beginning of the development of stream oxygen balance models (see Hatcher 1986 for historical review). The procedure was simply to measure the sediment oxygen demand (SOD) as an areal flux of oxygen to the sediment and use that consumption rate as a sink in the mass balance models. Where the contemplated control measures would not affect the SOD, this procedure is perfectly acceptable. However, most control alternatives affect the supply of organic particles to the sediment. The control of combined sewer overflows or the removal of nutrients from point sources directly reduces the supply of particulate organic matter (POM) to the sediment. Hence an important issue to be addressed in any of these studies is the effect this reduction has on the resulting SOD.

Attempts have been made to relate the SOD to the composition of the sediment itself--the expectation being that more organically rich sediments would have higher SODs. However, only weak correlations are usually found (e.g., Rolley and Owens 1967). Nevertheless, some dissolved oxygen (DO) models include a formulation where SOD is a linear function of the rate of decaying sedimentary carbon (see Porcella, Mills, and Bowie (1986) for a survey). In view of the conflicting observations of the relationship of SOD to sediment parameters, these assumptions are somewhat tenuous.

More often, models treat SOD as an exogenous variable to be externally specified. However, the flux of POM to the sediment is the terminal cause of SOD and other fluxes from the sediment. If the control measures being evaluated will significantly reduce the sediment POM flux then some quantitative connection between the POM flux, and the resulting SOD and other fluxes of concern is required for a proper analysis. The purpose of this paper is to present a model which predicts the SOD as a function of the rate of sedimentary POM decay and the transport and oxidation kinetics of methane and ammonia.

Fair, Moore, and Thomas experiment

This classical experiment, which shall be referred to as Fair et al. (1941), examined the variation of SOD in laboratory reactors as a function of sediment depth and time (Fair, Moore, and Thomas 1941). The sediment employed was a mixture of sewage sludge, sand, and diatomaceous earth. They concluded that SOD varied as approximately the one-half power of the initial areal volatile solids concentration, VS (kg/m^2) . Figure 1 illustrates the fit of the data to a square root dependency for both Fair et al. (1941) and data from Baity (1939). The relationship is $SOD = a_1\sqrt{VS}$ with a_1 a different constant for each time t after the start of the experiment.

The difficulty with applying this empirical result to natural sediments is that the dependent variable, areal volatile solids concentration in the experimental reactors, has no obvious field analog. The depth of sediment to be sampled in order to determine areal VS is undetermined. Therefore, although this work is widely known, it is not clear how the results are to be applied to field situations.

A similar relationship (Figure 1) has been observed in a set of field data from Green Bay (Gardiner, Aver, and Canale 1984). The SOD can be related to the square root of the surface sediment COD: $SOD = b_1\sqrt{COD}$ with b_1 constant. This relationship still implies a sampling depth which is difficult to specify.

In both these data sets a square root relationship is observed between SOD and measures of sediment organic matter concentration. This is quite different from the linear relationship of SOD to sediment organic carbon assumed in many DO models.

Models of the electron acceptors

A strategy that has been adopted for building models of SOD is to model only the concentration of the electron acceptors (O_2, NO_3, etc.) in the interstitial water of the sediment. The simplest model follows from assuming that the consumption of oxygen is zero order and constant with respect to depth z below the sediment-water interface (Bouldin 1968). The one-dimensional mass balance equation for DO in the interstitial water $O_z(z)$ is

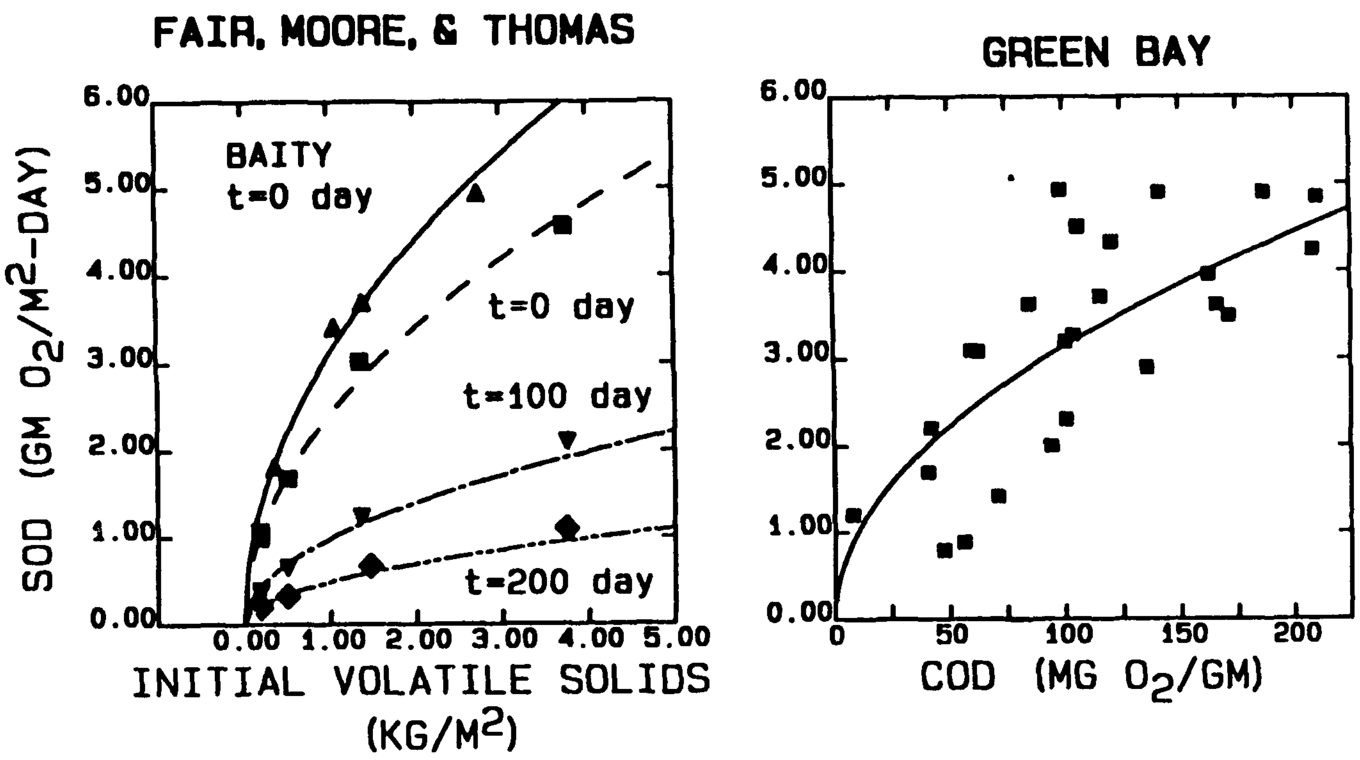

Figure 1. SOD versus initial areal volatile solids (left), Fair et al. (1941) and Baity (1938). The times t are days after the start of the experiment. SOD versus surface sediment COD (right) (Gardiner, Aver, and Canale 1984)

$$-D_{02}\frac{d^2O_2(z)}{dz^2} = R[O_2] \qquad (1)$$

where D_{02} is the diffusion coefficient for DO, and $R[O_2]$ is the zero-order consumption rate of oxygen. The solution follows from two integrations. The boundary conditions are

$$O_2(z)\,|_{z=0} = O_2(0) \qquad (2)$$

which specifies the overlying water DO concentration

$$c(L_{02}) = 0 \qquad (3)$$

which requires that the oxygen concentration is zero at the depth of the aerobic zone L_{02} ; and

$$\frac{dO_2(z)}{dz}\,|_{z=L_{02}} = 0 \qquad (4)$$

which follows from the requirement that below L_{02} the DO is zero. Since no oxygen is being consumed below $z = L_{02}$ the flux of DO at $z = L_{02}$ must be zero as well.

The flux of oxygen to the sediment is obtained from the slope of the DO profile at $z = 0$

$$SOD = -D_{02}\frac{dO_2(z)}{dz}\,|_{z=0} \qquad (5)$$

The result is (Bouldin 1968)

$$SOD = \sqrt{2D_{02}R[O_2]\,O_2(0)} \qquad (6)$$

This equation makes several interesting predictions. It requires that SOD varies as the square root of the zero-order oxygen consumption rate $R[O_2]$. If one supposes that the areal volatile solids concentration is proportional to the zero-order oxygen consumption rate, then this is just what Fair et al. (1941) found. However, this model gives no guidance for specifying or measuring the zero-order oxygen consumption rate $R[O_2]$. In fact at this level of development the model basically replaces a measurable flux, the SOD, with an unmeasurable quantity $R[O_2]$. The model also predicts that SOD should vary as the square root of the overlying water DO. As shown below, the observed variation of SOD with overlying water DO is more complicated than this model predicts.

Klapwijk and Snodgrass (1986) proposed a three-layer model where the layers are characterized by the electron acceptors used to react with the organic matter: oxygen (the aerobic layer); nitrate (the anoxic layer); and methane fermentation (the anaerobic layer). The SOD results from two reactions in the aerobic zone: the oxidation of carbonaceous reduced end products and the nitrification of ammonia to nitrate. Since zero-order sources and sinks are used, the SOD model is equivalent to Equation 6 with

$$R[O_2] = R_C[O_2] + 4.57R[NO_3] \qquad (7)$$

where $R_C[O_2]$ is the zero-order carbonaceous oxygen consumption rate and $R[NO_3]$ is the nitrification rate in the aerobic layer. The stoichiometric coefficient, 4.57 gm O_2/gm NH_4-N , is the oxygen consumed by nitrification. In order to determine $R[NO_3]$, the maximum nitrification rate, $R[NO_3]_{,max}$, is specified as a model parameter. Then the ammonia production is estimated in the aerobic, anoxic, and anaerobic layers. If this exceeds $R[NO_3]_{,max}$ then $R[NO_3] = R[NO_3]_{,max}$ and the remaining ammonia production escapes as an ammonia flux. Otherwise $R[NO_3]$ = total ammonia production, and no ammonia escapes.

The rate parameters in the model are: the aerobic carbonaceous oxidation rate $R_C[O_2]$, the maximum nitrification rate $R[NO_3]_{,max}$, and the anaerobic ammonia production rate. The use of this model requires either measurements or estimates of these three zero-order rates.

Models of interstitial water profiles

These models follow from the original models of concentration profiles in sediment interstitial water proposed by Berner (1971, 1980). Once the concentration profile is modeled the fluxes can be obtained from the slope of the profile at the benthic interface via differentiation, e.g., Equation 5.

Vanderborght, Wollast, and Billen (1977a, 1977b) proposed a two-layer model of this type. Oxygen is consumed at a zero-order rate in the upper layer and at a first-order rate in the lower layer. The model also considers the production of silica and ammonia, its nitrification to nitrate, and the consumption of sulfate. Eleven model parameters are required. Four are determined from the silica profile. The ratio of ammonia production to sulfate consumption is estimated from the reaction stoichiometry. The remaining six parameters are obtained from fitting the model to the ammonia, nitrate, and sulfate profiles. No measured interstitial water oxygen data or SOD were used to calibrate the model for the data set considered.

Similar models with zero-order (Jahnke, Emerson, and Murray 1982) and first-order (Goloway and Bender 1982) oxygen consumption rates have been proposed as part of more comprehensive nitrate reduction models for marine sediments. None appear to have been calibrated with actual SOD or interstitial water DO measurements.

Oxygen and temperature dependency

The dependence of SOD on temperature and overlying water DO has been the subject of several laboratory and field investigations (see Porcella, Mills, and Bowie 1986 for a summary). A mechanistic proposal by Walker and Snodgrass (1986) for the relationship is

$$SOD = \mu_{\beta}(T)\,\frac{O_2(0)}{K_{02} + O_2(0)} + k_c(T)\,O_2(0) \qquad (8)$$

where

$\mu_{\beta}(T)$ = the maximum biological SOD

K_{02} = the half saturation constant

$k_c(T)$ = the chemical SOD at temperature T

The latter is measured by poisoning a duplicate core and measuring the remaining oxygen uptake. This is assumed to be due to nonliving processes and is called chemical SOD. The biological SOD is the total SOD minus the chemical SOD.

Diagenesis models

A model has been proposed (Di Toro and Connolly 1980, Di Toro 1986) which focuses on the production of sediment fluxes as a consequence of the flux of particulate organic carbon to the sediment and its decomposition. The idea is to model the transport of the reduced species (i.e., the electron donors) produced by the decomposition of organic carbon (e.g., $CH_4(aq)$, HS^-, Fe^{2+}, etc.) rather than the electron acceptors (O_2, NO_3, etc.). The diagenesis reaction can be thought of as producing oxygen equivalents of various reduced species. A mass balance equation is used to compute the flux of oxygen equivalents to the sediment-water interface. It is assumed that a fraction $f_{O_2^{\cdot}}$ is oxidized to produce SOD. For situations where neither a gas phase nor solid phases are formed, and to the approximation that the diffusion coefficients of the various reduced species are equal, the identity of the reduced species produced by diagenesis is immaterial. The SOD which results from the oxidation of this flux of oxygen equivalents is

$$SOD = J_{PCOD} f_{O_2^{\cdot}} \frac{[O_2(0)]}{[O_2(0)] + \frac{5}{4}\,[NO_3(0)]} \qquad (9)$$

where J_{PCOD} is the flux of reactive particulate COD to the sediment, and $[O_2(0)]$ and $[NO_3(0)]$ are the molar concentration of DO and nitrate, respectively, in the overlying water. Increasing the overlying water nitrate concentration is predicted to decrease the SOD since denitrification consumes oxygen equivalents and reduces the flux to the sediment water interface.

The principal focus of this model is to couple SOD explicitly to the input of POM and the diagenetic reaction that makes it available for subsequent oxidation. The major weakness of the model is in not accounting for oxidation kinetics, other than including a parameter $f_{O_2^{\cdot}}$ to account for possible incomplete oxidation, and not explicitly considering ammonia oxidation.

Discussion

All the above models, except for the diagenesis models of SOD, are based primarily on modeling the transport and fate of the electron acceptors (O_2, NO_3, and SO_4) and specifying the oxidation or consumption rates as model parameters. But it is not clear how to measure or model consumption rates or how to relate them to the flux of POM to the sediment. This is a severe weakness since the causal chain starts with the input of POM to the sediment and result in sediment fluxes.

From a mass balance point of view the consequence of POM diagenesis is the generation of reduced species: CH_4, H_2S, and NH_4. Hence the model should focus on the transport and oxidation of these reduced species. The distribution and fluxes of the electron acceptors, in particular the oxygen flux, result as a consequence of these oxidations.

Perhaps the most severe shortcoming of all the models discussed above is that none take *explicit* account of methane gas formation. Methane gas flux can be a large part of the overall diagenesis, and models which attempt to relate SOD to the input of POM must account for this primary loss mechanism.

SOD Model Formulation

The focus of the model developed in this paper is the transport and oxidation of methane and ammonia and the SOD that results. The model explicitly considers methane gas formation. Oxidation of other reduced species (e.g., H_2S, FE^{2+}, and Mn^{2+}) is not considered. The reason is that no way has been found of determining how much of the diagenesis produces these chemical species as opposed to methane formation. Since the explicit consideration of H_2S and SO_4 is clearly required for marine sediments, the model presented below is restricted to freshwater sediments.

The exclusion of the other reduced species that are chemically oxidized may not be warranted in all situations. Walker and Snodgrass (1986) reported that $k_c(T)$ averaged 0.0397 m/d so that for $O_2(0) = 4$ to 8 mg/L the SOD due to nonbiological oxidation would be $k_c(T)O_2(0) = 0.16$ to 0.31 gm $O_2/m^2 \cdot day$ (Eq. 8). It appears, therefore, that the chemical (nonliving oxidation) component of SOD is important only if the biological SOD is small. In any case a sound analysis of the methane and ammonia oxidation reactions is a necessary part of any comprehensive SOD model and it may suffice for certain applications.

SOD model framework

The SOD model is based on a conventional diagenesis formulation for ammonia and methane, shown in Figure 2. The model uses a three-layer idealization of the sediment: an aerobic layer of depth L_{O2} , an anaerobic layer which is undersaturated with respect to methane solubility c_s to depth L_s , and a saturated layer to a depth H , the depth over which diagenesis is assumed to take place. Diagenesis produces ammonia and methane at zero-order rates S_N and S_C , respectively. Oxidation of ammonia and methane in the aerobic zone occurs as first-order reactions with rate constants K_N and K_C , respectively. Transport within the interstitial water is by diffusion with diffusion coefficients D_{NH4} and D_{CH4} , respectively. The analysis of this model begins with the consequences of the formation of a methane gas phase.

Methane production and maximum SOD

Stoichiometry and oxygen equivalents. Benthic fluxes of oxygen and oxygen-consuming chemicals are the terminal result of a series of reactions that begin with the diagenesis of particulate organic carbon, represented by CH_2O, and end with the formation of methane. The overall reaction in the anaerobic zone is

$$CH_2O \rightarrow \frac{1}{2}\, CO_2 + \frac{1}{2}\, CH_4 \tag{10}$$

The oxygen consumption reaction in the aerobic zone is

$$\frac{1}{2}\, CH_4 + O_2 \rightarrow \frac{1}{2}\, CO_2 + H_2O \tag{11}$$

A convenient way to quantify (1) the amount of organic material that reacts, (2) the methane produced, and (3) the oxygen consumed, is to use the oxygen equivalent of each reactant and end product. The definition of an oxygen equivalent, denoted by O_2^*, is the oxygen required for complete oxidation. The stoichiometric coefficients for the above reactions are all unity in this scheme. By contrast, if carbon units are used then 1 gm CH_2O as carbon [= 2.67 gm O_2^*] produces 1/2 gm of CH_4 as carbon [= 1/2 (5.33 gm O_2/gm CH_4-C) = 2.67 gm O_2^*] which consumes 2.67 gm of O_2. Using oxygen equivalents

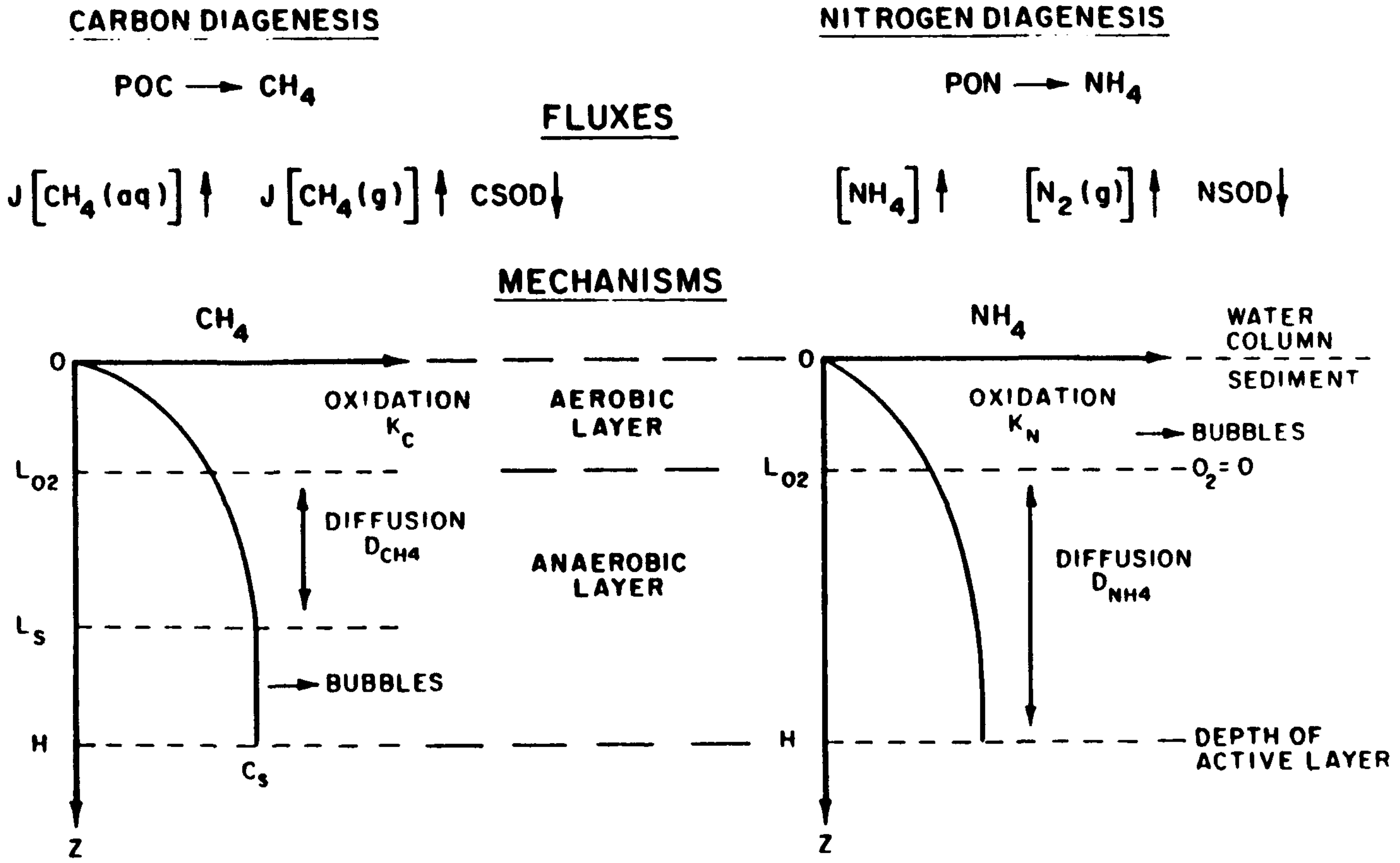

Figure 2. Schematic diagram of the SOD model. Diagenesis of POC and PON produce CH_4 and NH_4 in the interstitial water. Oxidation, diffusion, and gas phase formation combine to produce the resulting fluxes of carbon and nitrogen species to the overlying water, and the resulting SOD

simplifies the equations and expresses the concentrations in units that are appropriate for quantifying the impact on DO.

Gas phase formation. If the methane produced by diagenesis were conservative in the anaerobic layer, the only reaction of concern would be its rate of oxidation in the aerobic layer. However, methane is only slightly soluble in water. If its solubility, $c_s = 100$ mg O_2^*/L (at $T = 20°$ C), is exceeded in the interstitial water it forms a gas phase which escapes as bubbles (Reeburgh 1969; Kaplan 1974). Since this is an important sink, it is necessary to include it explicitly in the model structure.

Let S_C be the zero-order rate of carbon diagenesis in oxygen equivalents which produces methane via Equation 10. Assume that it is being produced in the active layer of the sediment with depth = H. Then the mass balance equation for the concentration of dissolved methane in the interstitial water c(z), is

$$-D_{CH4} \frac{d^2c(z)}{dz^2} = S_c \qquad 0 \le z \le L_s \tag{12}$$

where both the concentration of methane (gm O_2^*/m^3) and the diagenesis source (gm O_2^*/m^3-day) are in oxygen equivalent units. The appropriate boundary conditions are

$$c(O) = 0 \tag{13}$$

requiring the overlying water methane concentration to be zero;

$$c(L_s) = c_s \tag{14}$$

which specifies that the methane concentration reaches its solubility limit c_s at a depth L_s, the depth of methane saturation. Since the concentration of dissolved methane is constant and equal to c_s below L_s, the concentration gradient just below $z = L_s$ is zero. Hence flux continuity requires that the flux at $z = L_s$ also is zero.

$$\frac{dc(z)}{dz}\bigg|_{z=L_s} = 0 \tag{15}$$

The solution for the vertical distribution of methane, obtained by solving Equation 12, is a parabola with two arbitrary constants which are evaluated using Equations 14 and 15 to yield

$$c(z) = c_s - \frac{S_c}{2D_{CH4}}(L_s - z)^2 \tag{16}$$

The final boundary condition, Equation 13, can be used to determine the depth of methane saturation

$$L_s = \sqrt{\frac{2D_{CH4}c_s}{S_c}} \tag{17}$$

The upward flux of methane in oxygen equivalents at the sediment-water interface is

$$J[CH_4(aq)] = D_{CH4}\frac{dc}{dz}\bigg|_{z=0} = S_cL_s \tag{18}$$

which corresponds to all the methane production in the unsaturated region of the sediment: $z = 0$ to $z = L_s$. Substituting Equation 17 in Equation 18 yields

$$J[CH_4(aq)] = \sqrt{2D_{CH4}c_sS_c} \tag{19}$$

If the oxidation rate of methane in the aerobic zone were sufficiently large so that all the dissolved methane transported to the aerobic zone interface were oxidized, then the flux of dissolved methane in oxygen equivalents would be equal to the maximum carbonaceous SOD

$$CSOD_{max} = \sqrt{2D_{CH4}c_sS_c} \tag{20}$$

$CSOD_{max}$ is expressed in terms of the volumetric carbon diagenesis S_c (gm O_2^*/m^3-day). In order to relate it to the flux of carbon diagenesis

$$J_C = S_CH \tag{21}$$

it is convenient to define a diffusion mass transfer coefficient

$$\kappa_D = \frac{D_{CH4}}{H} \tag{22}$$

where H is the depth of the active sediment layer. Then the maximum carbonaceous SOD becomes

$$CSOD_{max} = \sqrt{2\kappa_Dc_sJ_c} \tag{23}$$

For small diagenesis fluxes, it is computationally the case that $CSOD_{max} > J_C$. However this is physically impossible since the maximum CSOD occurs when all the diagenesis flux J_C is being oxidized. In this case no gas phase is forming, Equation 23 is no longer valid, and

$$CSOD_{max} = J_C \tag{24}$$

for $J_c < 2\kappa_Dc_s$.

Equations 23 and 24 relate the carbon diagenesis flux J_C to the maximum CSOD. The addition of oxidation kinetics modifies the equations somewhat but their basic form is unchanged. They predict a linear dependency of CSOD on diagenesis, Equation 24, as assured in a previous model, Equation 9 (Di Toro 1986), until the formation of a methane gas phase. For larger diagenesis fluxes a square root dependence of CSOD on diagenesis flux is predicted, Equation 23.

Although Equation 23 bears a superficial resemblance to the models based on modeling oxygen diffusion, Equation 6, the square root dependency arises for a completely different reason. In Equation 6 it is the result of an oxygen mass transfer limitation since the parameter that controls is overlying water oxygen concentration, $O_2(0)$. For the model based on methane production and oxidation, however, the cause of the square root dependency is the limited solubility of methane.

Ammonia and methane oxidation kinetics

The preceding analysis examined the consequences of the formation of a methane gas phase. The kinetics of oxidation are also important. Ammonia is considered first, followed by methane.

Nitrogen stoichiometry and denitrification. Besides reduced carbon being liberated by diagenesis, ammonia nitrogen is also liberated. The oxidation of ammonia to nitrate is via the nitrification reaction

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \qquad (25)$$

If no further reaction occurred the sediment would provide a flux of nitrate to the overlying water. However denitrification can occur which reduces NO_3 to nitrogen gas. The conventional formulation is to include a layer below the aerobic layer in which denitrification occurs (Vanderborght, Wollast, and Billen 1977a, 1977b; Jahnke, Emerson, and Murray 1982; Goloway and Bender 1982). For the SOD model formulated in this paper no separate denitrification layer is included. Three sources of evidence are offered to support this formulation.

The first is the experimental results of Jenkins and Kemp (1984). An ammonia tracer, $^{15}NH_4^+$, was added to the water overlying sediment cores taken from two stations in the Patuxent River estuary in April and August. After 48 hr of incubation the partitioning of $^{15}NH_4^+$ among the nitrogen species was determined in the interstitial and overlying water. Approximately 10 to 20 percent remained as $^{15}NH_4^+$, the rest appeared either as $15N_2$ or 15PON. No appreciable $^{15}NO_3$ was observed (Jenkins and Kemp 1984, Figure 3). Their interpretation is that nitrification and denitrification occur in close spatial proximity. The suggestion (Brezonik 1977; Jorgensen 1977) is that "anoxic microsites" exist (for example, in the interior of larger organic particles), so that aerobic ($NH_4 \rightarrow NO_3$) and anoxic ($NO_3 \rightarrow 1/2\ N_2$) reactions can coexist in the same location.

The second source evidence is the consequence of assuming no denitrification in the aerobic layer. The result is that one half of the nitrate formed by the nitrification of diagenetically produced ammonia escapes as a nitrate flux to the overlying water. This can be seen by considering a simple model of nitrate in the aerobic layer. Let S_{NO3} be the source of nitrate due to ammonia oxidation. The mass balance equation for interstitial water nitrate $NO_3(z)$ is

$$-D_{NO3} \frac{d^2 NO_3(z)}{dz^2} = S_{NO3} \qquad 0 \le z \le L_{02} \tag{26}$$

The appropriate boundary conditions are $NO_3(0) = 0$ since the concern is the fate of internally produced nitrate and not the flux of nitrate from the overlying water. The simplest boundary condition at the aerobic-anaerobic boundary is

$$NO_3(L_{02}) = 0 \tag{27}$$

which corresponds to sufficiently rapid denitrification in the anaerobic zone to deplete the nitrate below $z = L_s$. The result is

$$NO_3(z) = \frac{J_{NO3} z (z - L_{02})}{2 D_{NO3} L_{02}} \tag{28}$$

where $J_{NO3} = S_{NO3} L_{02}$, the flux of nitrate due to ammonia oxidation. The flux of nitrate to the overlying water is

$$J[NO_3(aq)] = D_{NO3}\frac{dNO_3(z)}{dz}\Big|_{z=0} = \frac{J_{NO3}}{2} \qquad (29)$$

so that half of the nitrate flux produced by ammonia oxidation escapes to the overlying water. If the boundary condition at the aerobic-anaerobic boundary is $NO_3(L_{02}) > 0$, corresponding to a finite rate of denitrification in the anaerobic zone, then more than half of J_{NO3} escapes as $J[NO_3(aq)]$. No such nitrate was observed in the Milwaukee River although the sediment ammonia and nitrogen gas fluxes were substantial (SWRPC 1987).

The third source of evidence is the analysis of the measured gas flux data from the Milwaukee River which is presented below. It indicates that most if not all the nitrate produced by sediment nitrification must be denitrified to nitrogen gas. Otherwise the quantity of N_2 gas flux measured from the sediments cannot be explained.

It is assumed, therefore, that the nitrate produced in the aerobic zone of the sediment is denitrified to nitrogen gas via the reaction

$$\frac{5}{8}\,CH_4 + HNO_3 \rightarrow \frac{5}{8}\,CO_2 + \frac{1}{2}\,N_2 + \frac{7}{4}\,H_2O \qquad (30)$$

Since denitrification also consumes methane it reduces the quantity of methane that is available for direct oxidation via Equation 11. Substituting the equivalent oxygen for the methane consumed in Equation 30 and combining with Equation 25 yields

$$NH_3 + \frac{3}{4}\,O_2 \rightarrow \frac{1}{2}\,N_2 + \frac{6}{4}\,H_2O \qquad (31)$$

which is simply the oxidation of ammonia to nitrogen gas directly with a stoichiometry of $a_N = 1.714$ gm O_2 consumed per gm NH_4-N oxidized to nitrogen gas. This reaction can be thought of as the net oxidation of ammonia to N_2. If some of the NO_3 produced by nitrification is denitrified to ammonia instead of nitrogen gas, then there is no oxygen consumed and that reaction is not of concern.

The fact that ammonia is nitrified and then denitrified to nitrogen gas has an important consequence in terms of the nitrogeneous SOD. The other models discussed above account for the 4.57 gm O_2 consumed per gm NH_4^-N oxidized to nitrate. However since only the electron acceptors are considered in these models, Equation 25, and not the consumption of oxygen-demanding material, Equation 30, they compute a larger NSOD per unit of ammonia oxidized, but do not reduce the CSOD by the appropriate amount to account for the consumption of methane.

Ammonia and N_2 flux equations and NSOD. The schematization is shown in Figure 2. The mass balance equations for ammonia concentrations in the aerobic $n_1(z)$ and anaerobic $n_2(z)$ layers are

$$-D_{NH4} \frac{d^2 n_1(z)}{dz^2} = -K_N n_1 + S_N \qquad 0 \le z \le L_{02} \tag{32}$$

$$-D_{NH4} \frac{d^2 n_2(z)}{dz^2} = S_N \qquad L_{02} \le z \le H \tag{33}$$

where K_N is the first-order oxidation rate of ammonia and S_N is the zero-order rate of ammonia diagenesis production. The boundary conditions are

$$n_1(o) = 0 \tag{34}$$

which corresponds to negligible overlying water ammonia concentration compared with the interstitial waters. This is usually a reasonable simplification since interstitial water ammonia concentrations can easily exceed 5 to 15 mg NH_4-N/L (Di Toro 1986). However, no essential complication is introduced if a non-zero concentration is included.

The continuity conditions for concentration and flux at the aerobic-anaerobic layer boundary, which follow from the requirements of mass balance at the interface, yield

$$n_1(L_{02}) = n_2(L_{02}) \tag{35}$$

$$-D_{NH4}\frac{dn_1(z)}{dz}\Big|_{z=L_{02}} = -D_{NH4}\frac{dn_2(z)}{dz}\Big|_{z=L_{02}} \tag{36}$$

A zero ammonia flux condition at $z = H$ corresponds to the assumption that no ammonia is being produced below H, the depth of the active sediment layer

$$-D_{NH4}\frac{dn_2(z)}{dz}\Big|_{z=H} = 0 \tag{37}$$

The ammonia flux to the overlying water, $J[NH_4] = D\ dn_1/dz$ at $z = 0$, that results from the solution of these equations is

$$J[NH_4] = S_N(H - L_{02})\ sech\ (\lambda_N L_{02}) + \frac{S_N}{\lambda_N}\tanh\ (\lambda_N L_{02}) \tag{38}$$

where

$$\lambda_N = \sqrt{\frac{K_N}{D_{NH4}}} \tag{39}$$

and

sech(x) = 1/cosh(x) = 2/[exp(x) + exp(-x)] and

tanh(x) = [exp(x) - exp(-x)]/[exp(x) + exp(-x)], the usual hyperbolic functions.

An important simplification is possible because the depth of the aerobic layer L_{02} is usually small compared with the depth of the active sediment layer H. For this case the contribution of S_N in Equation 32 can be ignored when solving for n_1. The result is

$$J[NH_4] = J_N \,\mathrm{sech}\, (\lambda_N L_{02}) \tag{40}$$

where $J_N = S_N H$, the ammonia diagenesis flux. The equation for the flux of nitrogen gas $J[N_2]$ follows from the mass balance requirement
$J_N = J[NH_4] + J[N_2]$, i.e

$$J[N_2] = J_N\{1 - \mathrm{sech}\, (\lambda_N L_{02})\} \tag{41}$$

and the nitrogeneous sediment oxygen demand, NSOD, is the oxygen consumed in the process of oxidizing ammonia to nitrogen gas

$$NSOD = a_N J_N\{1 - \mathrm{sech}\, (\lambda_N L_{02})\} \tag{42}$$

where $a_N = 1.714$ g O_2/gm NH_4-N, the oxygen stoichiometry of the reaction, Equation 31.

Methane flux equations. The methane flux equations are similar to Equations 32 to 36 for the ammonia flux with Equation 37 replaced by Equation 14. For the simplification used above ($L_{02} \ll H$) the results for the dissolved $J[CH_4(aq)]$ and gaseous $J[CH_4(g)]$ methane fluxes are

$$J[CH_4(aq)] = \sqrt{2\kappa_D C_s J_C}\, \mathrm{sech}\, (\lambda_C L_{02}) \tag{43}$$

$$J[CH_4(g)] = J_C - \sqrt{2\kappa_D C_s J_C} \tag{44}$$

where

$$\lambda_C = \sqrt{\frac{K_C}{D_{CH4}}} \tag{45}$$

K_C is the first-order rate constant for methane oxidation and κ_D is the dissolved methane mass transport coefficient, Equation 22. The carbonaceous sediment oxygen demand, CSOD, is

$$CSOD = \sqrt{2\kappa_D c_s J_c}\,\{1 - \operatorname{sech}\,(\lambda_c L_{02})\} \tag{46}$$

If $J_c < 2\kappa_D c_s$, then the square root expression is replaced with J_C. Note that

$$J_c = J[CH_4(g)] + J[CH_4(aq)] + CSOD \tag{47}$$

so that diagenetically produced CH_4 either escapes as gas, or as unoxidized dissolved flux, or it is oxidized.

Total sediment oxygen demand

DO mass balance equation. In order to complete the model it is necessary to compute the vertical distribution of DO so that the flux of DO to the sediment can be determined. The DO mass balance equation is

$$-D_{02}\,\frac{d^2O_2(z)}{dz^2} = -a_N K_N n_1(z) - K_c c(z) \tag{48}$$

The solution is straightforward, requiring two integrations of the right-hand side forcing functions. Equations 2 and 4 are used to evaluate the two arbitrary constants and Equation 3 can be solved for L_{02}.

Figure 3 presents an example of the interstitial water profiles of ammonia, methane, and dissolved oxygen computed using Equations 32 and 33, the analogous methane equations, and Equation 48. The top panels are for the top millimetre of the sediment. The bottom panels are for the full depth of the active sediment layer. The solutions for ammonia and methane as conservative substances are shown as dotted lines. Note that the nonconservative solutions are quite different in the aerobic zone but not in the deeper portions of the sediment. It is for this reason that Equation 17 can still be used for computing the depth of methane saturation L_s. The most important feature of

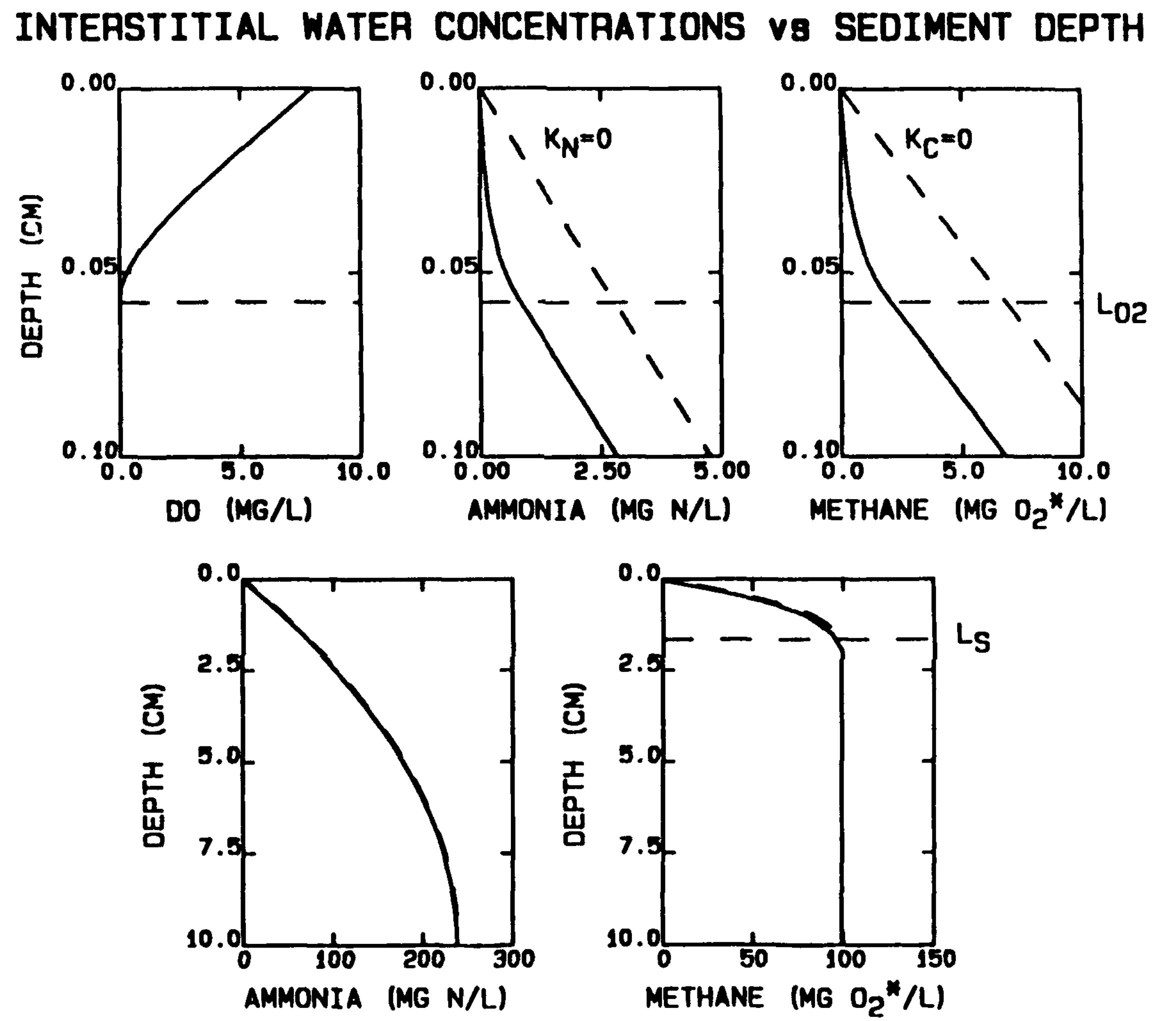

Figure 3. Interstitial water concentration profiles of DO, ammonia, and methane versus depth from $z = 0$ to $z = 0.10$ cm (top) and from $z = 0$ to $z = 10$ cm (bottom). Dashed lines are for $K_N = K_c = 0$. Aerobic zone depth L_{o2} and depth of methane saturation L_s are shown. Parameter values are given in Table 1

these solutions is the almost linear decrease of DO with respect to sediment depth in the aerobic layer. This observation is employed in the next section.

Depth of the aerobic zone. The total SOD is the gradient of the interstitial water DO concentration at the sediment water interface. The numerical solution in Figure 3 suggests that the DO profile can be approximated by a straight line so that

$$SOD = D_{02} \frac{dO_2}{dz} \Big|_{z=0} \approx D_{02} \frac{O_2(0)}{L_{02}} \tag{49}$$

This relationship has been suggested on many occasions (apparently first by Grote 1934--quoted by Hutchinson 1975) and verified by more recent measurements (Revsbech, Sorensen, and Blackburn, 1980; Jorgensen and Revsbech 1985). The utility of this equation is that it directly establishes the depth of the aerobic zone

$$L_{02} = D_{02} \frac{O_2(0)}{SOD} \tag{50}$$

which can be used in Equations 40 to 46 so that

$$\lambda_C L_{02} = \left(\sqrt{\frac{K_C}{D_{CH4}}}\right)\left(D_{02} \frac{O_2(0)}{SOD}\right) = \sqrt{K_C \frac{D_{02}^2}{D_{CH4}}}\left(\frac{O_2(0)}{SOD}\right) \tag{51}$$

$$\lambda_N L_{02} = \left(\sqrt{\frac{K_N}{D_{NH4}}}\right)\left(D_{02} \frac{O_2(0)}{SOD}\right) = \sqrt{K_N \frac{D_{02}^2}{D_{NH4}}}\left(\frac{O_2(0)}{SOD}\right) \tag{52}$$

The terms in the square root suggest the definitions

$$\kappa_C = \sqrt{K_C \frac{D_{02}^2}{D_{CH4}}} \tag{53}$$

$$\kappa_N = \sqrt{K_N \frac{D_{02}^2}{D_{NH4}}} \tag{54}$$

for the methane and ammonia oxidation parameter groups, respectively. The dimension (length per time) suggests that these parameters be termed reaction velocities.

SOD equation. Using these definitions and adding Equations 42 and 46 yields the final SOD model equation

$$\begin{aligned} SOD = \sqrt{2\kappa_D c_s J_c}\left\{1 - \operatorname{sech}\left(\kappa_c \frac{O_2(0)}{SOD}\right)\right\} \\ + \frac{a_N}{a_R} J_c \left\{1 - \operatorname{sech}\left(\kappa_N \frac{O_2(0)}{SOD}\right)\right\} \end{aligned} \tag{55}$$

The square root is replaced by J_C if $J_C < 2\kappa_D c_s$.

The first term on the right-hand side of Equation 55 is the CSOD, the second term is the NSOD. The ratio $a_R = J_C/J_N$ is the carbon (in oxygen equivalents) to nitrogen produced by diagenesis. It can be estimated from the Redfield ratio (Redfield, Ketchum, and Richard 1963) from which $a_R = 5.68$ gm C/gm N $= 15.2$ gm O_2^*/gm N .

Equation 55 has SOD on both sides of the equation. A simple iterative solution using back substitution has been found to be a satisfactory solution technique. A convenient starting value is $SOD_{max} = CSOD_{max} + a_N/a_R\ J_C$ corresponding to complete oxidation of methane and ammonia in the aerobic layer.

The four model parameters are: the carbon diagenesis flux J_C ; the dissolved methane mass transfer coefficient κ_D , and the two reaction velocities κ_c and κ_N . Note that the depth of the active sediment layer H is not an explicit model parameter. It is included in the definition of κ_D , Equation 22, but it is not explicitly required since the diagenesis sources are expressed as fluxes. The methane saturation concentration c_s is computed from

Table 1

Comparison of Exact and Approximate Solutions for SOD

J_c gm O_2^*/m^2-day	SOD gm O_2/m^2-day Approximate	Exact	Error (%)
	$\kappa_c = 0.5$ m/day		
1.00	0.637	0.633	-0.642
2.00	0.948	0.952	0.439
5.00	1.550	1.625	4.652
10.00	2.170	2.381	8.866
20.00	2.968	3.401	12.752
50.00	4.363	5.244	16.795
100.00	5.731	7.073	18.974
	$\kappa_c = 2.0$ m/day		
1.00	0.639	0.636	-0.475
2.00	0.970	0.965	-0.460
5.00	1.717	1.720	0.201
10.00	2.601	2.666	2.440
20.00	3.759	4.017	6.416
50.00	5.652	6.427	12.060
100.00	7.354	8.697	15.445

Other parameters: $\kappa_N = 0.8$ m/d ; $O_2(0) = 8.0$ gm/m^3 ; $\kappa_D = 0.139$ cm/day ; $c_s = 99$ gm O_2^*/m^3 ; $H = 10$ cm.

$$c_s = 100\left(1 + \frac{H_0}{10}\right)(1.024)^{(20-T)} \qquad (56)$$

for c_s in gm O_2^*/m^3 . H_0 (metres) is the depth of the water column over the sediment which corrects for the in situ pressure, and T is the sediment temperature in °C. This equation is within 3 percent of the reported methane solubility between 5° and 20° C (Yamamoto, Alcauskas, and Crozier 1976).

Accuracy of the approximation. The effect of the linear approximation on the accuracy of SOD computation is shown in Table 1. The exact SOD is obtained from analytical solutions of the mass balance equations Equations 32 and 33, the analogous methane equations, and Equation 48. A numerical procedure is used to solve Equation 3 for L_{02} . For all cases examined the error is never greater than 20 percent and for most of the cases the error is below

15 percent. As the approximate equations are much more convenient and intelligible, they are preferable unless high accuracy solutions at large SODs are required for some other reason. Both the exact and approximate equations conserve mass exactly so that this is not a criterion for choice.

Flux of the other components. The equations for the ammonia and dissolved methane fluxes are

$$J[NH_4] = \frac{J_C}{a_R} \operatorname{sech}\left(\kappa_N \frac{O_2(0)}{SOD}\right) \tag{57}$$

$$J[CH_4(aq)] = \sqrt{2\kappa_D C_s J_C} \operatorname{sech}\left(\kappa_C \frac{O_2(0)}{SOD}\right) \tag{58}$$

The equivalent dissolved nitrogen gas flux $J[N_2(aq)]$ is ignored since surface waters are almost completely saturated with respect to nitrogen gas (the atmosphere is 78 percent nitrogen gas) so that very little N_2 production is required to saturate the interstitial waters. Hence the production of N_2 via denitrification is assumed to immediately partition into the gas phase. The gas fluxes of methane and nitrogen are

$$J[CH_4(g)] = J_C - \sqrt{2\kappa_D C_s J_C} \tag{59}$$

$$J[N_2(g)] = \frac{J_C}{a_R}\left\{1 - \operatorname{sech}\left(\kappa_N \frac{O_2(0)}{SOD}\right)\right\} \tag{60}$$

and the total gas flux (L/m^2-day) is

$$J_{GAS} = 22.4\left(\frac{\frac{1}{2}J[CH_4(g)]}{32} + \frac{\frac{1}{2}J[N_2(g)]}{14}\right) \tag{61}$$

where one mole of gas = 22.4 litres, the molecular weights are for O_2 and N_2 as N are 32 and 14, respectively, and the coefficients of one half are from Equations 10 and 31.

Data Analysis

Sediment dilution experiment

The SOD model makes a specific prediction for the relationship between diagenesis flux J_C and SOD. It should be linear for small diagenesis fluxes and approximately a square root relationship for larger fluxes. In order to perform a direct test, it is necessary to design an experiment in which the diagenesis flux can be varied systematically and the SOD observed.

The use of different depths of sediments--as was done by Fair et al. (1941)--was not chosen because another experimental variable, sediment depth, varies together with diagenesis flux. Instead, a dilution procedure was employed. A sediment sample from the Milwaukee River was diluted with clean sand to produce a sequence of sediments with known relative amounts of reactive organic matter. The diagenesis fluxes for these sediments are, therefore, in proportion to the fraction of active sediment they contain.

Methods and materials. The SOD reactor vessels consisted of plexiglass cylinders (12.7 cm high by 7 cm in diameter) with an inflow and outflow tube connected 1 cm below the top of the reactor (Mueller and Jin-lung Su 1972). The reactor lids were plexiglass plates with an annular ring the size of the reactor walls machined into its surface to improve the seal and a hole the size of a dissolved oxygen probe drilled off center to provide access for making dissolved oxygen measurements. A magnetic spin bar was supported in a small plastic cage that was attached to the underside of the lid. This caged spin bar was used to mix the supernatant water when the reactor was sealed.

Surface sediment samples were collected with an Ekmann dredge from an area in Milwaukee Harbor known to have high sediment gas evolution rates. The samples were iced and transported to the laboratory within 24 hr. At the laboratory the samples were mixed to insure homogeneity and twigs and large gravel were removed. Serial dilutions of sediment mixed with acid washed, baked sand were then placed in the SOD reactor vessels to a depth of approximately 6 cm. The dilution fractions were computed from the ratio of the wet weight of active sediment that was added to each vessel to the wet weight that was added to the 100 percent sediment reactor. Clean sand was added to bring the total volume to about 250 mL in each reactor.

After the sediment-sand mixtures were added to the reactors, deionized water that had been passed through a carbon column was pumped through them at a rate of 3 to 4 mL/min using a peristaltic pump. The supernatant waters were aerated with an air stone diffuser during this period of flow-through operation. After several volume displacements of the overlying water the air stones were removed and time zero samples collected. Makeup water was then added from the feed source, the inflow and outflow lines were closed, and the reactor lids were sealed in place. Dissolved oxygen measurements were subsequently made over time to compute the SOD. Ammonia samples were collected to compute the ammonia flux over the duration of both the aerobic and anaerobic periods. The reactor lids were sealed with a rubber stopper between probe readings. Following the time of dissolved oxygen depletion, the volumetric gas generation rate in the sealed reactors was measured by the volume of water displaced into covered beakers.

Results. The results of two replicated experiments are shown in Figure 4. The initial linear behavior is shown in the inset. The dotted line is the extrapolated linear dependency. The model results, the solid lines, are computed from the SOD model, Equation 55. The diagenesis flux is in proportion to the quantity of active sediment in each reactor. Table 2 lists the parameters estimated from the nonlinear least squares fit to these data (Marquardt 1956).

The nonlinear (approximately square root) relationship between SOD and diagenesis flux is clearly confirmed by the results. The fact that the lowest experimental SOD value is slightly larger than the linear relationship may be due to a small residual organic carbon in the sand that was not removed by the cleaning procedure. Since the active sediment concentration for this SOD is 1 percent, a small contamination could add a significant additional diagenesis flux.

Calibration using paired fluxes

Plotting related fluxes against each other is a commonly used technique to analyze sediment nutrient and oxygen fluxes (Nixon, Oviatt, and Hale 1975). It happens that this procedure is ideally suited for analyzing data using the SOD model.

The fundamental relationship in the SOD model is between the diagenesis flux and the resulting benthic fluxes. It would seem, therefore, that in

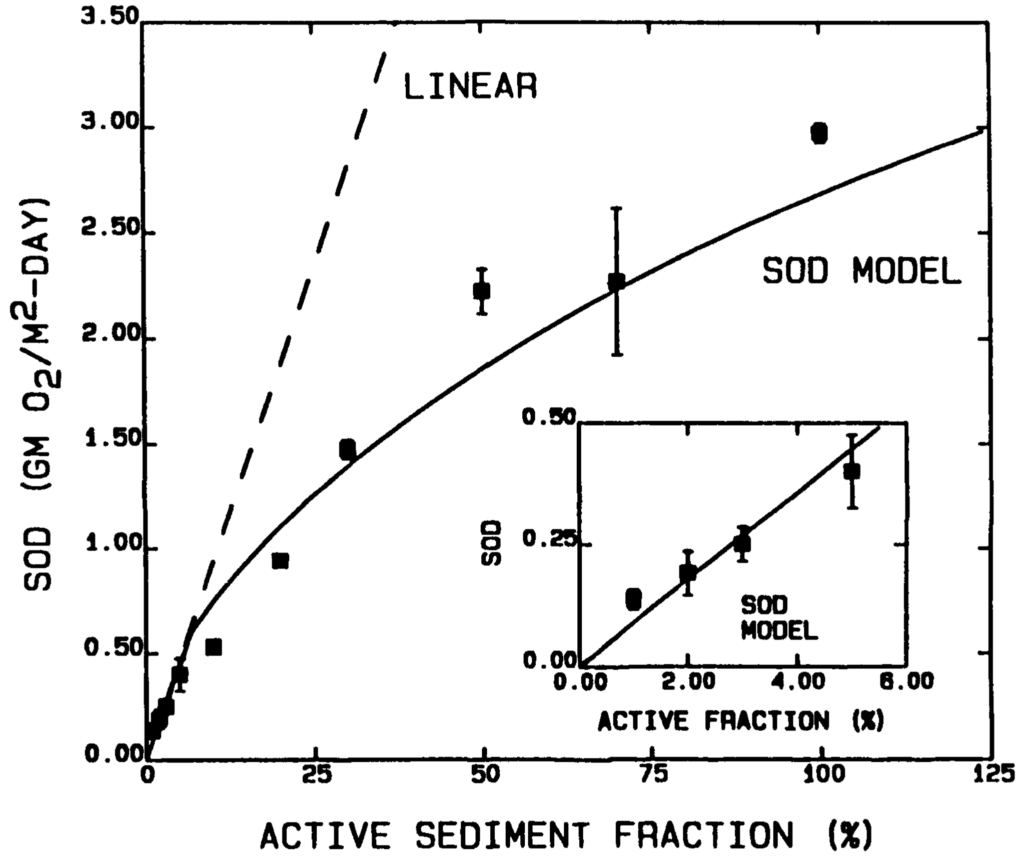

Figure 4. Results of the sediment dilution experiment. Solid lines are computed from SOD model, Equation 55. Parameters are listed in Tables 2 and 3. Dashed line is an extrapolation of the linear portion of the model result, shown in the inset figure

Table 2

Kinetic and Transport Parameter Estimates

(Standard Error of the Estimate in Parentheses)

Data Source	κ_C (m/d)	κ_N (m/d)	κ_D (cm/d)	θ_N, θ_C	J_C gm O_2*/m -d	Reference
Lab Reactor Sewage Sludge	0.839 (0.19)^a	0.894 (0.097)^a	0.268 (0.024)^a	-	-	Fair, Moore, and Thomas (1941)
Sediment Dilution Experiment	>2.0	0.894^b	0.268^b	-	8.0^a	This Work
Milwaukee River	0.575 (0.156)^a	0.897 (0.151)^a	0.139 (0.047)^a	1.079 (0.031)	-	This Work
Eel Pond	>2.0	0.393 (0.141)	0.301 (0.177)	1.079^b	-	Rowe et al. (1975)
Potomac River						Callendar and Hammond (1982)
Saginaw River						Chiaro and Burke (1980)
Laboratory Reactor						Fillos and Swanson (1975)
River Ivel	0.519 (1.54)	0.879^b	0.139^b	-	32.4 (48.2)	Edwards and Rolley (1965)
River Gade	2.60 (0.64)	"	"	-	41.6 (3.2)	" "
River Hiz	2.93 (0.62)	"	"	1.079^b	31.4 (2.4)	" "
Spring Lake	4.75 (1.40)^a	"	"	"	22.2 (1.9)^{a,c}	McDonnell and Hall (1969)
Lake Erie	0.409 (0.77)^a	"	"	"	10.9 (29)^{a,d}	Davis and Herdendorf (1986)
Hamilton Harbor	1.41 (0.67)^a	"	"	"	10.4 (4.4)^{a,d}	Polak and Haffner (1978)

[a] At 20° C.

[b] Parameter value is assumed.

[c] Estimated θ_c = 1.122 (0.015) .

[d] Assumed θ_c = 1.1.

order to estimate the model reaction velocities and mass transport coefficient it is necessary to have an independent measurement of the diagenesis flux. However the model not only relates the SOD to the diagenesis flux but it also predicts dissolved, $J[CH_4(aq)]$, $J[NH_4]$, and gaseous, $J[CH_4(g)]$, $J[N_2(g)]$, fluxes as well. Thus any set of laboratory or field measurements that determines any two of these fluxes can be used to calibrate the model parameters.

The diagenesis flux J_C can be expressed in terms of one of the measured fluxes. For example, the methane gas flux can be used, Equation 59. The total gas flux, Equation 61, can also be used to solve for the diagenesis flux by substituting Equation 60 for $J[N_2(g)]$. Either of these expressions can be substituted for J_C in Equation 55. The result is a relationship between SOD and either methane or total gas flux.

It is important to note that the relationship between any two fluxes is independent of the magnitude of the diagenesis flux. It depends only on the parameters that apportion the total methane and ammonia fluxes to SOD and dissolved and gaseous fluxes. Although the diagenesis flux is determined as part of the computation, the relationships between the fluxes are controlled entirely by the reaction velocities κ_c and κ_N and the mass transfer coefficient κ_D . Hence it is not necessary to have an independent estimate of the diagenesis flux in order to calibrate the model. In order to use the model to predict SOD, however, the diagenesis flux is required.

For data sets with reported gas fluxes the model is calibrated as follows. The three parameters to be estimated are reaction velocities κ_C and κ_N and the mass transfer coefficient κ_D . The κ_C and κ_D determine the CSOD and the methane fluxes; κ_N determines the NSOD, ammonia, and N_2 fluxes. Given a measured gas flux it is possible to solve either Equation 59 or Equations 59 to 61 for the diagenesis flux. This can then be used in the other flux equations, Equations 55, 57, and 58, to predict SOD, ammonia, and dissolved methane fluxes. A nonlinear least squares procedure (Marquardt 1956) is employed to estimate the reactions velocities. For the more restricted data sets certain of the parameters are fixed.

SOD, ammonia, and gas fluxes--Laboratory data. The Fair et al. (1941) experiment varied depth and examined fluxes over time. Estimates of the SOD and gas fluxes were made at $t = 20$ days , which corresponds to the initiation of the gas flux measurements, and at $t = 30$, 50, 75, and 100 days after the start of the experiment. The ammonia fluxes are geometric means of slopes estimated by differences from the reported data. Figure 5 presents the SOD

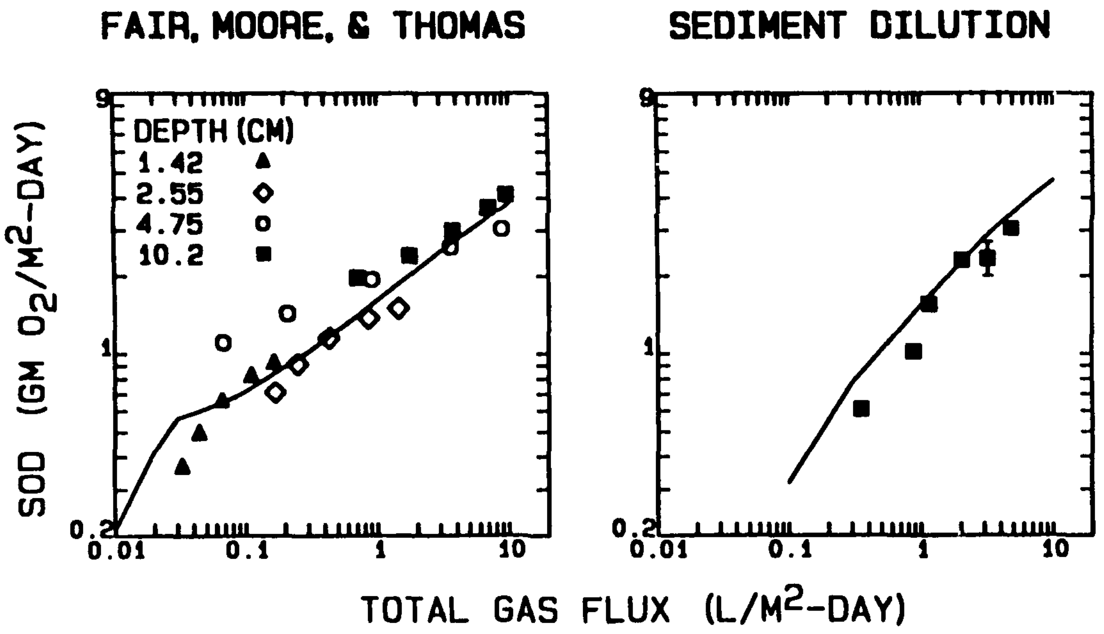

Figure 5. SOD versus total gas flux for the Fair et al. (1941) data (left) and the sediment dilution experiment (right). Lines are computed using Equations 55 and 59 to 61. Parameter values are given in Tables 2 and 3

versus total gas flux data from Fair et al. (1941) and for the sediment dilution experiment discussed above. The lines are computed from Equations 55, 59, 60, and 61 with the parameters listed in Table 2.

The Fair et al. (1941) data are remarkable in the following respect. Even for the wide range of depths employed for the reactors (1.42 to 10.2 cm) and the wide range of observed gas fluxes over the duration of the experiment (0.03 to 10 L/m^2-day), the relationship between SOD and gas flux is remarkably consistent. No depth effect is evident. It is these data, the sediment dilution experimental results, and a similar although less direct finding for the Milwaukee River field data discussed below, that prompted the definition of the mass transfer coefficient κ_D which appears to be constant, independent of the depth of the active diagenesis layer H . It is for this reason that H plays no role in the SOD model.

Figure 6 presents the ammonia flux versus total gas flux observed in these experiments and the model computation using Equations 57 and 59 to 61. The fits are not very satisfactory although for the sediment dilution experiment the ammonia flux fits reasonably well to the aerobic flux prediction. The experiment was done in such a way that the ammonia flux cannot be uniquely associated with either aerobic or anaerobic conditions since during the observation period the oxygen in the reactor was depleted.

Field data - Milwaukee River. As part of an investigation of the effects of combined sewer overflows in the Milwaukee River (SWRPC 1987) an extensive set of simultaneous field observations of SOD and gas fluxes was collected (Gruber et al. 1987). It is this data set that initiated the development of the model presented above. The relationship of SOD and gas composition versus total gas flux is shown in Figure 7. The SOD-total gas flux relationship is similar to the Fair et al. (1941) and sediment dilution experiments, Figure 5: a total gas flux of 1 L/m^2-day corresponds to an SOD of approximately 1 gm O_2/m^2-day in the three data sets.

The SOD and gas composition data are used to estimate the reaction velocities and mass transfer coefficient using a nonlinear least squares regression (Marquardt 1956). The individual *in situ* DO and temperature and water column depth at each station are used in the computation. The latter parameters are important since the saturation concentration of methane is a function of both temperature and pressure, Equation 56. It happens that it is possible to estimate the temperature dependency of κ_C and κ_N as well (assumed to be equal since it was not possible to discriminate between the two

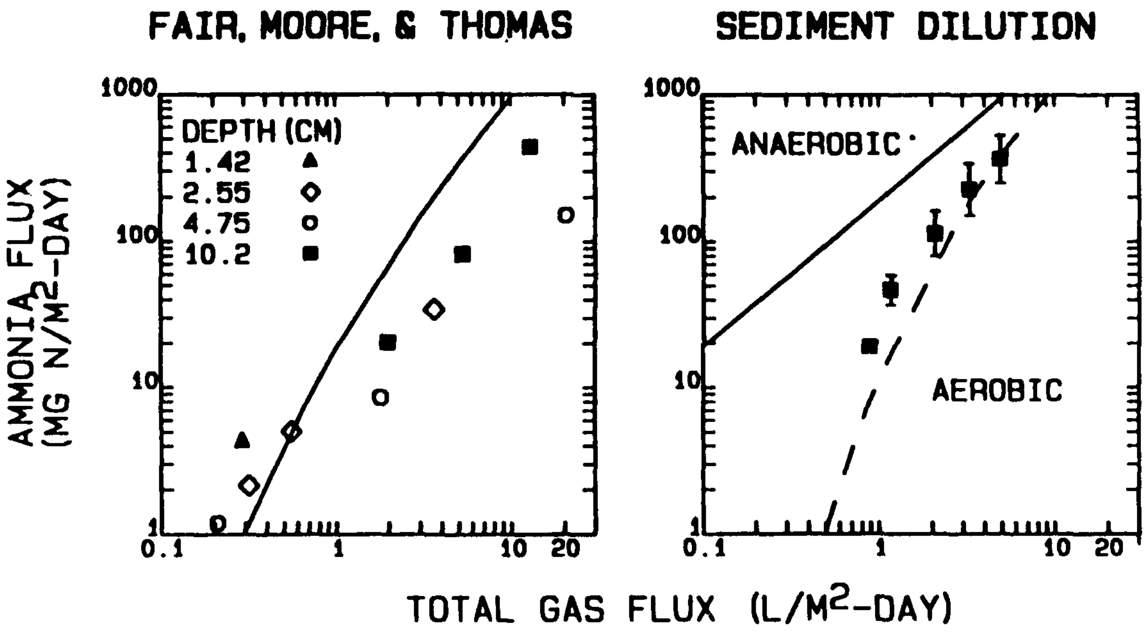

Figure 6. Ammonia flux versus total gas flux for the Fair et al. (1941) data (left) and the sediment dilution experiment (right). Lines are computed using Equations 57 and 59. Parameter values are given in Tables 2 and 3. For the sediment dilution data, both the anaerobic J_N (solid line) and aerobic $J[NH_4]$ (dashed line) fluxes are shown

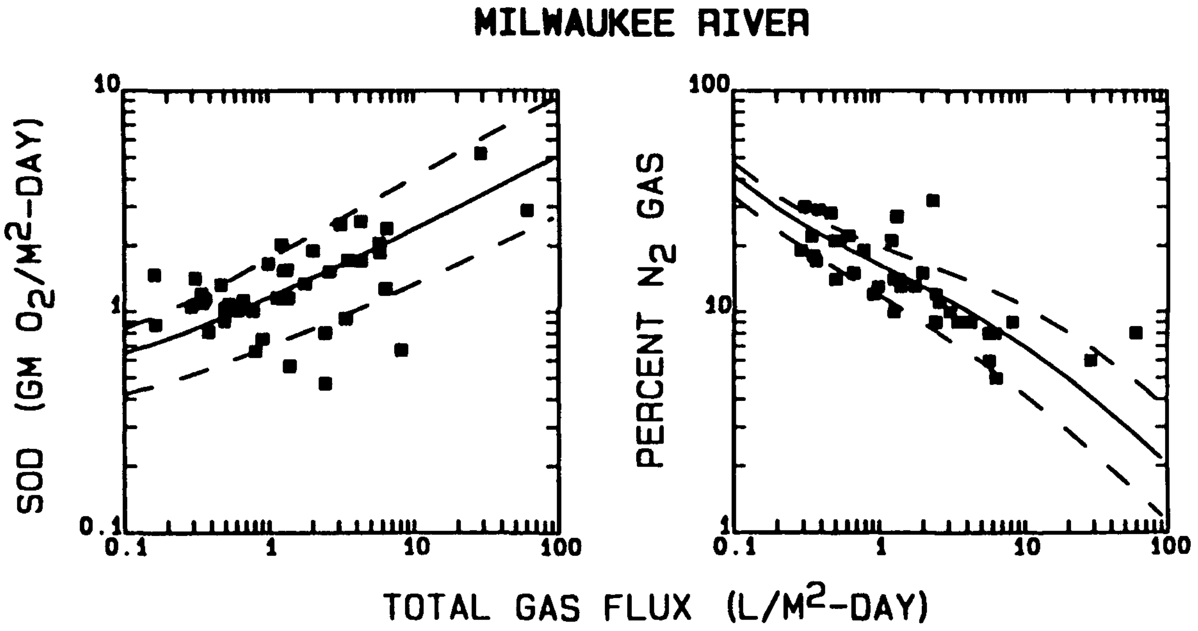

Figure 7. SOD (left) and percent nitrogen in the gas flux (right) versus total gas flux. Lines are computed using Equations 55 and 59 to 61. Parameter values are given in Table 2. Model results are evaluated using the median (solid lines) and the median plus and minus the standard deviation (dashed lines) of DO, temperature, and methane saturation concentration, Table 3

temperature coefficients). The lines in Figure 7 are the model results evaluated using the median (solid lines) and the median plus and minus the standard deviation (dashed lines) for DO, temperature, and methane saturation concentration, Table 3.

The regular decrease in the percentage of nitrogen gas with increased total gas flux, shown in Figure 7, can be explained by examining Equations 59 and 60. The nitrogen gas flux is proportional to the diagenesis flux, Equation 60. However the methane gas flux, Equation 59, can be zero at a finite diagenesis flux: $J_C < 2\kappa_D C_s$. This corresponds to undersaturation of methane in the interstitial water. Hence for small diagenesis fluxes the gas flux is essentially all N_2 gas. As diagenesis increases, the methane gas flux increases but less than linearly due to the square root term in Equation 59. Thus nitrogen gas still makes up a large proportion of the total gas flux.

At larger diagenesis fluxes, and therefore larger total gas fluxes, the composition would approach a constant, the Redfield ratio = 13.2 percent, if all the methane escaped without oxidation and all the ammonia was oxidized to nitrogen gas. However as gas flux increases the SOD increases which decreases the fraction of ammonia that oxidizes to nitrogen gas, Equation 60. Hence the percentage of N_2 can decrease further. All these features are represented in the Milwaukee River field data in Figure 7.

SOD and ammonia fluxes. Just as total gas flux can be used to estimate the diagenesis flux, so also can the ammonia flux, using Equation 57. Hence, it is possible to use field data sets for which SOD and ammonia fluxes are determined simultaneously to calibrate the reaction velocities. Figure 8 presents the results of a search of the literature for reported freshwater field data of paired fluxes (Rowe, Clifford, and Smith 1975, Callender 1982; Chiaro 1980) and a few laboratory measurements (Fillos 1975), together with a model fit. Since these data represent various temperatures, DO concentrations, and water column depths, the parameter estimates in Table 2 are not very reliable. However, it is interesting to note that the parameters are in the range of those estimated from the more complete data sets listed in Table 2.

Component fluxes. The behavior of the flux model is illustrated in Figure 9. The Milwaukee River parameters are used for these computations. The left panel presents the components of the total SOD. At diagenesis fluxes of less than $J_C = 2\kappa_D C_s = 0.54$ gm $O_2^*m^2$-day , no gas phase forms and CSOD is equal to J_C . As diagenesis increases SOD increases but a gas phase forms

Table 3

Mean and Standard Deviations of Environmental Parameters

(Standard Deviation is in Parentheses)

Figure Number[a]	Data Source	Temperature T (° C)	Methane Saturation c_s (mg O_2^*/L)	Dissolved Oxygen $O_2(0)$ (mg/L)
4, 5, 6	Sediment Dilution Experiment	20.	100	6.0
5, 6	Lab Reactor-Sewage Sludge (Fair et al. 1941)	22.5	93.1	6.0
	Milwaukee River			
7	SOD vs Gas Flux	15.3 (4.29)	180 (37.5)	4.48 (2.98)
7	% $N_2(g)$ vs Gas Flux	15.7 (4.17)	178 (36.5)	5.67 (3.07)
12	Fraction NH_4 Oxidized	15.7 (4.17)	--	--
9	--	20.	100	6.0
10	McDonnell & Hall Edwards and Rolley	20.	100	6.0
11	Hamilton Harbor	14.7 (1.7)	267 (11)	--
11	Lake Erie	10.3 (3.6)	430 (38)	--

[a]Figure 8: T = 15 (5) °C, H_o = 5 (5) m, $O_2(0)$ = 6.0 (2.0) mg/L.

and methane gas flux begins. At J_C = 10 gm O_2^*/m^2-day most of the carbon diagenesis is escaping as methane gas, and the SOD is 34 percent NSOD due to ammonia oxidation. At J_C = 100 gm O_2^*/m^2-day , a very large diagenesis flux, the SOD is only 6.8 gm O_2^*/m^2-day with 63 percent due to NSOD.

It is remarkable that for a two-orders-of-magnitude change in diagenesis flux the SOD increases only eight-fold, Figure 9. This may explain the often observed fact that SODs do not strongly correlate with sediment properties (e.g. Rolley and Owens 1967). One might reasonably expect a correlation between sediment properties such as POC concentration and diagenesis flux. However the SOD is related to the diagenesis flux via a square root. Hence the range of possible SODs is compressed. Even if a correlation existed it might be difficult to detect.

The behavior of the nitrogen fluxes in illustrated in the right panel of Figure 9. At low diagenesis fluxes almost no ammonia escapes oxidation and the gas flux, which would be small, is all nitrogen gas. As diagenesis

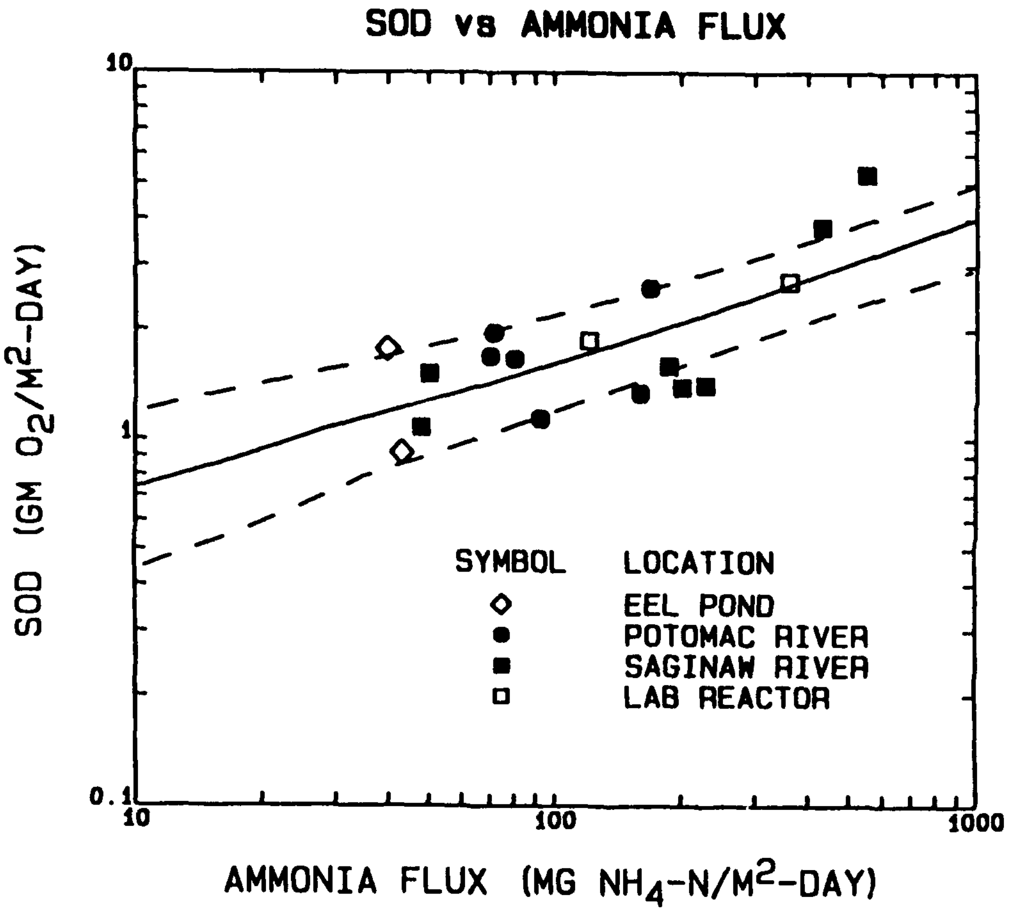

Figure 8. SOD versus ammonia fluxes for paired observations in fresh waters. Parameter values are given in Table 2. Model results are evaluated using the median (solid line) and the median plus and minus the standard deviation (dashed lines) of DO, temperature, and methane saturation concentration, Table 3

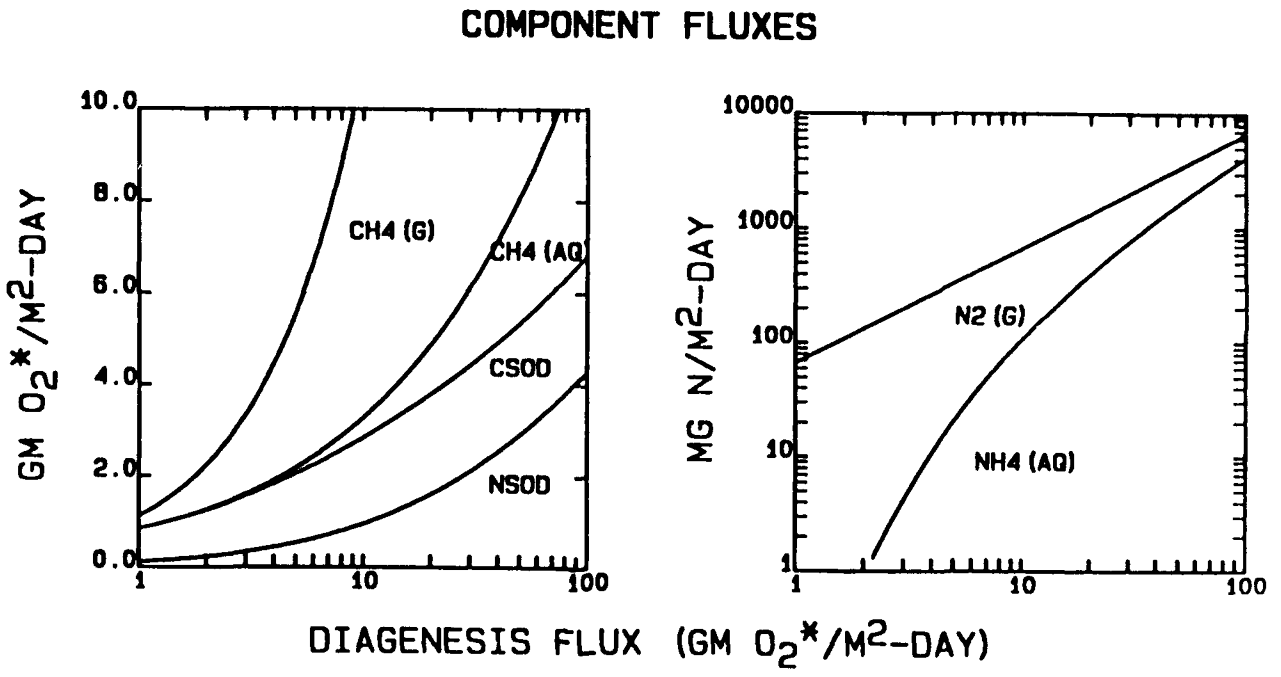

Figure 9. Component fluxes versus diagenesis flux. Cumulative plot of NSOD, CSOD, dissolved methane flux, and gaseous methane flux (left). Cumulative plot of ammonia and nitrogen gas flux (right). Parameter values are given in Table 2

increases the ammonia flux increases until it approaches two thirds of the nitrogen flux. This suggests several points of interest.

First, the quantity of nitrogen that escapes into the atmosphere via nitrification-denitrification spans the range of essentially 100 percent to 37 percent at high diagenesis fluxes. This is a significant terminal sink of nitrogen in sediments. Direct measurements of nitrogen gas fluxes from sediments confirm that a significant percentage of the total nitrogen flux from sediments is nitrogen gas (Chen et al. 1972; Seitzinger et al. 1980).

Second, the ammonia flux increases more rapidly than the diagenesis flux. As a log-log relationship between $J[NH_4]$ and J_C the exponent exceeds two at low diagenesis flux rates and is always greater than one. From the point of view of predicting ammonia fluxes this suggests that whereas SOD is less than linear with respect to diagenesis flux the ammonia flux would increase more rapidly than linearly. Finally, the combination of less than linear relationship of SOD, and the greater than linear relationship of ammonia flux versus diagenesis flux produces the flat relationship between SOD and ammonia flux illustrated in Figure 8.

SOD and dissolved oxygen concentration variation

The SOD model, Equation 55, predicts an explicit dependence of SOD on overlying water DO concentration. Several data sets exist which examine this relationship. Figure 10 (right panel) presents the results of fitting the model to an extensive set of laboratory measurements for river sediment cores (Edwards and Rolley 1965). The fitting parameters for these data are the carbon diagenesis flux J_C , which is presumed to be constant for all cores from each river, and κ_C , the methane reaction velocity. Figure 10 (left panel) presents the results of McDonnell and Hall (1969), for which both the DO and the temperature were varied. The fitting parameters in this case include the methane reaction velocity κ_C , the diagenesis flux at 20° C, and a temperature coefficient for the diagenesis reaction θ_C , so that J_C at any temperature is $J_C(T) = J_C(20°\ C)\theta_C^{(T-20)}$.

The estimates for κ_C listed in Table 2 are within the range for the other data sets if the standard errors are considered. The estimated diagenesis fluxes are large, which are required by the large SODs found at the high DO concentration. It is interesting to note that for the larger SODs there is a DO dependency even at DO concentrations which are much larger than concentrations known to limit biological oxidations (~10 percent of saturation - see

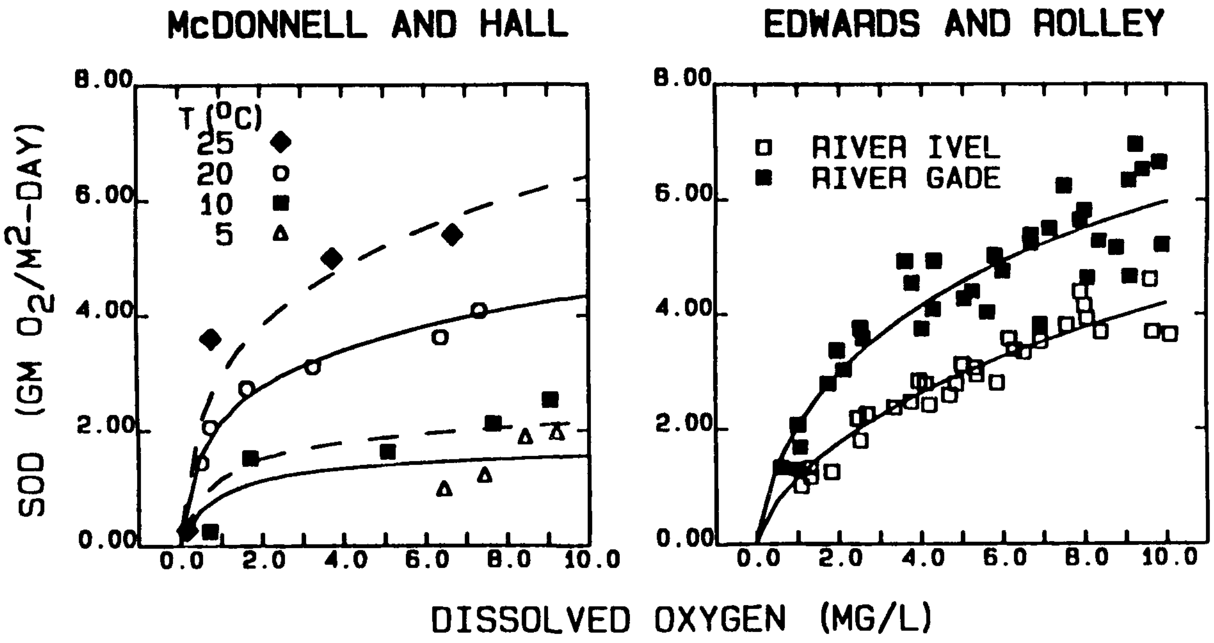

Figure 10. SOD versus DO observed in laboratory experiments. Data from McDonnell and Hall 1969 (left) and Edwards and Rolley 1965 (right). Lines are model fits to the data. Parameter values are given in Table 2

HMSO, 1964, for a review). Equation 55 predicts an oxygen dependency even at high oxygen concentrations because the depth of the aerobic zone depends on both the DO in the overlying water and the SOD itself, see Equation 50. The ratio of $O_2(0)$/SOD is the critical parameter. When the SOD is large, higher DO concentrations still affect the fraction of methane and ammonia that is oxidized to produce SOD. On the other hand if the SODs are low, then the model predicts a rather flat SOD versus DO profile. This is nicely demonstrated in McDonnell and Hall's data for which the lower temperature data are virtually flat above a DO concentration of 3 mg/L whereas the higher temperature data show a dependency at higher DO as do the Edwards and Rolley data.

Two field data sets relating SOD to DO concentrations are shown on Figure 11. Parameter estimates for κ_C and J_C are listed in Table 2. The lines are for the medians (solid lines) plus and minus the standard deviation (dashed lines) of DO, temperature, and saturated methane concentration (Table 3). The Hamilton Harbor parameter estimates are within the previous ranges. The Lake Erie parameters are on the low side although the large standard errors of the estimates make a judgment difficult.

Ammonia oxidation and dissolved oxygen concentration

The Milwaukee River nitrogen gas flux data provide a means to test the oxygen dependency of ammonia oxidation since nitrogen gas flux is equivalent to the flux of oxidized ammonia. If it were possible to estimate the ammonia diagenesis flux J_N, then the fraction of the ammonia diagenesis flux that is oxidized is

$$f_{NH4} = \frac{J[N_2(g)]}{J_N} \qquad (62)$$

J_N can be estimated from the carbon diagenesis flux J_C, and the Redfield ratio $a_N = J_C/J_N$. The carbon diagenesis flux J_C could be estimated directly from the methane gas flux using Equation 59. However, that estimate depends on the reliability of the model and the fitted parameter κ_D. Instead, an estimate is employed which uses only measured fluxes. The methane gas flux is almost equal to the total carbon diagenesis. The other fluxes are the diffusive methane flux, for which no observation is available but which is expected to be negligible (see Figure 9), and the CSOD, which can be estimated

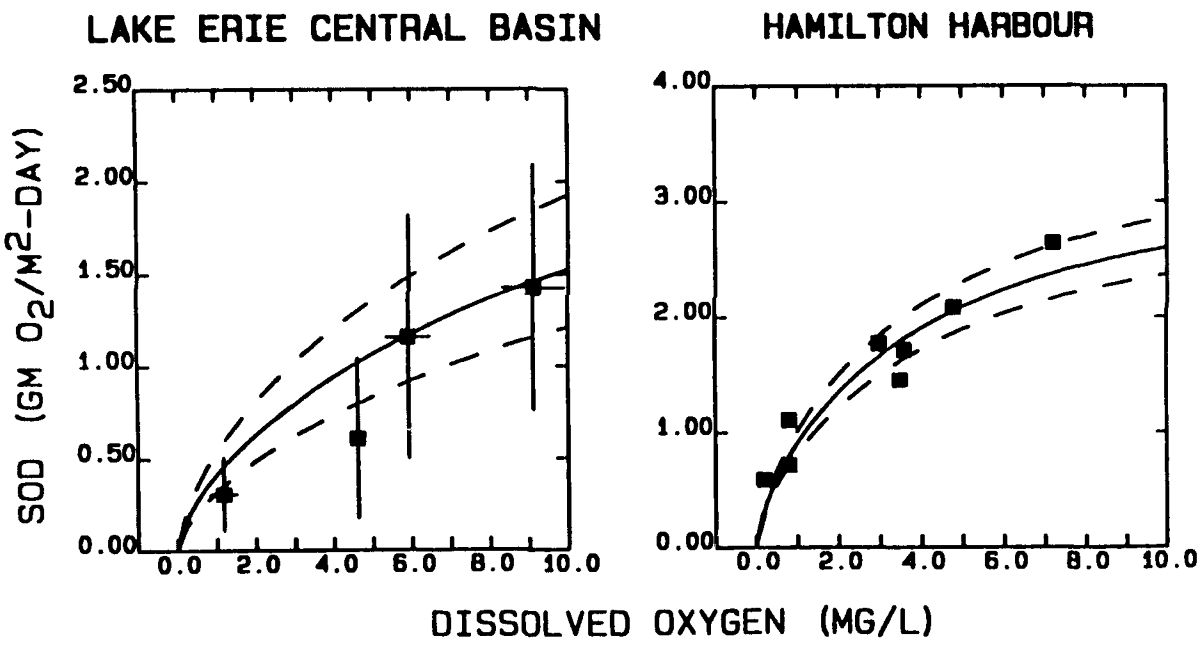

Figure 11. SOD versus DO observed in field data. Data from Davis and Herdendorf 1986 (left) and Polak and Haffner 1978 (right). Parameter values are given in Table 2. Model results are evaluated using the median (solid line) and the median plus and minus the standard deviation (dashed line) of DO, temperature, and methane saturation concentration, Table 3

from the measured SOD minus the NSOD. The nitrogen gas flux provides a direct estimate for NSOD. Thus, the estimate is computed from

$$f_{NH4} = a_R \frac{J[N_2(g)]}{J[CH_4(g)] + \{SOD - a_N J[N_2(g)]\}} \tag{63}$$

which is compared to the theoretical expression from Equation 60

$$f_{NH4} = 1 - sech\left(\kappa_N \frac{O_2(0)}{SOD}\right) \tag{64}$$

in Figure 12. The bars are the standard deviations of the ordinate and abscissa variables. The model lines correspond to the median (solid line) plus and minus the standard deviation (dashed lines) of the temperature (Table 3). The predicted dependency is observed although the scatter in the data is substantial. Thus, the DO dependency of both SOD and ammonia flux appear to conform to the model formulation.

Temperature dependence

An interesting point was made by Fair et al. (1941) concerning the temperature dependency of SOD and anaerobic reactions. They tabulated temperature coefficients for SOD, θ_{SOD}, and anaerobic digestion θ_C, and pointed out that $\theta_{SOD} < \theta_c$. The SOD model offers an explanation based on the square root dependency of CSOD with respect to diagenesis. If CSOD is proportional to $\sqrt{J_C}$ then

$$\theta_{SOD} = \sqrt{\theta_C} \tag{65}$$

A similar result is found here, Table 2. The temperature dependency for the diagenesis flux in McDonnell and Hall's experiment is $\theta_C = 1.122$, whereas the coefficient for SOD is $\theta_{SOD} = 1.053$ which is almost exactly $\sqrt{1.122} = 1.059$.

For the case where no gas flux is forming, however, one would expect $\theta_{SOD} = \theta_c$ since the relationship between SOD and J_C is linear. Since the formation of a gas phase is itself a function of SOD the temperature dependency is more complex than just a constant θ_{SOD}.

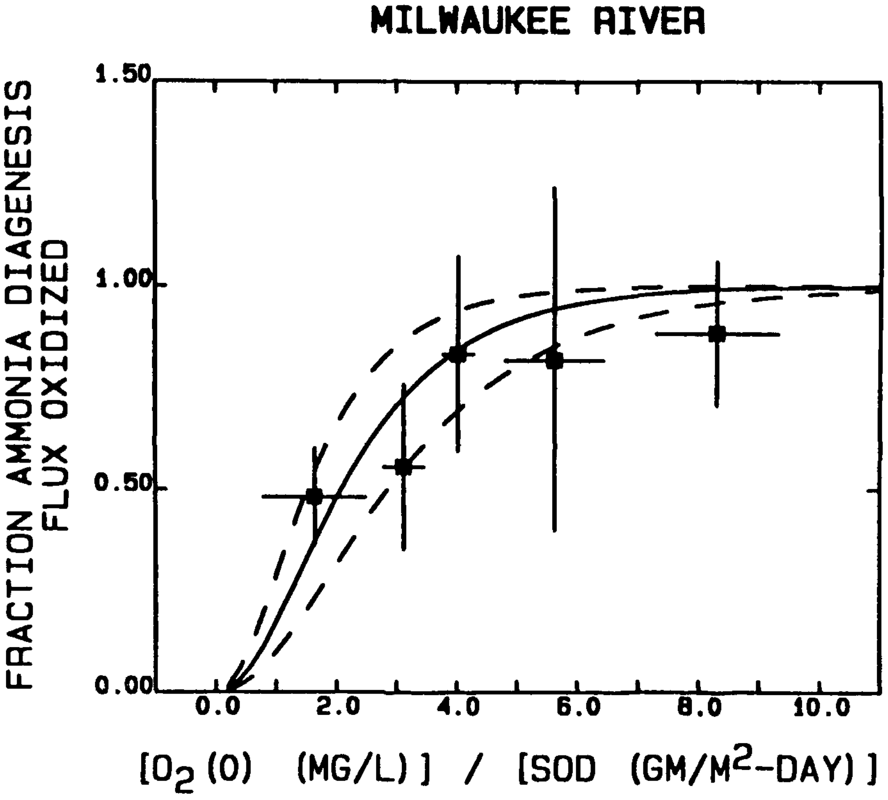

Figure 12. Fraction of the ammonia diagenesis flux that is oxidized to nitrogen gas. Parameter values are given in Table 2. Model results are evaluated using the median (solid line) and the median plus and minus the standard deviation (dashed lines) of DO, temperature, and methane saturation concentration, Table 3

Practical Applications

The use of this SOD model in water quality investigations requires certain modifications of standard field data collection and modeling practice. Simultaneous measurements of SOD, ammonia flux, and, above all, methane and nitrogen gas fluxes are required for calibration of the reaction velocities and mass transport coefficient. The gas flux measurements are critical since they are directly related to the diagenesis flux. The procedure for measuring these fluxes has been described elsewhere (Gruber et al. 1987). If possible the other nitrogen and carbon species fluxes should also be determined.

Using this SOD model in a predictive mode requires a specification of the diagenesis flux. For problem frameworks where predicting changes in SOD and other fluxes is necessary, a model that predicts the accumulation rate of sedimentary particulate organic matter (POM) is required. This quantifies the supply of POM available for diagenesis. In addition a model for diagenesis kinetics (e.g., Westrich and Berner 1984) is required to quantify the rate of decomposition of POM. Thus two additional components are required for a comprehensive coupled water column-sediment model of DO. Such a model has been constructed using a simpler SOD model (Di Toro and Connolly 1980).

An additional point to consider is the fate of dissolved and gaseous methane that is transferred to the overlying water. The former represents a dissolved BOD which must be considered in the DO balance. The flux of gaseous methane in the form of bubbles can also transfer methane to the water column where it contributes to the oxidizable carbon. We expect to report in the near future on the model constructed for the Milwaukee River, which includes a POM fate and diagenesis kinetic model, and the SOD model.

The present model formulation has certain limitations. The most important of these is its restriction to freshwater sediments. The evident importance of sulfide in marine waters as an intermediate reduced specie requires that its behavior be explicitly considered. To a lesser extent the role played by other intermediate reduced species such as iron and manganese may be important in some cases, especially where the SOD is small. In addition the contribution from the respiration of benthic macrofauna is not incorporated. The nitrogen flux model should be extended in order to explicitly include nitrate fluxes to and from the sediment. Finally there is a need for comprehensive field data sets of fluxes so that more rigorous calibrations and extensions can be made to the model.

Conclusions

The model described above presents a comprehensive analysis of the relationship between the diagenesis flux, the dissolved and gaseous methane fluxes, ammonia and nitrogen gas fluxes, and SOD. The square root dependency between diagenesis flux and SOD has been attributed to the formation and escape of methane gas. Although the ammonia flux-total gas flux relationships are less clear, the relationship between SOD and ammonia flux predicted by the model is observed in paired field and laboratory measurements. The model reproduces observed SOD-DO dependencies from laboratory and field data sets, as well as ammonia oxidation inferred from N_2 gas flux measurements. The model computes an internally consistent set of fluxes to the overlying water. Carbon diagenesis flux is either oxidized to become CSOD, or escapes as dissolved or gaseous methane flux. Nitrogen diagenesis is converted to either NSOD and N_2 or ammonia flux. Thus a rigorous mass balance is maintained.

The model is based upon a distinction between diagenesis fluxes that supply the reduced end products on the one hand, and the transport and oxidation kinetics that consume oxygen and modify the fluxes. The choice of parameter groups (dissolved methane mass transfer coefficient κ_D , and the reaction velocities κ_C and κ_N) is made so that the model fits within the framework of a flux prediction model rather than an interstitial water prediction model.

The use of paired flux plots to calibrate the kinetics independently of the diagenesis flux neatly eliminates the need to have direct measurements of diagenesis for use in calibration of the reaction velocities and mass transfer coefficient. Nevertheless they would be useful particularly in the calibration of a model for diagenesis kinetics (Westrich and Berner 1984). The three kinetic parameters have been estimated from various data sources and do not appear to vary too greatly.

The effect of overlying water DO and SOD and NH_4 fluxes arises naturally from the formulation. An additional half saturation constant for DO is not introduced. Actually it is assumed to be very small since oxidation proceeds up to $O_2(0) = 0$. The important parameter group is $O_2(0)/SOD$ so that the quantity of SOD itself influences the magnitude of dependency.

The temperature dependence of SOD is primarily related to the variation of J_C with respect to temperature. The principal effect is the temperature variation of anaerobic decomposition.

The use of this SOD model requires calibration data sets which include field gas flux measurements as well as the more conventional sediment fluxes.

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List of Symbols

Symbol	Definition	Units	Equation No.
a_N	= 1.714 gm O_2 consumed per gm NH_4^-N oxidized to nitrogen gas	gm O_2/gm N	31
a_R	= 15.2 gm O_2^* produced per gm NH_4^-N produced, the Redfield ratio	gm O_2^*/gm N	55
COD	Surface sediment COD concentration	mg O_2/gm	(Fig. 1)
$CSOD_{max}$	Maximum carbonaceous SOD corresponding to complete oxidation of dissolved methane in the aerobic layer	gm O_2^*/m^3-day	20
c_s	Methane solubility	gm O_2^*/m^3	14
c(z)	Methane concentration at depth z	gm O_2^*/m^3	12
D_{CH4}	Diffusion coefficient for CH_4 in interstitial water	m^2/day	12
D_{NH4}	Diffusion coefficient for NH_4 in interstitial water	m^2/day	32
D_{NO3}	Diffusion coefficient for NO_3 in interstitial water	m^2/day	26
D_{O2}	Diffusion coefficient for O_2 in interstitial water	m^2/day	1
f_{NH4}	Fraction of ammonia diagenesis that is oxidized to $N_2(g)$	-	62
$f_{o_2^*}$	Fraction of J_{PCOD} oxidized to produce SOD	-	9
H	Depth of the active layer of the sediment	m	12
H_o	Depth of the water column over the sediment	m	56
$J[CH_4(aq)]$	Flux of dissolved methane to the overlying water	gm O_2^*/m^2-day	18 43
$J[CH_4(g)]$	Flux of methane gas	gm O_2^*/m^2-day	44
J_{GAS}	Total gas flux	L/m^2-day	61
$J[NH_4]$	Ammonia flux to the overlying water	gm NH_4-N/m^2-day	38

Symbol	Definition	Units	Equation No.
$J[N_2(g)]$	Flux of nitrogen gas from the sediment to the overlying water	gm N_2-N/m^2-day	41 60
J_c	$= S_cH$, the carbon diagenesis flux in oxygen equivalents	gm O_2^*/m^3-day	21
J_N	$= S_NH$, the ammonia diagenesis flux	gm NH_4-N/m^2-day	40
J_{NO3}	Nitrate production flux	gm NO_3-N/m^2-day	26
J_{PCOD}	Flux of reactive particulate COD to the sediment	gm O_2^*/m^2-day	9
$k_c(T)$	Chemical SOD at temperature T	gm O_2/m^2-day	8
K_c	First-order reaction rate constant for ammonia oxidation	day^{-1}	45
K_N	First-order reaction rate constant for ammonia oxidation	day^{-1}	32
K_{02}	Half saturation constant for O_2	gm O_2/m^3	8
κ_c	Reaction velocity for methane oxidation	m/day	53
κ_D	Methane diffusion mass transfer coefficient	m/day	22
κ_N	Reaction velocity for methane oxidation	m/day	54
L_{02}	Depth of the aerobic zone	m	3
L_s	Depth of methane saturation, $c(L_s) = c_s$	m	14
λ_c	$= \sqrt{K_c/D_{CH4}}$	m^{-1}	45
λ_N	$= \sqrt{K_N/D_{NH4}}$	m^{-1}	39
$\mu_\beta(T)$	Maximum biological SOD	gm O_2/m^2-day	8
$n_1(z)$	Ammonia concentrations in the aerobic layer	gm NH_4-N/m^3	32
$n_2(z)$	Ammonia concentrations in the anaerobic layers	gm NH_4-N/m^3	33
$NO_3(z)$	Nitrate concentration at depth z	gm NO_3-N/m^3	26

Symbol	Definition	Units	Equation No.
$[NO_3(0)]$	Molar concentration of nitrate in the overlying water	moles/L	9
NSOD	Nitrogeneous sediment oxygen demand	gm O_2/m-^{2}-day	42
O_2^*	Oxygen equivalents--the oxygen required for complete oxidation	gm O_2	1
$O_2(z)$	Interstitial water-oxygen concentration at depth z	gm O_2/m^3	1
$[O_2(0)]$	Molar concentration of oxygen in the overlying water	moles/L	9
$R[NO_3]$	Zero-order nitrification rate in the aerobic layer	gm NO_3-N/m^3-day	7
$R[NO_3]_{,MAX}$	Maximum nitrification rate	gm NO_3-N/m^3-day	7
$R[O_2]$	Zero-order rate of oxygen consumption	gm O_2/m^3-day	1
$R_c[O_2]$	Zero-order carbonaceous oxygen consumption rate	gm O_2/m^3-day	1
sech(x)	$= 2/[\exp(x)+\exp(-x)]$	-	39
S_c	Zero-order rate of carbon diagenesis in oxygen equivalents	gm O_2^*/m^3-day	13
S_N	Zero-order rate of ammonia diagenesis production	gm NH_4-N/m^3-day	32
S_{NO3}	Zero order rate of nitrate production	gm NO_3-N/m^3-day	26
SOD	Flux of O_2 to the sediment	gm O_2/m^2-day	5
T	Sediment temperature	°C	56
tanh(x)	$=(\exp(x)-\exp(-x))/(\exp(x)+\exp(-x))$	-	39
θ_c	Temperature dependents for carbon diagenesis. $J_c(T) = J_c(20°C)\theta_c^T$	-	65
θ_{SOD}	Temperature dependence for SOD. $SOD(T) = SOD(20°C)\theta_{SOD}^{T-20}$	-	65
VS	Sediment areal volatile solids concentration	kg/m^2	(Fig. 1)

Symbol	Definition	Units	Equation No.
z	Depth, positive downward, from the sediment water interface	m	1

Role of Sediment Oxygen Demand in Oxygen Metabolism of Large Lakes

by

William J. Snodgrass[1]

Abstract

This paper presents a perspective on the magnitude of sediment oxygen demand (SOD) in different freshwater bodies (mainly large lakes) to assist in an understanding of its potential role in the Chesapeake Bay.

Five water bodies in the Southern Ontario area are used as a reference for this paper, including the two lower St. Laurentian Great Lakes. Basically the data suggest that SOD constitutes up to 50 percent of the oxygen metabolism of thin hypolimnia (2-4 m), such as in Lake Erie, to less than 20 percent in Lake Ontario whose hypolimnia mean thickness is in excess of 80 m, and whose maximum depth is three times larger.

Methods for characterizing the relative importance of SOD are examined in this paper. They include *in situ* measurements, statistical analysis of vertical oxygen profiles, and modeling assessments.

A particle-based model is used as a basis for examining the depth dependency of SOD. Data from one lake with several basins of varying depths are used to provide some evidence to support the hypothesized role of basin depth on SOD.

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Fatty Acid Production During Decomposition of Marsh Detrital Sources: Implementation for Seasonal Controls of Sulfate Reduction Rates in Salt Marsh Sediments

by

Myrna Jacobson[1]

Abstract

The biomass of reactive carbon to marine sediments influences reaction rates of diagenesis. A comparison of fatty acid production rates in anaerobic sediment amended with both fresh and leached *Spartina* and *Ulva* was made. Differences in production were expected to reflect lability of these substrates. Ammonia production, sulfide production, and sulfate depletion were measured. 13C CPMAS solid phase NMR was measured on samples of both *Spartina* and *Ulva*. No difference was seen between NMR spectra for the substrates measured. Fatty acid production was similar in both substrates; however, leaching caused a decrease in fatty acid production in *Spartina* but not *Ulva*. The relative contribution to early diagenesis by these substrates may be estimated from the production rates fostered by the labile fraction of these substrates.

In addition, experiments were conducted in which sulfate reduction rates were measured in sediment removed from the marsh seasonally and incubated at 10, 20 and 30° C. Results indicate that temperature variation alone can be used to characterize sediment sulfate reduction in this system.

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Spatial and Temporal Characterization of Sediment Oxygen Consumption (SOC) Rates in Chesapeake Bay

by

Jonathan H. Garber[1]

Maryland Chesapeake Bay Monitoring Program

Since its inception in 1984 the Maryland Chesapeake Bay Water Quality Monitoring Program has sought to provide a synoptic characterization of the causes and consequences of water quality problems in Chesapeake Bay. Components of this on-going program have compiled records of nutrient loadings, water quality parameters, plankton activities, and ecosystem processes (including primary productivity, organic matter deposition, and sediment oxygen and nutrient fluxes). These data support water quality modeling efforts aimed at improving our understanding of the process of estuarine eutrophication as well as guiding management actions taken to improve water quality. The purpose of this presentation is to (1) describe techniques developed by the Ecosystem Processes Component (EPC) of the Chesapeake Program for monitoring organic matter deposition and benthic fluxes; (2) describe spatial, annual, and interannual patterns of sediment oxygen consumption (SOC) and nutrient flux rates in Chesapeake Bay; and (3) show evidence in support for a hypothesis that links annual rates of SOC to nutrient loading of the main-stem bay rates via the processes of organic matter production and deposition.

Benthic Flux and Sediment Deposition Measurement Techniques

Benthic fluxes of oxygen and dissolved nutrients were determined four (five beginning in 1989) times annually at ten (now eight) monitoring stations located in the Maryland portion of Chesapeake Bay and its major northern tributaries (SONE Program). Benthic fluxes were also determined at additional stations located along the entire main-stem axis of the bay (BEST Program) during the period of April 1988-April 1989 and on thirteen occasions at Station R64 in 1987 (MiniSONE Program). Sediment deposition measurements are made almost continuously during spring, summer, and fall at Station R64.

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Details of the intact core procedure used for benthic flux measurements and sediment trap array used to determine sediment deposition rates can be found in Figure 4 of Boynton et al. (1990).

Variability of Flux Measurements

Variability in benthic flux measurements was determined by comparing the coefficients of variation (CV) computed for all measurements of a constituent flux at an individual station (therefore including seasonal and interannual variation) with the CV for a typical set of triplicate flux determinations made at an individual station. Variability associated with each set of triplicate SOC determinations was typically in the range of 10-20 percent. Averaged over several years (over 450 individual flux determinations), the CV of SOC in Northern Bay data base was 67 percent. For comparison, the CV's for determinations of other water quality parameters at a typical midbay monitoring station (R64), such as the concentrations of dissolved oxygen, ammonium, water temperature, and salinity, determined at a sampling frequency identical to that of the flux measurements range from about 15 percent for salinity to over 90 percent for dissolved oxygen. Over an annual cycle, measurements of benthic fluxes are about as "highly variable" as most routinely measured physical and chemical monitoring variables.

Characterization of SOC Rates in Chesapeake Bay

The year-long survey of benthic fluxes along the main-stem bay revealed that SOC rates are generally less than 0.5 g $O_2/(m^2*day)$ when water temperatures are less than 10° C. Analysis of four years of monitoring data (1985-1989), which by design concentrated sampling effort in spring and summer, revealed two basic patterns in the annual cycle of SOC rates. These corresponded to regions of tributaries and main-stem bay that experienced seasonal depletion of dissolved oxygen in near-bottom water and those that remained oxic year-round. The latter, which included most of the SONE monitoring stations, peaked in May and June, declined through the remainder of the summer, then increased in October. Seasonal patterns of SOC rates at stations subject to periodic anoxia were strongly influenced by the timing and duration of low oxygen conditions in late spring and summer as well as the occurrence of reaeration events. These factors contributed to generally higher variability and lower summer rates of SOC at midbay stations.

Five-year averages for SOC rates at SONE monitoring stations (n = 60 SOC determinations per station) for the period of 1985-1989 ranged between 0.54 and 1.57 g $O_2/(m^2*day)$. The range for an individual year was generally considerably greater. For example, in 1989, station-averaged SOC rates ranged from 0.02 to 2.00 g $O_2/(m^2*day)$. Although within-station seasonal variations obscured between-station differences, SOC rates tended to be highest at shallow tributary stations and lower in the deeper main-stem bay.

Interannual trends in SOC and inorganic nutrient fluxes were examined by computing arithmetic annual means for constituent fluxes at each monitoring station. Mean annual station SOC rates ranged from 0.3 to 2.6 g $O_2/(m^2*day)$ and in nearly all cases exhibited a significant decrease since 1985. A working hypothesis linking nutrient inputs to sediment metabolic processes via organic matter production and deposition has been developed to account for the observed interannual pattern.

Conclusions

1. The intact core technique has reliable methods for routine shipboard monitoring of SOC and sediment-water fluxes of other dissolved constituents.
2. Spatial, temporal, and interannual trends of SOC and nutrient fluxes in Chesapeake Bay are ecologically interpretable and can be shown to be linked to nutrient loading and other environmental forcing.
3. Both water column and sediment oxygen consumption contribute to oxygen depletion. The role of SOC is probably most important in spring and early summer. Accumulation of reduced products in sediments is also an important contributor to SOC.
4. Better techniques are needed to determine TOTAL BENTHIC RESPIRATION: either H2S flux (which can be done) or TOTAL DIC Flux (best option).

Acknowledgment

The data presented here are the result of a large interdisciplinary effort involving investigators from the Maryland Department of the Environment, University of Maryland, Philadelphia Academy of Sciences, VERSAR, Inc., Virginia Institute of Marine Science, Old Dominion University, and US EPA Chesapeake Bay Liaison Office. Among the principals contributing to this effort I especially acknowledge my co-workers W. R. Boynton and W. M. Kemp and their technical staff; J. Barnes, J. Watts, S. Stammerjohn, and L. Matteson. M. Haire, R. Magnien, N. Panday, R. Summers, K. Sellner, F. Holland, P. Sampou, J. Cornwell, F. Jacobs, G. Brush, D. Burdige, and R. Wetsel all made substantial contributions to the monitoring program and our thinking about estuarine processes.

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Seasonal Variations in Sediment-Water Nutrient Exchanges in Estuarine Systems

by

C. N. Farris[1]

Introduction

Nutrient fluxes across the sediment-water interface have been a topic of much investigation in many nearshore studies (e.g. Fisher, Carlson, and Barber 1982; Keizer, Hargrove, and Gordon 1989). These fluxes are thought to be an important seasonal component of nutrient cycles in coastal and estuarine waters (Asmus, Asmus, and Reise 1986; Bodungen 1986; Van Klump and Martens 1989). Additionally, these fluxes may be associated with significant changes in the structure and development stage of the benthic community (Rhoads 1974). Finally, these nutrient fluxes can be strongly influenced by natural and anthropogenic changes in the physical environment. These fluxes can be associated with changes in the nutrient and organic loading in the water column and the benthic habitat (Kelly et al. 1985). Thus, the pattern of flux rate variations in the benthos is directly related to the dissolved and nutrient species in the overlying water column, which also reveals clear seasonal trends (Pilson 1985).

In estuaries, there are two broad categories of dissolved chemical species. Those whose concentration is determined only by the contributing proportions of riverine and offshore water are conservative in character; an example is the chlorinity of natural waters. Those species whose concentration is determined by chemical or biotic interactions and transformations are nonconservative in character; an example would be in oxygen or phosphate concentration. Frequently, the interaction of the benthos with the water column determines the type of non-conservative behavior of the nutrient.

Sources of Alteration in Nutrient Flux Variation

There are several factors, both biotic and abiotic, that can effect variations in flux rates. Among the physical factors are temperature, wave

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and current action, and the sediment type (both the vertical profile of the pore water concentration, and the grain size distribution) (e.g. Walker and O'Donnell 1981; Helder and DeVries 1986). The nutrient concentration of the overlying water column has also been implicated in the nutrients' net flux (e.g. Fisher, Carlson, and Barber 1982).

The biotic factors are much more complex and less easily quantifiable. Usually biotic factors are the direct result of the activity of the fauna as it exploits its environment, broadly described as bioturbation (Rhoads 1974; Rhoads and Young 1970), or the change in nutrient concentration in the water just over the benthos due to metabolic activity (Sundback and Graneli 1988). Certain organisms can also alter the character of the sediment surface by secretions or other depositions (e.g. Rhoads, Yingst, and Ullman 1978).

Bioturbation has been the subject of many studies; until recently these have been mostly descriptive in nature (Rhoads and Young 1970). There are several studies that have advanced theoretical and quantitative hypotheses. These include quantifying the effect of benthic fauna on the nutrient concentration in its microhabitat (Rhoads 1973), and defining aspects of pelagic-benthic coupling in the effect of macrofauna on dissolved and particulate species in the overlying water column (Asmus, Asmus, and Reise 1990). This last phenomenon is implicated in far-reaching changes in the phytoplankton and long-term community structure in the water column (cf. Cloern 1982; Officer and Ryther 1980; Doering et al. 1989).

Another hypothesis suggests that the character and degree of nutrient exchange is associated with the developmental stage of the benthic community (Rhoads, Yingst, and Ullman 1978). The developmental stage progresses from the pioneer species associated with a physically disturbed or highly polluted site to the equilibrium species associated with a fully established or recovered benthic community. The nutrient exchange rates can be said to track these stages as well; if so, this could be an important relationship. However, much more study needs to be done.

Methods

Three different techniques have been used to measure nutrient fluxes across the sediment-water interface. Fluxes have been estimated from the application of theoretical differential constants to the nutrient concentrations of the water just over the benthos and the vertical profiles of the interstitial pore water (e.g. Van Klump and Martens 1989). This technique is widely used both from water column sampling studies and pore water concentration studies from sediment cores. It has been shown that the calculated fluxes from this technique are significantly different from other techniques that directly measure benthic fluxes. These differences have been associated with the processes of exchange from the sediment to the adjacent water and must be taken into account in any study (Lerat, Lasserre, and le Corre 1990).

The most widely used measurement of nutrient exchange is from the measurement of changes in the nutrient concentration in the water layer directly over the benthos, either from the use of the benthic chambers in *in situ* (Pamatmat 1971; Hale 1974) and in microcosms (Pilson, Oviatt, and Nixon 1980), or from the measurement of nutrient concentrations in sediment cores taken from the field and held at natural conditions (Thomas et al. 1976). The direct measurements are more intuitively indicative of the present benthic conditions. However, the variability can be a persistent problem in the analysis of the resultant data.

Seasonal Trends in Sediment-Water Nutrient Exchange

For most estuarine systems and their adjacent coastal waters, the seasonal trends in the flux rates can be typified by such studies as Bodungen (1986). In the spring, winter, and fall, rates of pelagic nutrient regeneration are quite low. In the spring, pelagic nutrient uptake rates are greater than the release of the nutrients from the benthos. In the fall, the rates of benthic release are greater than the rates of pelagic nutrient regeneration. From spring to summer, most of the sediment nutrient release is retained or recycled by the pelagic food web.

In the summer, the sediments of the water below the thermocline exhibit sediment release and exchange rates associated with the decline in oxygen concentration. In the late fall, nutrient concentrations reach stable levels and remain relatively constant until the spring. These nutrient concentrations are thought to be maintained by abiotic mechanisms, such as physical conditions and chemical diffusion rates (e.g. Bodungen 1986; Helder and DeVries 1986).

In an estuary, in the late spring to late fall, these nutrient flux rates can change as one moves down the estuary from sources of natural and anthropogenic organic and nutrient loading (Pamatmat 1971; Kelly et al. 1985).

Resuspension by current regimes can also cause perceptible changes in the nutrient exchange rates (Aussie stuff). A multitude of studies have shown the increase in nutrient exchange rates by the benthic community (Callender and Hammond 1982; Hopkinson, Hopkinson, and Wetzel 1982; Asmus 1986); microphytobenthos (e.g. Sundback and Graneli 1988); and macrofauna (e.g. Hale 1974).

Conclusions

Nutrient exchange rates have been shown to be indicative of and affected by many estuarine processes. These flux rates may help quantify the structure, developmental processes, and vigor of the benthic communities (Widbom and Elmgren 1988). Furthermore, the nutrient flux rates are indicative of the crucial role that the sediment-water interface plays in the estuary. This role not only is reflected in the flux rates but ultimately may be affected by these rates (McCaffrey et al. 1980). These nutrient exchange rates across the interface may exert a stabilizing effect on the transfer of nutrients within the estuary, and help define the processes by which estuaries act as net contributors to adjacent coastal waters.

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Studies on the Comparison of In-Situ and Laboratory Sediment Oxygen Demand Measurement Techniques

by

Ray C. Whittemore[1]

Introduction

A uniform procedure for the measurement of sediment oxygen demand (SOD) has not been agreed upon by water quality modelers. In order to assess this critical sink of dissolved oxygen (DO) in assimilative capacity studies, modelers use one or more methods which include *in situ* respirometry, undisturbed laboratory cores, and simply varying SOD to achieve model calibration. The 1983 Water Pollution Control Federation Annual Conference sponsored four sessions on SOD theory and measurement (Hatcher 1985). Those participating in these sessions generally agreed that *in situ* measurements were more reliable than the other methods because they least disturbed the sediment water column interface, or did not rely upon complete knowledge of other DO sinks (model calibration). Others at the conference, however, suggested that undisturbed laboratory cores could be effectively used because both field and personnel time are minimized when compared to the *in situ* techniques. They also suggested that sediment cores could be collected by trained divers with minimal disturbance of the sediment-water column interface.

Because there are few controlled studies that directly compare *in situ* with laboratory core measurements, the general utility of laboratory SOD methods has not been properly evaluated. NCASI concluded from an analysis of existing literature that there was no general correlation of laboratory with *in situ* measurements (NCASI 1982). A further review of these studies indicated that the measurement techniques were not well described or documented in the literature. Thus, the effect of measurement technique on individual *in situ* or laboratory based SOD values was not known.

This paper describes a controlled study designed to evaluate *in situ* and laboratory SOD measurements at two river locations with considerably different sediment characteristics and river hydraulics. The results of the study were

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designed to provide modelers with a basis for (a) judging the utility of laboratory-core measurements as surrogates for *in situ* respirometry, (b) evaluating river specific laboratory core/in situ respirometry SOD correlations, and (c) compiling an improved data base for quantifying the variability in SOD rates measured by each technique.

Experimental Procedures

In-situ respirometry

The *in situ* respirometer is schematically shown in Figure 1. A more detailed description of its design and operation is given in NCASI Technical Bulletins Nos. 317 and 321 (NCASI 1978, 1979). Important operational details of the device include:

(1) Use of KCL to elevate conductivity for use as a tracer to insure continuous seal of the respirometer with the trapped sediment.

(2) A submersible d-c voltage pump to provide controlled internal circulation of water without resuspending sediment.

(3) Depletion of dissolved oxygen by at least 1 mg/l during test.

(4) Ability to exclude light from the chamber to prohibit photosynthesis by covering it with black plastic.

(5) Determination of background water column respiration using dark/light bottle techniques.

The pumping rate was controlled by adjusting the voltage to the pump. A turnover rate was defined as the volume of the respirometer/pumping rate). This method was demonstrated in a laboratory to develop a reliable calibration of pumping rate with d-c volts. The method was reliable as long as the pump was new. Consequently, the pump was frequently replaced during use in the field.

Laboratory SOD cores

The device for the laboratory core measurements is shown schematically in Figure 2. It was modeled after work performed by the TVA (Hatcher 1985). The device consisted of a 16-litre polyethylene container fitted with an airtight cover. A 12-volt d-c pump was used to control circulation of the water at a known rate. The entire apparatus was immersed in a water bath to maintain integrity of the seal and to minimize temperature variations during testing.

The sediment samples were collected in plexiglass cylinders, 2-3/4 in. (70 mm) in diameter and 6 to 8 in. deep (150 mm to 200 mm). Six to eight

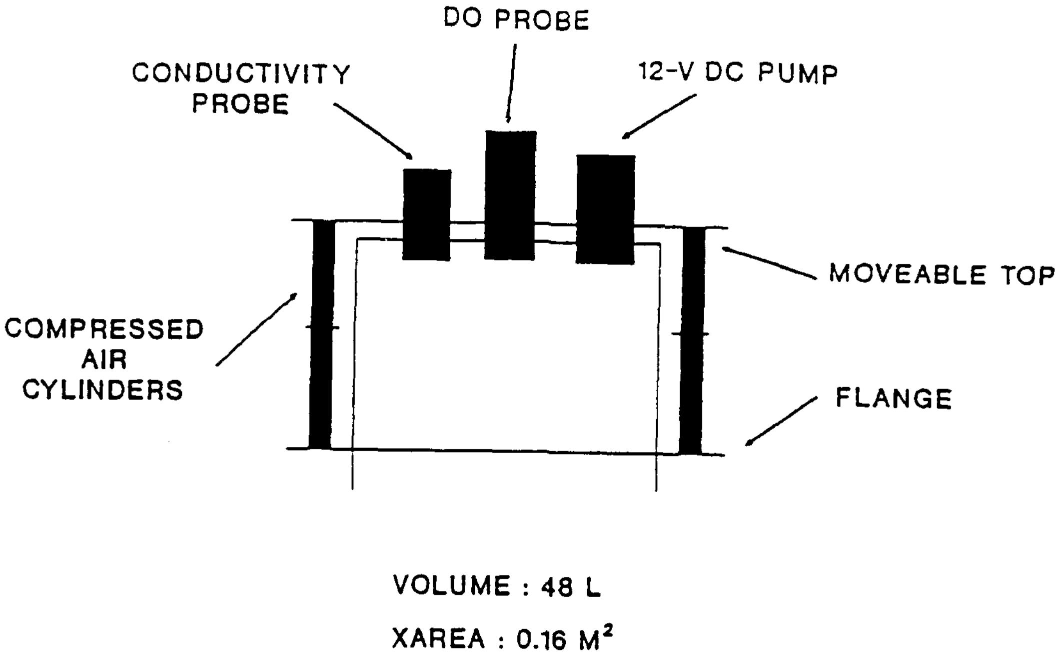

Figure 1. *In situ* sediment oxygen demand respirometer

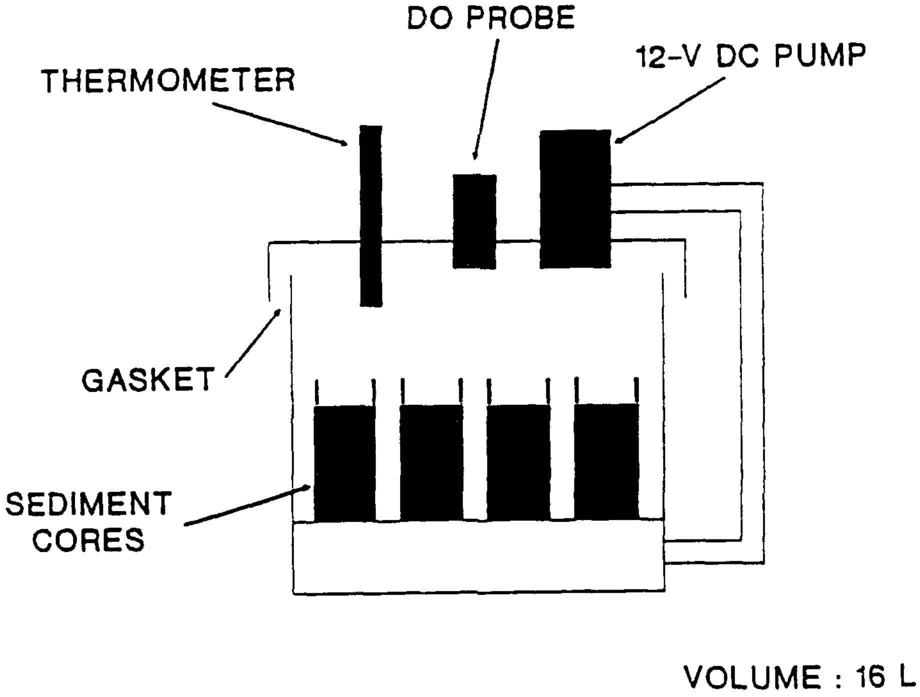

Figure 2. Laboratory core sediment oxygen demand apparatus

cores were usually collected at a stream site within a 3- to 9-ft (1- to 3-m) radius. In all cases, the diver moved in the upstream direction to insure that the sediment being collected was not affected by his downstream movements. For the sites selected in this study, it was possible for the diver to carefully insert the core into the sediment to a depth of 6 to 8 in. (150 to 200 mm). The core was then slowly removed and a large rubber stopper covered with aluminum foil was inserted into the bottom end. During development of the procedure it was noted that the SOD rate was significantly lowered when the sediment-water column interface was allowed to drain prior to measurement. Thus, the cores were placed upright in a pail by the diver before bringing them to the surface. In this way, the sediments were always kept wet prior to testing. For this study, the sediment cores were transported to the laboratory with a supply of fresh river water and testing was started within a 2-hr period.

Other major features of the laboratory testing include:

(1) Adjustment of circulation rates to achieve turnover times (volume of water in vessel/circulation rate of pump) comparable to the *in situ* tests.

(2) DO depletion of at least 1 mg/l during tests

(3) Determination of background water column respiration rate.

(4) Device placed in a water bath to minimize air leaks and temperature variations caused by room temperature changes and heat input from the circulation pump.

Discussion of Results

The tests were conducted on sediments from two New England sites with widely different sediment characteristics as shown in Table 1. The first site had sediment with low organic carbon content (< 7 percent), small particle size forest litter (< 0.5 in.) (13 mm), and tight consolidation of the stream bed. The second site, on the other hand, had a higher organic content (up to 94 percent), larger particle size forest litter including pieces of bark. The largest particles were 1 in. (25 mm) long and loosely consolidated in the bed which also contained gravel. These samples were more to difficult to collect in the plexiglas cores. Anaerobic activity in the sediment bed was evident at both sites. These anaerobic gases were detected upon disturbing the sediment.

The results are summarized by site location in Tables 2 to 4. Each table contains the length of the test, the initial DO concentration, the DO

Table 1

Site and Sediment Characteristics

Characteristic	Site A	Site B
Water temperature (°C)		
Laboratory	23-26	19-24
In situ	26-28	21-24
Approximate flow, cfs	200	2000
(cms)	(6)	(60)
Depth, ft (m)	3 to 6 (1-2)	3 to 6 (1-2)
Approximate current, fps	0.5	< 0.1
(m/s)	0.15	< 0.03
Sediment organic content, percent	1 to 7	54 - 94

depletion, average test temperature, turnover time, SOD at average test temperature, and SOD corrected to 20° C. The latter was calculated by assuming a correction factor of 1.06 and using Equation 1. The factor 1.06 is a midrange of those values reported in the literature (Bowie 1985).

$$SOD\ (@\ T) = SOD\ (@\ 20^\circ C) * 1.06 * \exp\ (T - 20) \qquad (1)$$

The data in the tables are grouped according to decreasing turnover time (increased pumping rate) up to 2 min. It is interesting to note that the average SOD values for both *in situ* and laboratory tests increased with increasing pumping rates or decreased turnover times. This observation supports the findings of NCASI and others (NCASI 1978; Hatcher 1985).

The most important observation is that the laboratory and *in situ* SOD rates are more comparable when compared at the same or similar turnover time. A paired t-test at the 95 percent confidence level was used on both Site A and B data sets to support this conclusion.

The coefficient of variation (standard deviation/mean) of each set of measurements was generally consistent with previous NCASI and EPA experience (NCASI 1985). For Site A, the values ranged from 9 to 37 percent for the laboratory tests and from 18 to 21 percent for the *in situ* tests. The results from Site B were not as extensive as those from Site A because the sediment at

Table 2

Site A - Laboratory SOD

Test ID	Delta Time hr	Initial DO mg/l	Delta DO mg/l	Tempera-ture °C	Turn-over Rate min	SOD	SOD @20C
						gm/m^{2}day	
L1a	10.8	7.9	0.60	23.0	NC*	0.81	0.68
L2a	12.9	8.3	0.85	22.0	NC	0.95	0.85
L4a	15.5	7.6	0.95	23.0	NC	0.89	0.75
L5a	14.0	7.8	0.80	24.0	NC	0.83	0.66
L6a	8.8	6.8	0.95	24.0	NC	1.57	1.25
L8	12.0	5.9	0.46	25.0	NC	0.56	0.42
L9b	12.0	5.3	1.20	24.0	NC	1.45	1.15
				MEAN			0.82
				STANDARD DEVIATION			0.27
				COEFFICIENT OF VARIATION (%)			33
L9d	12.0	4.1	1.00	22.0	10	1.21	1.08
L9	18.0	6.8	1.40	24.0	10	1.13	0.89
				MEAN			0.98
				STANDARD DEVIATION			0.09
				COEFFICIENT OF VARIATION (%)			9
L9c	13.0	5.1	1.00	22.0	4	1.12	0.96
L8c	12.0	5.5	1.26	24.0	4	1.51	1.21
				MEAN			1.09
				STANDARD DEVIATION			0.12
				COEFFICIENT OF VARIATION (%)			11
L1	4.4	8.5	0.60	23.0	2	1.99	1.67
L2	1.8	8.8	0.45	22.0	2	3.57	3.17
L3	8.0	7.5	1.00	23.0	2	1.81	1.52
L4	3.1	8.6	0.70	24.0	2	3.31	2.78
L5	3.5	8.4	0.60	24.0	2	2.49	1.97
L6	4.0	7.3	0.65	24.0	2	2.36	1.87
L8a	12.0	6.9	1.01	25.5	2	1.22	0.89
L8b	8.0	5.1	0.75	24.0	2	1.36	1.08
L9a	8.0	7.7	1.20	24.0	2	2.18	1.72
				MEAN			1.85
				STANDARD DEVIATION			0.69
				COEFFICIENT OF VARIATION (%)			37

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* No circulation.

Table 3

Site A - *In Situ* SOD

Test ID	Delta Time hr	Initial DO mg/l	Delta DO mg/l	Temperature °C	Turnover Rate min	SOD	SOD @20C
						gm/m^{2}day	
IS2a	12.3	5.4	1.9	26.5	NC	0.97	0.66
IS3a	6.5	7.1	1.4	27.0	NC	1.40	0.93
IS4a	9.2	7.3	2.1	27.0	NC	1.50	1.00
IS7a	12.0	6.7	2.9	27.0	NC	1.59	1.06
IS9	4.0	6.5	1.1	27.0	NC	1.83	1.22
				MEAN			0.97
				STANDARD DEVIATION			0.18
				COEFFICIENT OF VARIATION (%)			18
IS2	7.7	9.3	3.9	26.5	2.6	3.50	2.40
IS3	4.8	8.8	1.7	26.5	2.6	2.43	1.66
IS4	2.7	8.4	1.1	27.0	2.6	2.79	1.85
IS5	4.7	8.5	1.6	27.5	2.6	2.30	1.49
IS7	3.3	8.7	2.0	27.5	2.6	4.17	2.70
IS8	3.7	7.8	1.3	27.0	2.6	2.45	1.63
				MEAN			1.93
				STANDARD DEVIATION			0.41
				COEFFICIENT OF VARIATION (%)			21

Site B was more easily disturbed during placement of the *in situ* device as well as during the collection of the laboratory cores. The high coefficient of variation of 47 percent is consistent with this observation.

The laboratory data for Site B had coefficients of variation in the range of 2 to 22 percent. Since no *in situ* tests were conducted at this site, the effect of circulation on SOD could not be evaluated. The *in situ* work was limited because circulation resulted in leakage of water within the respirometer to that in the underlying sediment trapped by the chamber.

The findings of this study suggest that there is some justification for using laboratory core methods as surrogates for in-situ respirometry. Table 6 summarizes the overall results of significance.

Previous work in this area has not adequately dealt with the effect of circulation or turbulence on SOD values. Consequently, both laboratory and *in situ* results from the same site could not be fairly evaluated. In many of these earlier studies, laboratory results were either consistently higher or lower than corresponding *in situ* results. The measurement devices and test

Table 4

Site B - Laboratory SOD

Test ID	Delta Time hr	Initial DO mg/l	Delta DO mg/l	Temperature °C	Turnover Rate min	SOD gm/m²day	SOD @20°C gm/m²day
L12	4.2	6.3	0.85	24.0	NC	2.38	1.88
L12b	12.0	4.8	2.70	22.5	NC	2.74	2.37
L13	3.2	7.2	0.85	20.0	NC	3.27	3.27
L14	6.0	5.9	1.45	21.0	NC	2.98	2.81
L15	5.6	7.4	1.10	19.5	NC	2.33	2.39
L15b	12.2	6.6	2.25	20.0	NC	1.73	1.73
				MEAN			2.41
				STANDARD DEVIATION			0.52
				COEFFICIENT OF DEVIATION (%)			22
L12a	3.0	4.8	0.90	22.5	2	2.83	3.31
L13a	0.8	5.9	0.20	21.0	2	3.34	3.16
				MEAN			3.23
				STANDARD DEVIATION			0.08
				COEFFICIENT OF VARIATION (%)			2

Table 5

Site B - *In Situ* SOD

Test ID	Delta Time hr	Initial DO mg/l	Delta DO mg/l	Temperature (°C)	Turnover Rate min	SOD gm/m²day	SOD @20°C gm/m²day
IS10	13.0	7.2	2.70	24.0	NC	1.23	0.98
IS11	4.8	6.3	2.20	23.0	NC	3.07	2.58
IS12	4.0	7.9	2.00	22.0	NC	3.34	2.97
IS13	12.0	6.9	2.30	22.0	NC	1.12	1.00
IS14	4.8	6.8	1.70	21.0	NC	2.31	2.18
IS15	13.8	6.7	2.40	21.5	NC	1.00	0.91
				MEAN			1.77
				STANDARD DEVIATION			0.84
				COEFFICIENT OF VARIATION (%)			47

Table 6

Summary of *In Situ* and Laboratory SOD Measurement Comparison

Site	Method	NOB	Turn-over Rate min	Mean SOD @ 20°C	Standard Deviation	Coefficient of Variation
A	Lab	7	NC	0.82	0.27	33
A	*In situ*	5	NC	0.97	0.18	18
A	Lab	9	2	1.85	0.69	37
A	*In situ*	7	2.6	1.93	0.41	21
B	Lab	6	NC	2.41	0.52	22
B	*In situ*	6	NC	1.77	0.84	47

conditions could not be properly documented from the literature article or in some cases following conversations with the lead investigator. It is likely that turbulence levels varied significantly. Thus, it was proper to conclude that the results were not comparable.

The utility of this study to water quality modelers is that laboratory tests are easier to conduct, utilize fewer field personnel, and generally require less expensive equipment than *in situ* testing. Hence, it is likely that implementation of a laboratory-based SOD measurement protocol would significantly reduce the cost of SOD work.

Before this recommendation can be universally adopted, further demonstration is needed to more fully document the comparability of *in situ* respirometry and laboratory core measurements. The demonstration should be made on a wider range of sediment types and river hydraulic conditions. This work was limited in that only two sites were included in the study.

Conclusions

Study conclusions are summarized below.

(1) A laboratory SOD measurement procedure was developed that produced SOD rates comparable to those obtained from *in situ* respirometry at two New England sites.

(2) SOD rates using both measurement procedures increased with increasing mixing in the chambers.

(3) Mixing levels were defined as the ratio of the vessel volume/pump circulation rate.

(4) For site A measurements, the coefficients of variation ranged from 9 to 37 percent for laboratory results and from 18 to 21 percent for *in situ* based results.

(5) For site B measurements, the coefficients of variation ranged from 2 to 22 percent for laboratory results, and the coefficient of variations 47 for *in situ* based results.

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Environmental Protection Agency Region IV Perspective on SOD

by

Delbert B. Hicks[1]

Introduction

Descriptive studies of sediment oxygen demand (SOD) are found in the literature dating back to the early 1900's. These assessments were often laboratory studies. Later, the techniques for *in situ* measurements were published in the 1950's (Davis and Davis 1986). Since then, the basic approaches to measuring SOD have remained unchanged and still involve laboratory treatment of sediments removed from the natural setting or *in situ* measurements using chamber devices. Among these two approaches, a variety of methods are found as indicated in the proceedings of a national/international SOD workshop conducted in 1986 (Institute of National Resources 1986).

The purpose of this paper is not to debate the pros and cons of these methods but rather to identify some research objectives which in my judgment would significantly add to our ability to provide accurate and representative SOD rates for environmental decisions. To start my discussion, I'll provide you with a brief review of EPA Region IV's approach to measuring SOD. Drawing from my experience in Region IV, which spans 20 years, I'll attempt to identify some salient concerns I have with the present approach to SOD measurements.

Approach to SOD

From the late 1960's to the present, efforts to measure SOD rates in Region IV have been with *in situ* chambers. This method was selected for several reasons which are discussed elsewhere (Murphy and Hicks 1986). In brief, the sediment core/laboratory approach was viewed as too radical a departure from "normal" conditions naturally associated with the sediments and water interface. The *in situ* use of chambers was viewed as less disruptive to these conditions. In addition, the *in situ* chamber method allows for an on-site assessment regarding the quality of the data before leaving the study site.

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Should the data be suspect of excessive variation or indicate peculiar trends, additional sampling can be conducted to aid in explaining the observations.

Through the course of our work in Region IV, chamber design has varied from prism-shaped devices, hemispheric domes, and presently to an annular configuration (shown in Figures 1, 2, and 3, respectively). The experimental nature of this earlier work was part of our efforts to provide a "uniform" method with standardized equipment design for the measurement of SOD in the streams, rivers, lakes, and estuaries of Region IV. In these efforts, the goal was to develop equipment and procedures which featured ease of deployment, provided reproducibility of data, yielded precision in data, and minimized the disturbance of the natural dynamics of the sediment-water interface. Presently, a "uniformed" method is employed for SOD determinations in Region IV.

In this experience of developing a means to determine SOD rates, some questions still require resolution while new concerns must be examined.

Throughout the history of the SOD experience in Region IV, the assumption has been made that the SOD measurements yielded an accurate estimate of the rates. We all know that reproducible and precise data do not assure accuracy. To my knowledge, a means to validate the accuracy of an SOD rate has yet to be examined. Over the years, a "comfort zone" has developed and it now surrounds the accuracy question. The "comfort zone" emerges each time the output from a calibrated model is field validated. Possibly such a comfort zone is adequate for the business at hand. Unfortunately, not all model outputs are field validated.

Substrate Diversity

In the early years of conducting waste load allocation assessments in Region IV, the water bodies of interest were typically the large rivers, lakes and estuaries. Today an increasing number of small wadeable streams are now subjects of waste load allocation. Unlike the large rivers and lakes, sand/mud type sediments are not the predominant substrate feature of the stream bottom. Instead, boulders, rubble, gravel, bedrock, submerged logs, stumps, and other irregular substrates are the predominant component of the streambed.

Associated with these submerged substrates is the attached *Aufwuchs* community which is generally comprised of microscopic plants and animals, and

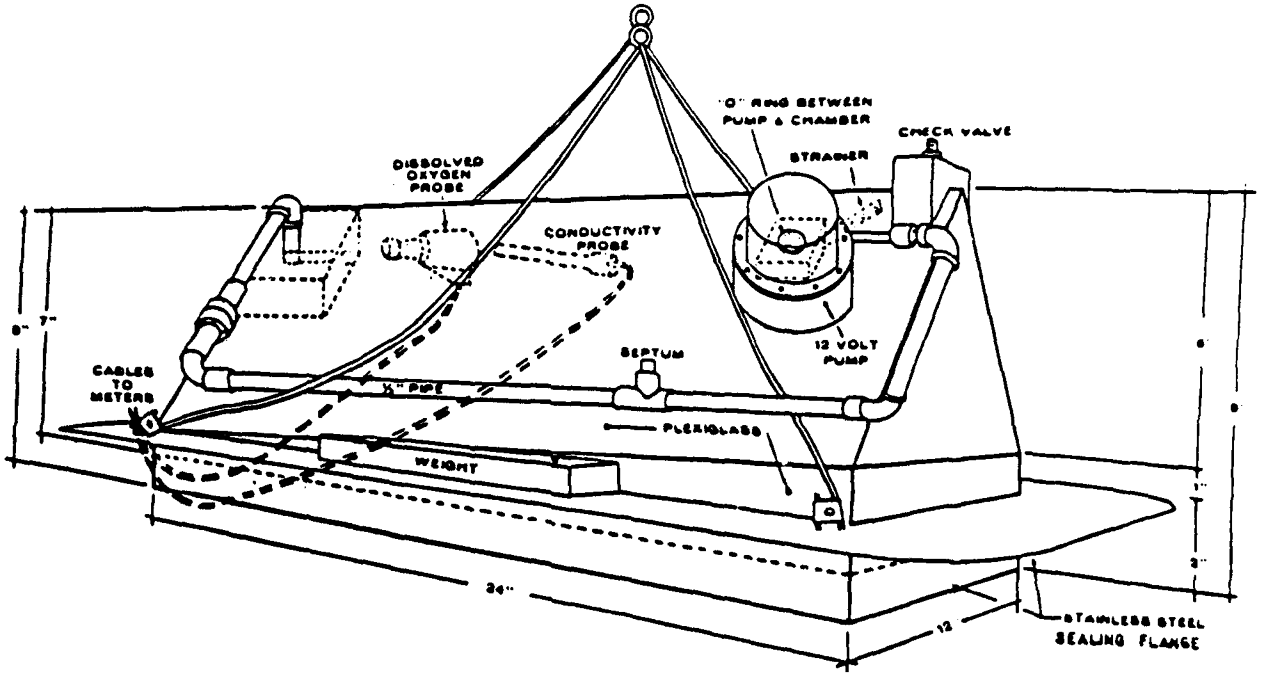
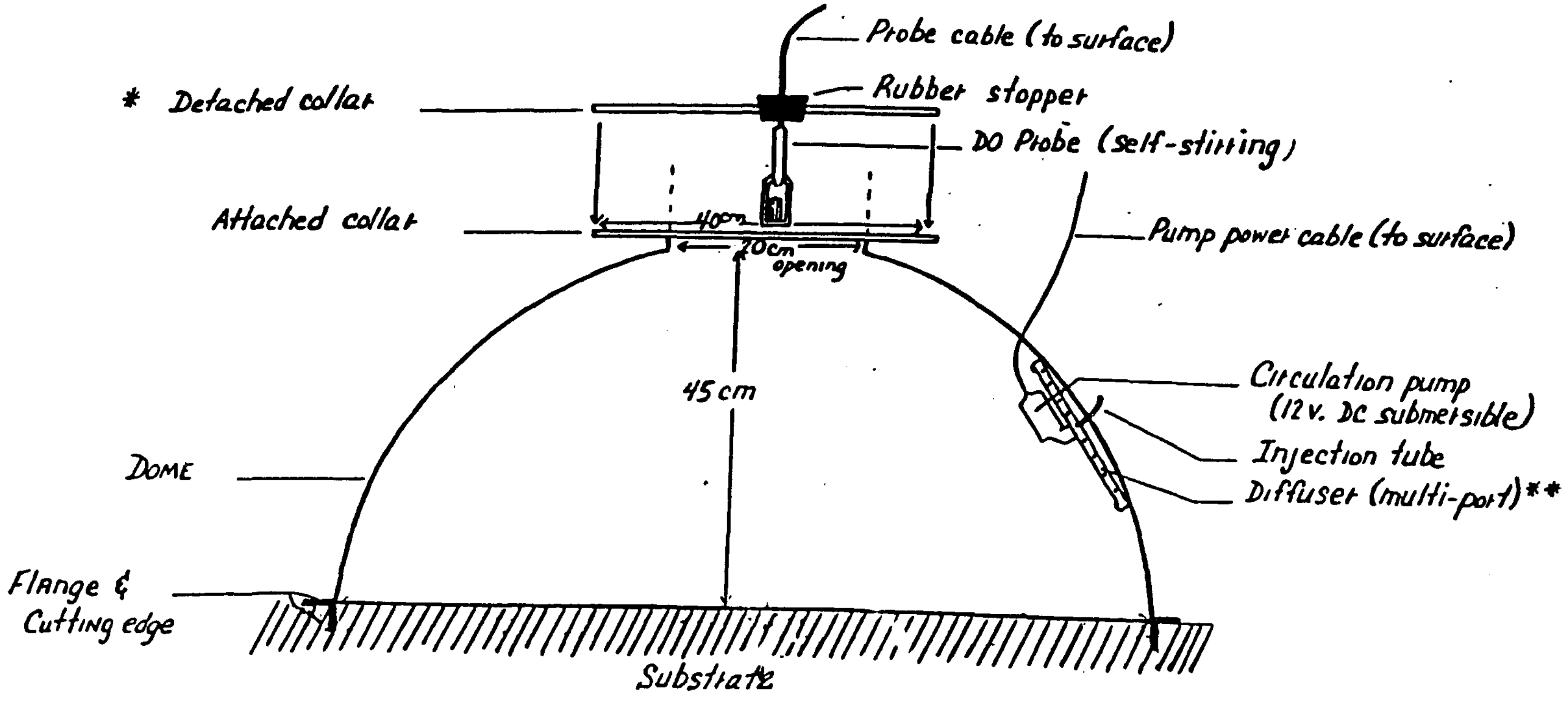


Figure 1. Prism-shaped SOD chamber, 1972 (after Lucas and Thomas 1972)



* Detached collar is lowered in place and secured to attached collar with C-clamps

** Ends of diffuser are capped

Figure 2. Hemispheric dome, 1973

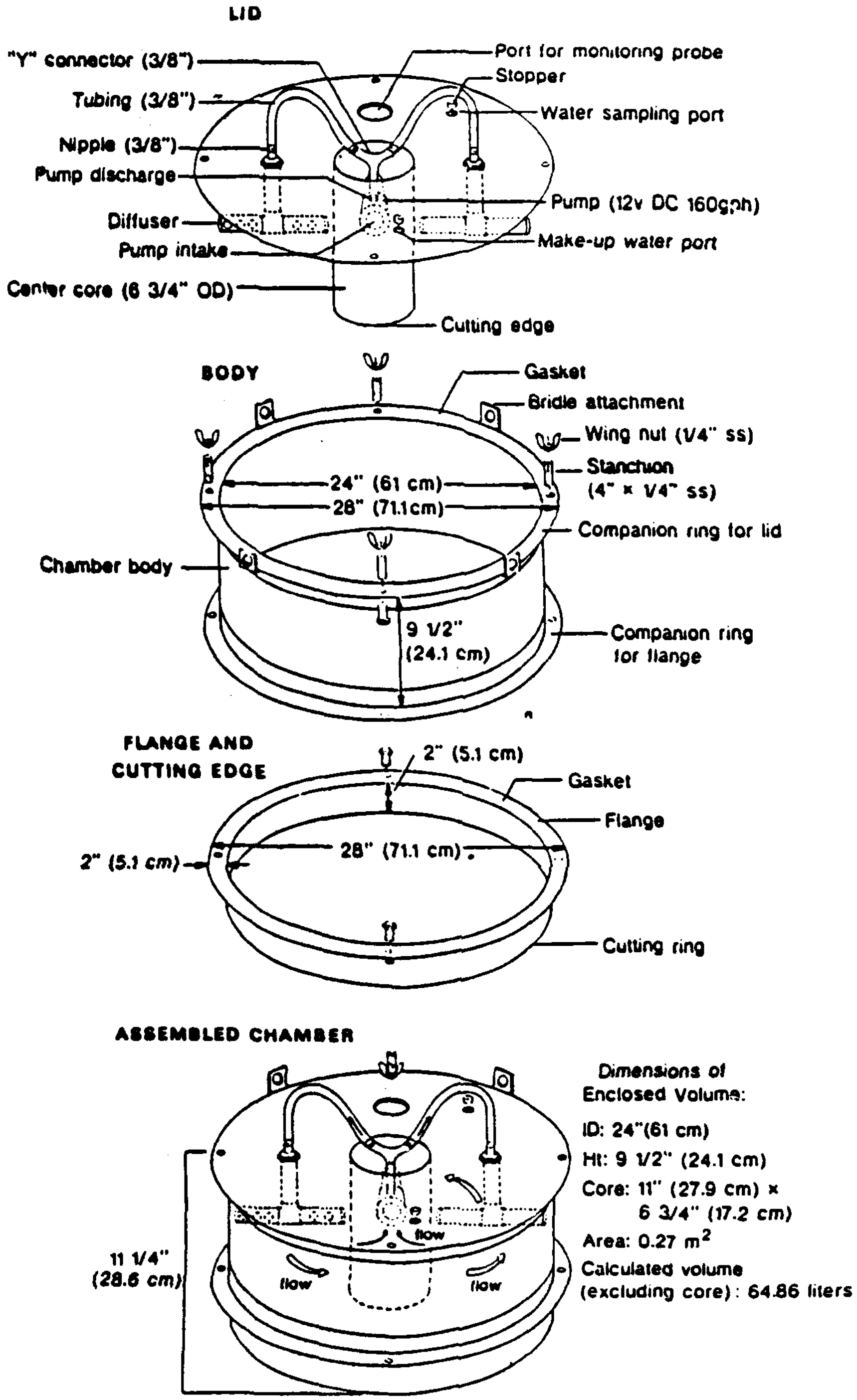


Figure 3. Annular chamber, 1976

bacteria which are all important elements affecting the dissolved oxygen regime of the stream. Such communities, however, are typically excluded from the waste load allocation assessments. The reason for this exclusion is simple. They don't normally fit within an *in situ* chamber or a sediment core.

With these small streams and possibly all other water bodies, the traditional approach to measuring SOD may need to be reconsidered. For example, the work of Odum (1956) and Odum and Hoskin (1958) makes available techniques to assess diel dissolved oxygen curves for the purpose of estimating total community respiration and gross primary production. The significance of the diel oxygen assessment provides an estimate of the dissolved oxygen production or respiration for the entire stream segment. The estimate is an integrated value for all sources of respiration or oxygen production relating to the water column, Aufwuchs, and benthic oxygen demand. The community sources of respiration or production could be partitioned by providing separate estimates of water column BOD or oxygen production. By subtracting water column effects from total community respiration, the remaining respiration could be redefined as total sediment oxygen demand which would include both biological and chemical uptake of oxygen. This approach to determining SOD, however, may have little utility in water bodies where the physical and chemical history of the water mass is unknown or more importantly where diel changes in dissolved oxygen concentration are apparent.

Oxygen Equivalent Approach to SOD

When dissolved oxygen concentrations are absent or generally less than 1 mg/L near the bottom, the use of *in situ* chambers is not practical. To use sediment cores and laboratory procedures for SOD determination would also appear as not practical because of the inherent difficulty of maintaining the testing environment at low or anaerobic conditions.

DiToro (1986) offers an alternative means of determining SOD rates regardless of the ambient state of the oxygen regime at the water-sediment interface. He provides a model framework which considers the COD flux of the sediment-interstitial water interactions. DiToro further demonstrates that the dissolved COD flux of the interstitial water and the SOD at the sediment-water interface are equal and for this reason the SOD rate is reported as an oxygen equivalent of the combined COD flux.

The DiToro oxygen equivalents model of SOD would be a useful assessment tool. The input data for such a model are collected in the field and not simulated under laboratory conditions. Further, the tools to collect the input data appear available as indicated by the work of Smith and Fisher (1986) and Lauria and Goodman (1986). These authors used a simple "stake" like device (Figures 4 and 5) which is vertically inserted into the sediments and left for a prescribed period of time, such as a week. As indicated in the figures, the membrane-covered cavities which are distributed along the length of the "stake" are sites where COD components collect via diffusion processes. The cavities are prefilled with deionized water. Upon retrieval of the "stakes," aliquots of each cavity solution are analyzed for COD or specific products of chemical reduction and respiration.

The oxygen equivalents model plus the "stake" type sampling device could provide a most useful approach to SOD measurements. Ambient dissolved oxygen concentrations are of no consequences to the procedure. Furthermore, sampling efforts could be expanded in a cost-effective manner. With the use of *in situ* chambers, a week of field effort may result in a maximum of six to eight stations being sampled. Even fewer stations would likely be assessed by the laboratory core methods because of limited lab space and time. The use of the *in situ* sampling "stakes" is very appealing since a much greater area of sediments can be assessed.

Temperature Compensation of SOD Rates

The dissolved oxygen concentrations of water overlying the sediments can be considered to be a factor affecting SOD rates (Hickey 1986, Edwards and Rolley 1965). The observed effects are that the SOD rate decreases with reduced concentrations of dissolved oxygen. Although the observations have yet to be explained, the observed effects should be carefully considered when attempting to demonstrate temperature compensation effects on SOD rates. In most instances, temperature effects on SOD are described in a mathematical formulation which generally shows direct proportional response of SOD to a measured increase or decrease in temperature.

Using temperature compensation effects only to describe seasonal responses, SOD would appear to be inappropriate given the view that SOD rates also appear to be dependent on dissolved oxygen concentration. For example, two seasonal SOD studies were conducted by Region IV personnel in Florida and Louisiana (Table 1). These data show the SOD rates to be inversely related to temperature and more directly affected by dissolved oxygen concentration. Obviously, two diverging effects are possible. The question is how valid is a temperature-compensated SOD rate without considering dissolved oxygen as a factor in the compensation calculations.

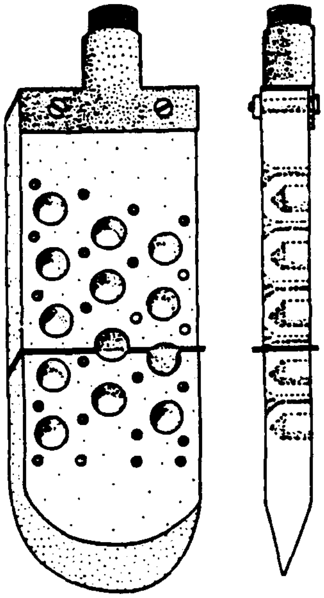


Figure 4. Sediment interstitial water sampler (after Smith and Fisher 1986)

Table 1

Comparison of Summer-Winter SOD Rates Relative to DO and Temperature

Location	Season	Water Temperature, °C	SOD $gO_2/m^2/hr$	Ambient DO mg/L
Charlotte Harbor, Florida	Summer	28.8	0.043	1.9
Charlotte Harbor, Florida	Winter	17.0	0.062	8.0
Calcasieu River, Louisiana	Summer	24.0	0.020	2.4
Calcasieu River, Louisiana	Winter	17.3	0.048	4.8

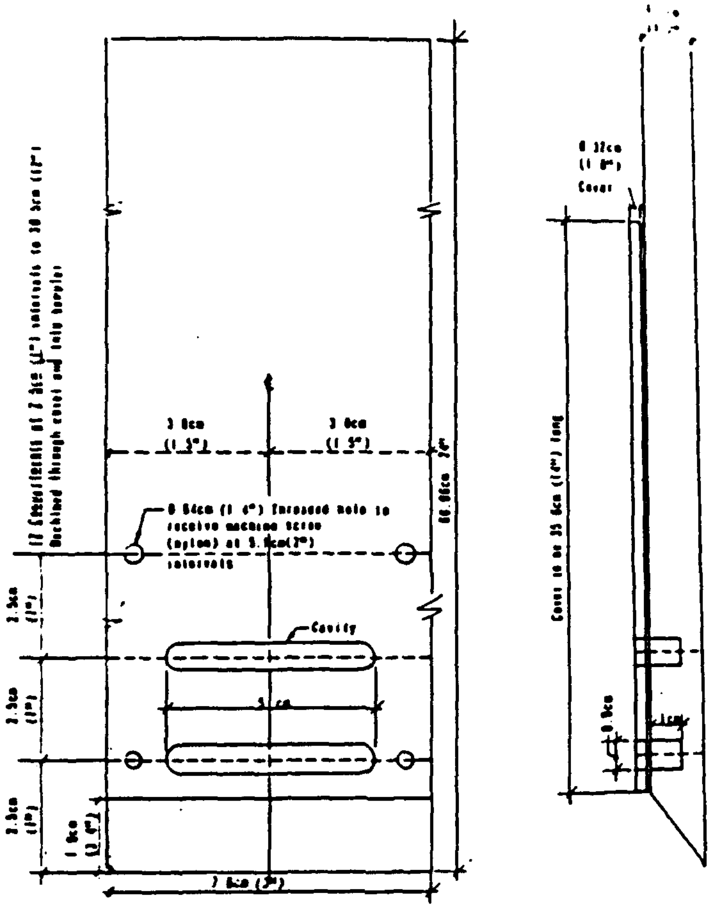


Figure 5. Sediment interstitial water sampler
(after Lauria and Goodman 1986)

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Chamber Measurements of Benthic Metabolism: Insights from Deep Sea Floor Studies

by

Richard A. Jahnke[1]

Introduction

The sea floor is recognized as an important location for the decomposition of organic materials and the consumption of metabolic oxidants in many marine environments. As such, reactions in the bottom sediments may exert considerable control on the chemical characteristics and biological habitability of the overlying water column. Quantifying chemical exchange across the sediment-water interface, therefore, is an important goal for assessing and monitoring water quality.

During the last four years, I have been involved in the development and use of a free vehicle instrument capable of performing benthic flux chamber incubations at the sea floor. To date, the instrument has been deployed at numerous sites adjacent to the central California continental margin and the California Borderland basin region.

In the following, I describe the instrument and discuss some of the rationale for the final design. Particular attention is given to the chamber stirring mechanism and methods used to evaluate the turbulence characteristics at the sediment surface within the chamber. Following the instrument description, results from the margin and basin regions are presented.

Instrument Design

The overall tubular frame of the Benthic Experimental Chamber Instrument (BECI) (Figure 1) is a smaller version of the design originally constructed by K. L. Smith, Jr. It consists of an upper section which contains large glass floatation spheres. The lower section is triangular in shape. Adjacent to each of the three "feet" are thin-walled open-ended cylinders in which expendable ballast is suspended from the jaw releases location directly above them. Each of these releases is connected to a central release by steel cables.

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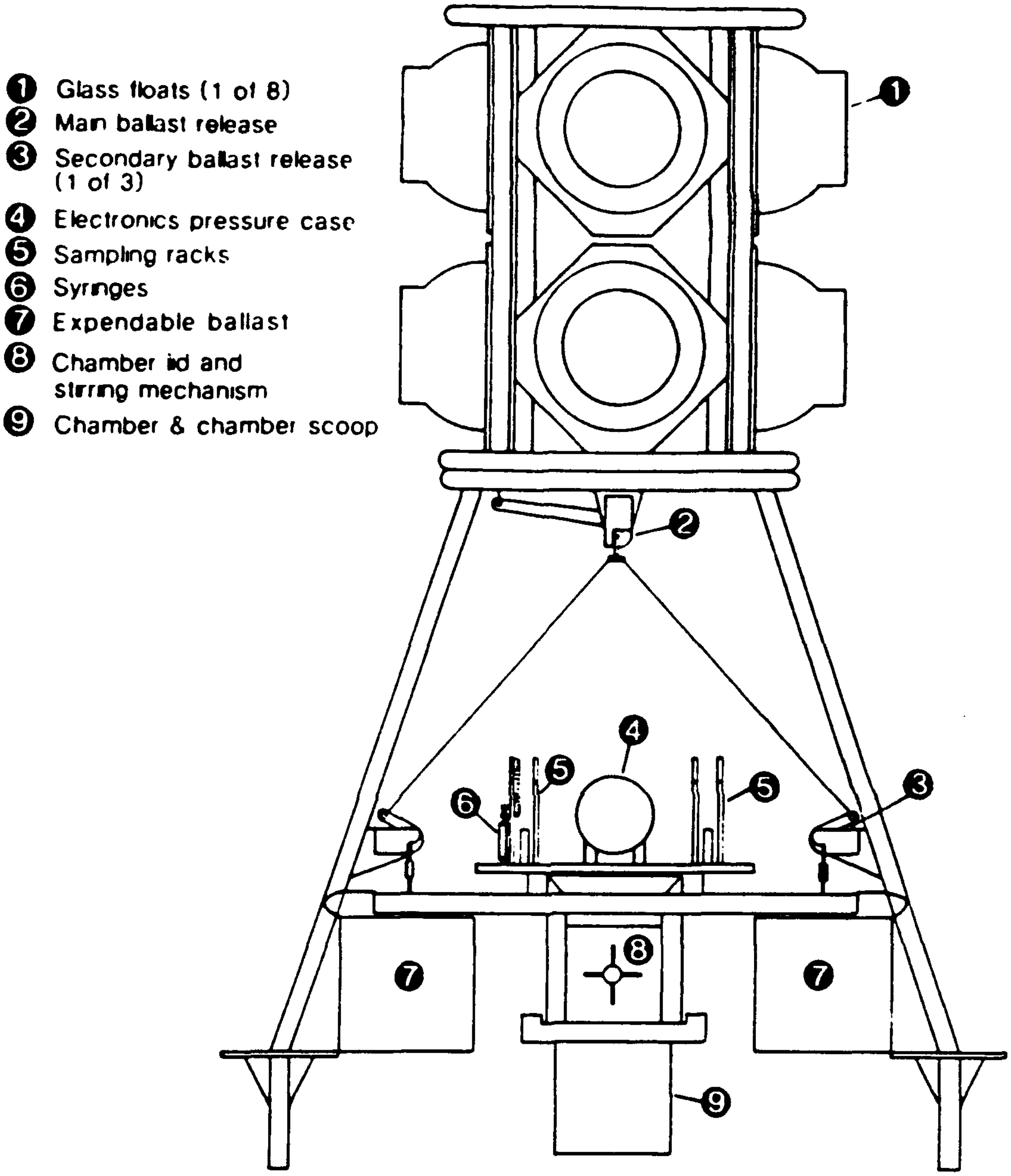


Figure 1. Schematic drawing of the benthic experimental chamber instrument. Note that one of the legs of the triangular frame has been omitted for clarity

The experimental chamber is located in the middle of the triangular base and the required electronics case, sample holders, and battery are secured directly above it.

The chamber consists of a 30- by 30-cm box constructed from thin-walled titanium that is open on the top and bottom (Figure 2). Hinged along one of the top edges is a lid constructed from polyvinylidene fluoride, a trace-metal

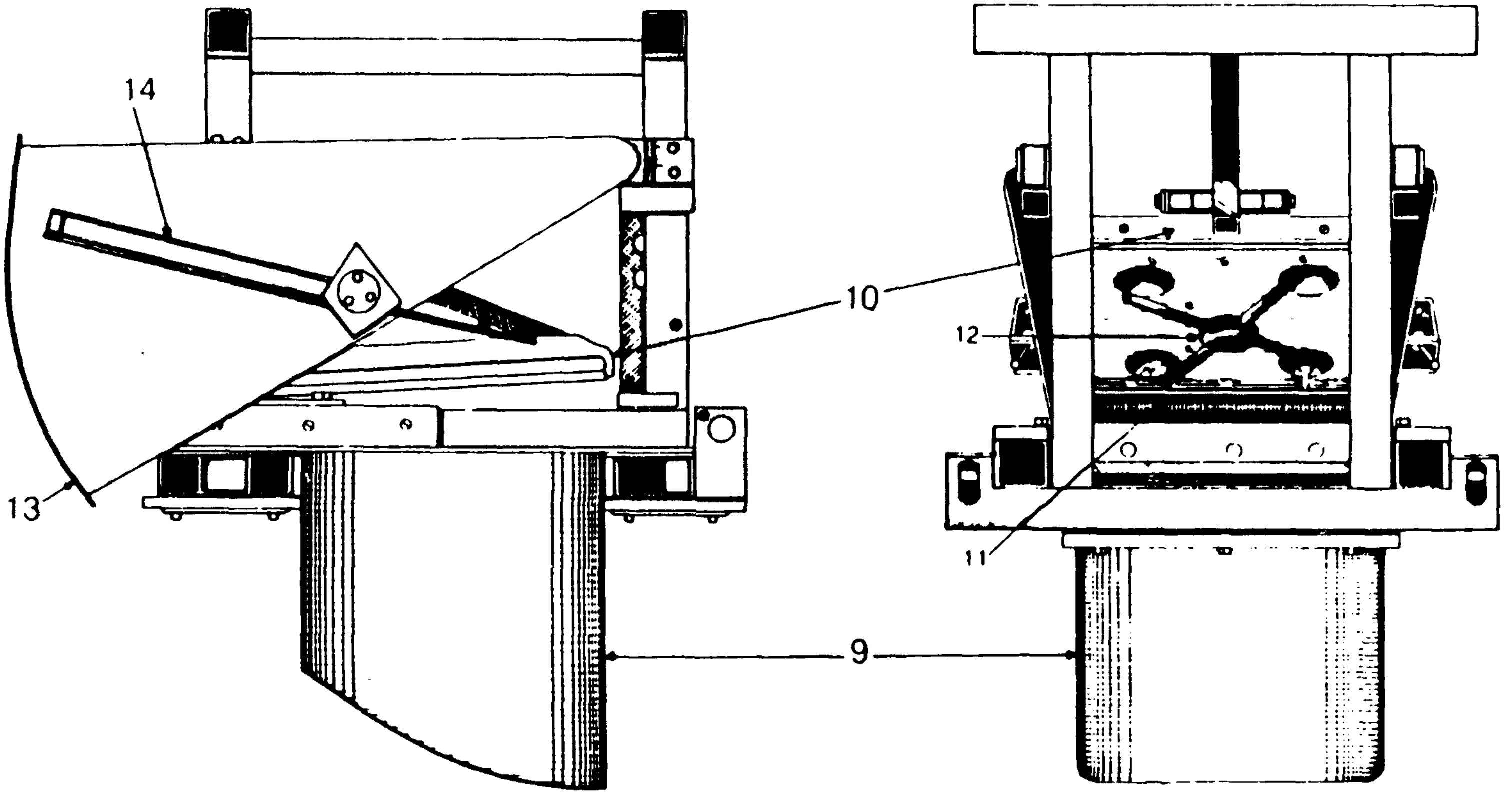


Figure 2. Side and front views of the chamber assembly. Numbered features are the titanium chamber (9), chamber lid (10), gaskets on the upper edge of the chamber against which the lid seals (11), chamber stirring mechanism (12), scoop for recovering the sediments within the chamber (13), and the hydraulic cylinder (one of two) that closes the scoop (14)

clean plastic of low gas permeability. An hydraulic ram closes the lid against a rubber gasket on the camber top to insure a watertight seal. Hinged to the sides of the chamber is a scoop which when rotated to its vertical position captures the sediment in the chamber.

The sampling system consists of inexpensive spring-driven syringes attached to the relatively simple release assembly (Figure 3). A spring (not shown in Figure 3) located on the back of the main mounting plate is oriented to pull the syringe piston upward if a sample is to be recovered or downward if a tracer is to be injected. A threaded rod, which is rotated by a d-c motor, is used to drive a small pin along the back side of the plate and sequentially release each syringe. When the sample has been fully recovered, the syringe piston is locked, preventing sample exchange during the remainder of the experiment or during vehicle recovery. As presently configured, two motor assemblies are used, each with ten syringes. Thus, twenty timed operations are performed for each deployment. A simple timer circuit in the central pressure case controls the experimental operations.

A variety of conditions must be met to achieve accurate chamber flux measurements. Many sources of uncertainty such as chamber water leakage or exchange and sediment disturbance can be easily assessed. Perhaps the most difficult criterion to assess is the influence of chamber water stirring rate on the measured fluxes. Besides mixing the chamber water so that a representative sample can be withdrawn, stirring also controls the hydrodynamic state and hence the diffusive sublayer thickness at the sediment surface. If reaction rates in the sediment are very rapid, supply or removal of solutes by diffusion across the diffusive sublayer may limit the benthic flux. Possible examples of diffusion-limited diagenetic systems are the dissolution of $CaCO_3$ below the lysocline, trace metal adsorption onto surface sediments, and oxygen fluxes into nearshore anoxic sediments.

In considering chamber stirring, it is important to recognize that much of the transport across the sediment-water interface may occur during fluctuations of the diffusive sublayer. Thus, to mimic the natural system, the mean and fluctuating characteristics of the near-bottom turbulent field must be reproduced within the chambers. It is likely that an exact matching of the turbulent characteristics within and outside of the chamber can never be attained.

A variety of different stirring devices were tested within the chambers (Figure 4). The bottom stress and equivalent film thickness that each

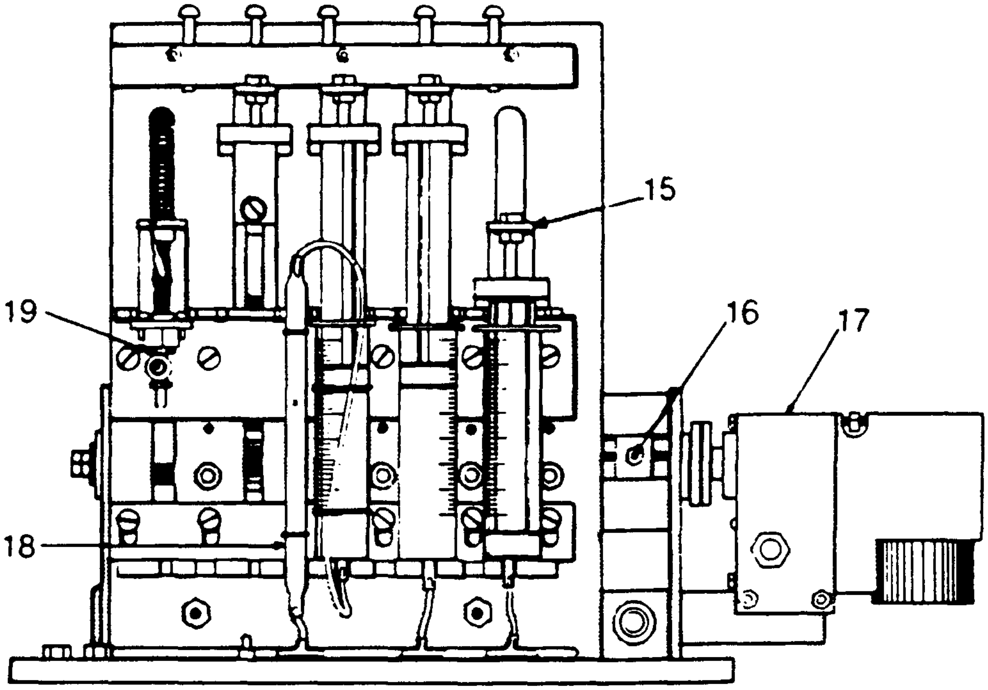


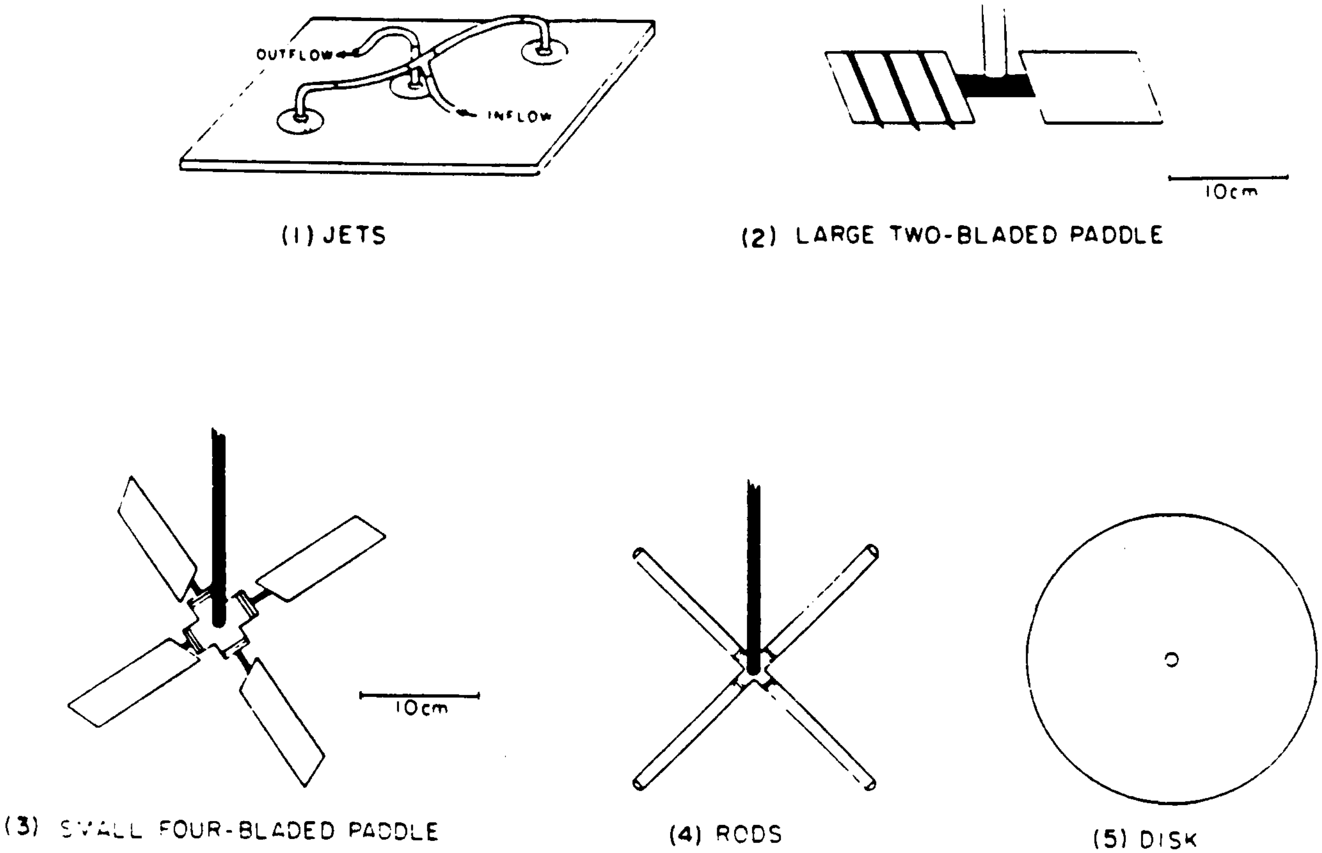
Figure 3. Sampling system. Numbered features are the elevator used to raise and lower the syringe pistons (15), the trip-pin that travels between the plates holding the syringes and releases the elevator latching mechanism (16), the housing in which is located the d-c motor used to drive the trip-pin (17), a glass ampule for gas and dissolved organics samples (18), and a valve used to control the hydraulics systems (19)

generates were determined for a variety of chamber volumes and stirring or flow rates. No one device mimics nature perfectly. For example, while the large double paddle provides an acceptable mean sublayer thickness, the turbulence intensities are much larger than those reported for natural conditions. The hydrodynamic conditions produced by the small paddles and the rods most closely approached those of natural systems. Examples of the mean diffusive sublayer thickness at different stirring rates and chamber depth of 10 cm are provided in Figure 5. The results are estimated from alabaster dissolution experiments. The shaded area represents the diffusive sublayer thickness estimated for many deep sea floor areas.

Case Studies

Central California slope

Over the last three years, a study of the benthic exchange along the California continental margin has been conducted. Study locations are displayed in Figure 6. Examples of benthic flux chamber results are provided



(1) JETS

(2) LARGE TWO-BLADED PADDLE

(3) SMALL FOUR-BLADED PADDLE

(4) RODS

(5) DISK

Figure 4. Examples of the types of stirring devices tested

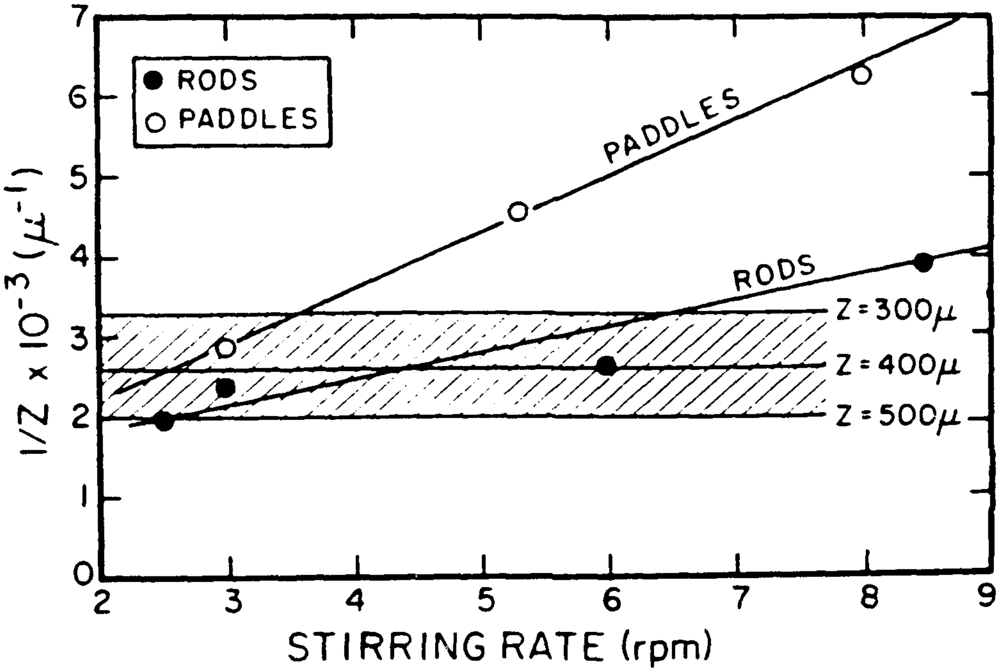


Figure 5. Results from alabaster dissolution rate studies for the indicated stirring devices as a function of stirring rate with a chamber depth of 10 cm

in Figure 7. In general, sediments consume oxygen and release silica, inorganic carbon, and phosphate. Nitrate is consumed in the sediments strongly in the oxygen minimum zone (where the oxygen content of the overlying bottom water is <10 umol/kg) but exhibits nearly no net flux at the other stations.

At the same locations, interfacial profiles of dissolved oxygen were measured *in situ* using the free-vehicle *In situ* MicroProfiler (IMP) (Figure 8). Oxygen fluxes were calculated from the measured interfacial gradient, effective sedimentary diffusion coefficients (corrected using the square of the porosity), and a one-dimensional form of Flick's first law.

Benthic oxygen fluxes estimated from chamber and microelectrode results are displayed in Figure 9 along with an oxygen hydrographic profile measured at GEOCSECS 202 that illustrates the well-developed oxygen minimum zone in this region. There is a large range in flux estimates even between

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* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page iv.

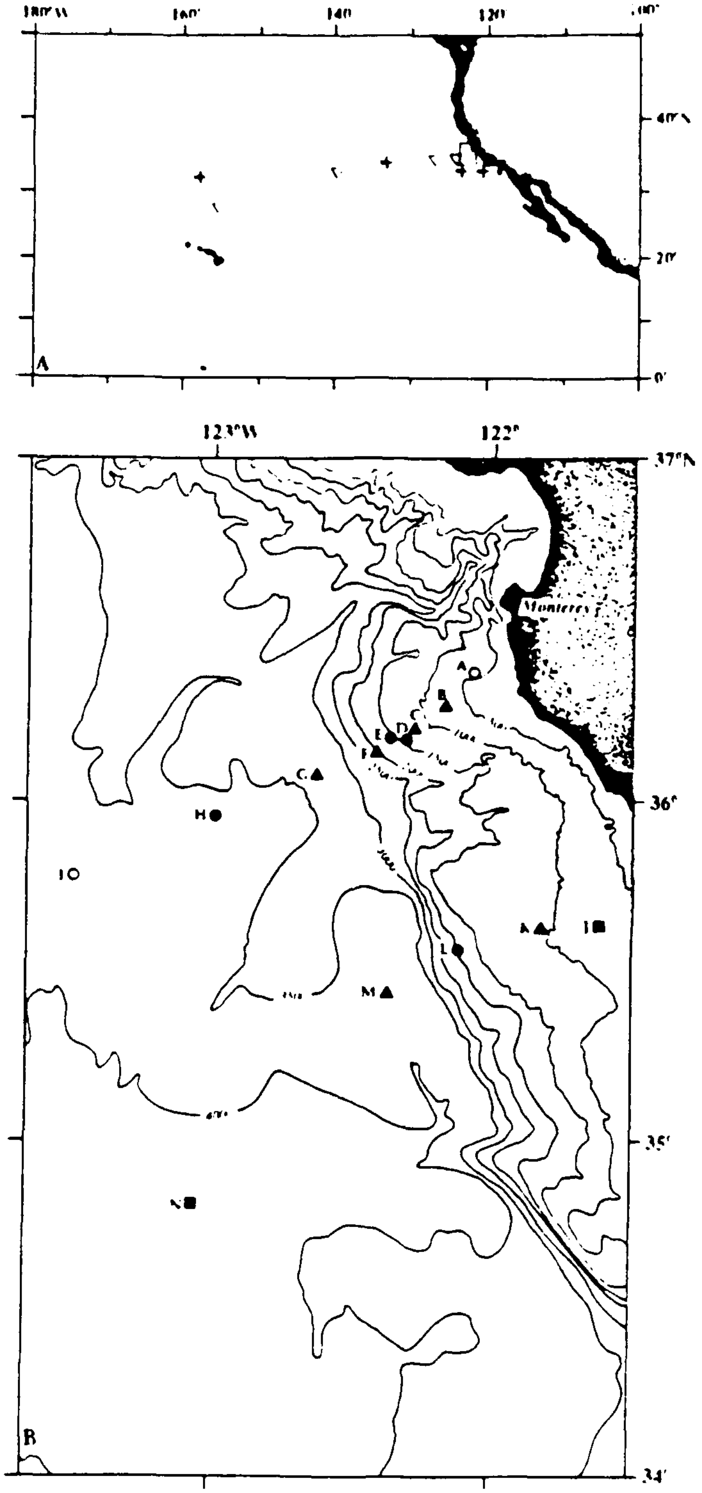
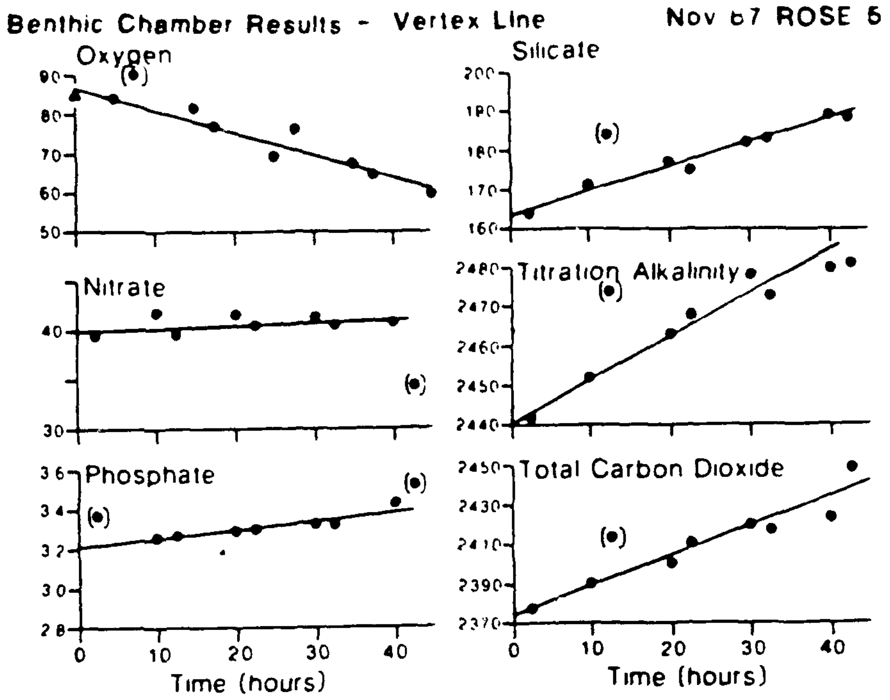


Figure 6. Sampling locations on the central California continental margin



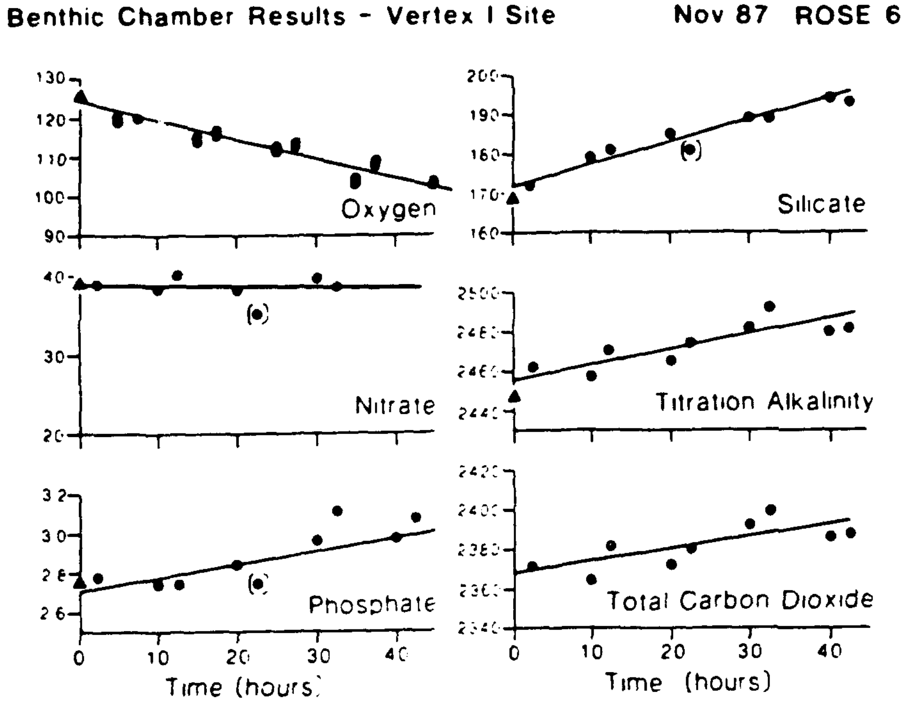


Figure 7. Examples of benthic flux chamber results on the California continental margin at a water depth of 2000 m (ROSE 5) and 3300 m (ROSE 6)

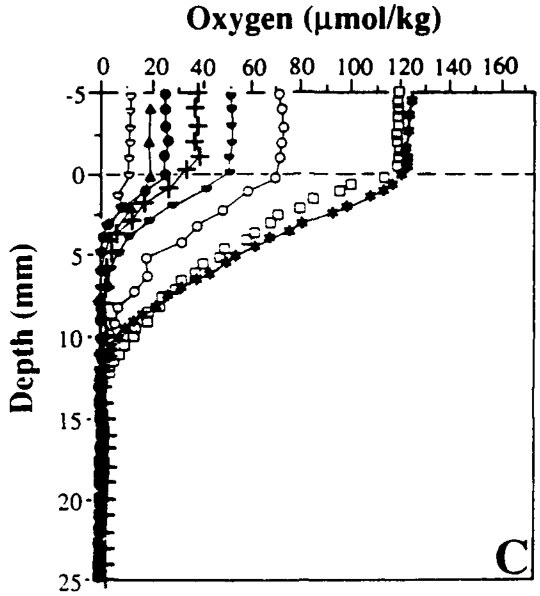


Figure 8. Representative oxygen profiles measured *in situ* by microelectrode at a subset of the study sights

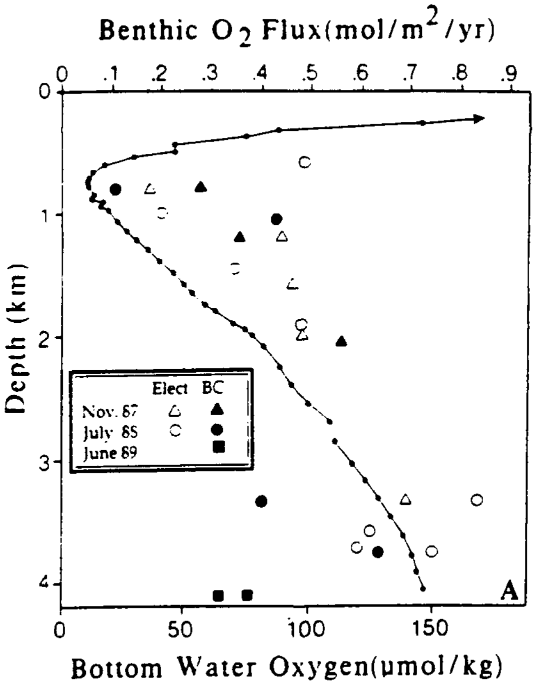


Figure 9. Benthic oxygen fluxes versus water depth for the indicated expeditions and techniques. Fluxes into the sediments are represented by positive values. Included is the GEOSECS 202 oxygen minimum zone in the northeast Pacific

measurements made less than a kilometer apart at similar water depths. This variability was expected considering the uncertainties of both techniques, the heterogeneous nature of surface sediments, and the patchiness of macrobenthic organisms in this region. Two important findings, however, are that the intra-site variability is smaller than the overall range of values and that no consistent difference between techniques is observed for benthic flux estimates.

In general, the lowest oxygen fluxes are observed in the oxygen minimum zone and tend to increase with increasing water depth and increasing bottom water oxygen content. The general correlation observed between bottom water oxygen content and benthic flux could result if fluxes are limited by diffusive transport. Estimates of diffusive sublayer thicknesses made by alabaster dissolution and oxygen microelectrode at a subset of these stations are <1 mm. Because pore water oxygen gradients extend to >4 mm, it does not appear the transport across the diffusive sublayer limits oxygen exchange at these sites. The general agreement between pore water calculated fluxes and benthic chamber measured fluxes supports this conclusion. If diffusive transport was limiting, the chamber fluxes would be systematically biased by the chamber stirring rate which was set to nominally maintain a diffusive sublayer thickness of 200-400 um.

Santa Monica Basin

Santa Monica Basin is a deep (>900 m), steep-sided, flat bottomed basin in the California Borderland directly adjacent to the continental shelf offshore of Los Angeles (Figure 10). Bottom water oxygen concentrations are less than 10 umol/kg. Although the bottom waters do contain some oxygen, the pore waters are everywhere anoxic as indicated by the presence of ferrous iron in all pore water samples (Figure 11). Decreasing sulfate concentrations indicate the occurrence of sulfate reduction in these sediments. Examples of the benthic chamber results (Figure 12) indicate the release of phosphate, silicate, and inorganic carbon from the sediments and the uptake of oxygen and nitrate.

Summary of all benthic flux estimates is presented in Table 1. Two important comparisons can be made to assess the internal consistency of the results. First, the pore water and benthic chamber silicate fluxes are similar suggesting that gross discrepancies do not exist in the methodologies. Second, the flux of oxidants (oxygen, nitrate, and sulfate) into the sediments can be used to predict the flux of inorganic carbon and titration alkalinity

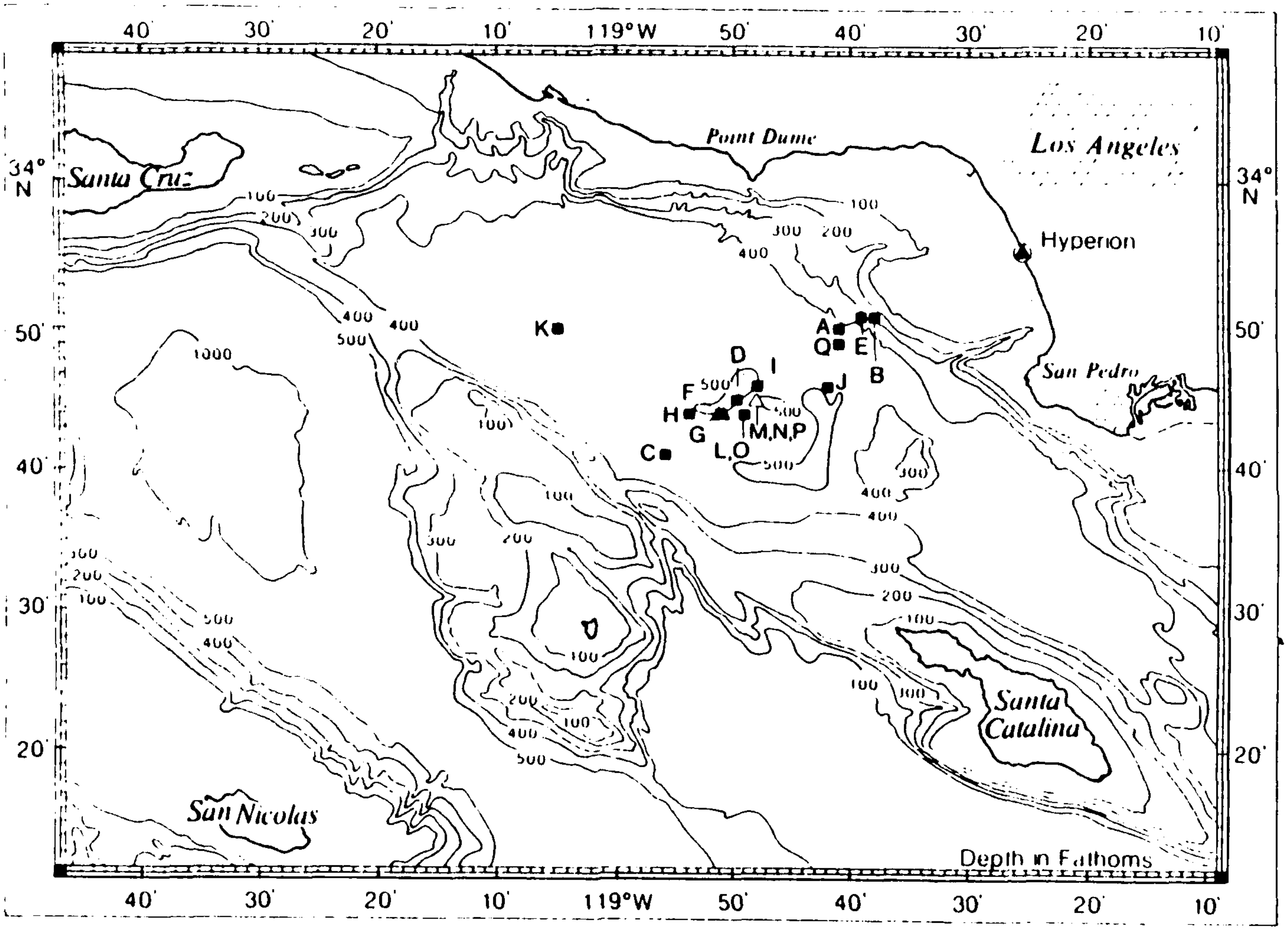


Figure 10. Sampling locations and bathymetry of Santa Monica Basin and adjacent areas

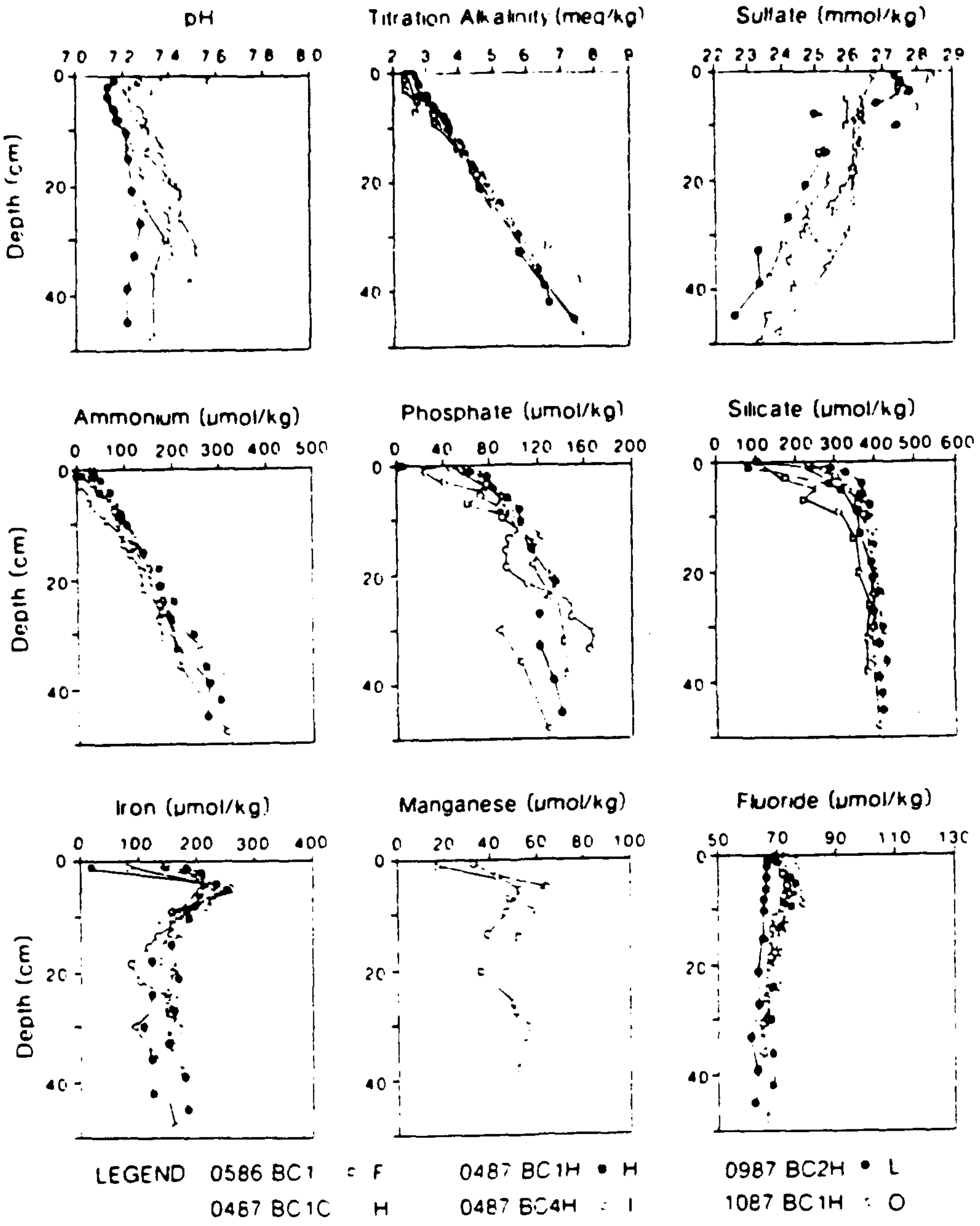
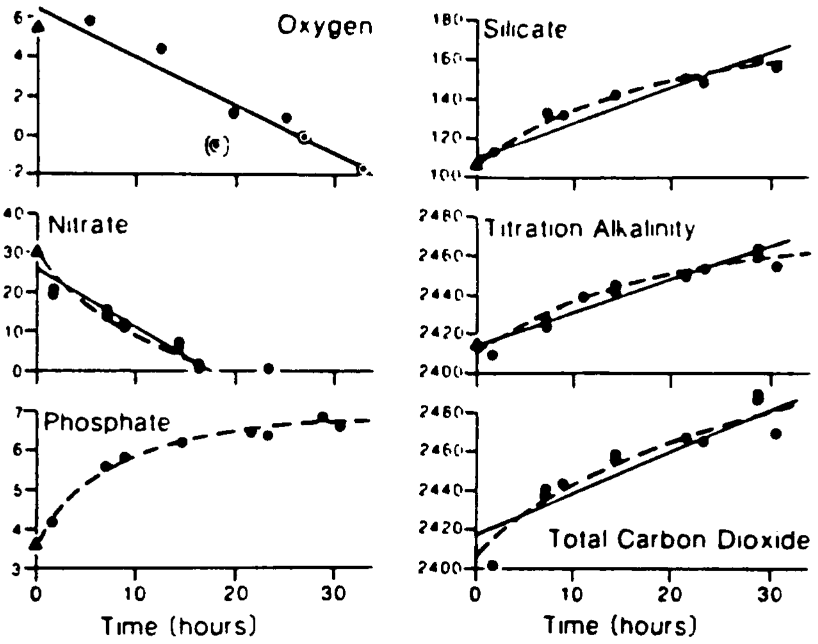
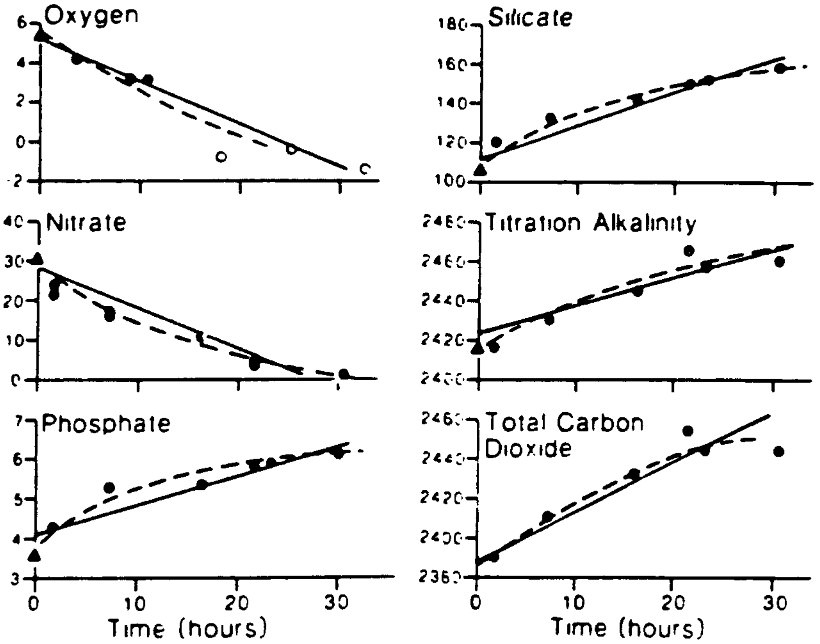


Figure 11. Pore water results for the indicated solutes at the center of the basin

from the sediments. The calculated values are sufficiently close to the measured results to suggest that an internally consistent data set has been obtained.



a. October 1987, ROSE 2



b. October 1987, ROSE 3

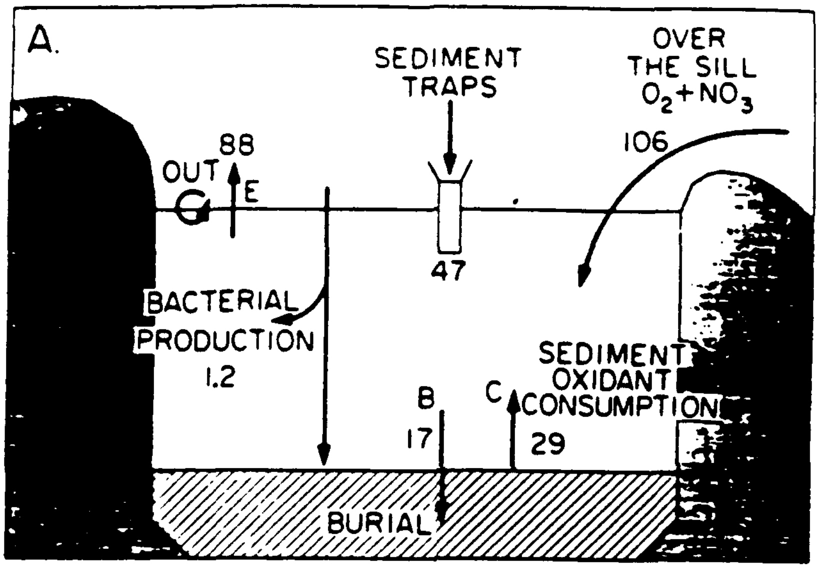
Figure 12. Examples of benthic chamber results for Santa Monica Basin

Table 1

Benthic Flux Summary (mmol $m^{-2}d^{-1}$)

Pore Water		O_2 (-0.6)	NO_3^-	SO_4^{2-} -0.4±0.08 n = 7	TCO_2	T.A.	$Si(OH)_4$ 1.9±0.5 n = 4	PO_4^{3-}
MANOP Lander	Ch1	--	-1.09	--	4.4	3.2	1.20	0.073
	Ch2	--	-0.81	--	--	--	1.38	0.055
	Ch3	--	-0.94	--	4.3	3.7	1.10	0.054
Shipboard Incubation			-0.81	--	--	2.6	1.24	--
BECI	#2	-0.2	-1.10	--	1.63	1.30	1.37	--
	#3	-0.25	-0.88	--	2.50	1.93	1.32	0.073
	#4	-0.35	-1.10	--	--	--	1.53	0.104
	#5	-0.34	-1.72	--	1.44	0.90	2.02	0.162
	#6	-0.66	-1.47	--	1.95	1.45	1.81	0.157
Average Measured *in situ* fluxes		-0.36±0.18	-1.10±0.31	--	2.70±1.33	2.15±1.04	1.47±.31	0.097±0.046
Calculated based on O_2, NO_3^-, SO_4^{2-} fluxes					2.36	1.98		

Because this is an enclosed basin, models of deep water exchange also provide estimates for the consumption of oxygen in the sediments (Figure 13). Recognizing that the hydrographic models do not include organic mineralization by sulfate reduction, the sum of oxygen and nitrate fluxes compares well with the sea floor fluxes. However, the hydrographic results suggest different relative contributions of nitrate and oxygen reduction to the total oxidant consumption than the sea floor data.



CARBON FLOW FOR BASIN
(Units of mg-C $m^{-2}d^{-1}$)

Figure 13. Summary of the deep water oxidant balance for Santa Monica Basin. To facilitate comparisons, oxidants are represented on an organic carbon equivalent basis assuming that the organic carbon would be oxidized completely to carbon dioxide

One explanation for the results is the oxidation of reduced chemical species (such as ammonia and ferrous iron) in the water column. Such reactions would increase the oxygen demand of the deep water of the basin without increasing the interfacial flux and provide an unaccounted source of nitrate to support the higher benthic nitrate fluxes. Another explanation is that the benthic oxygen flux is sensitive to stirring rate.

Thus, from the results, we make two general observations. At sites where significant quantities of reduced solutes are not present in the pore waters, benthic fluxes measured by flux chamber are not extremely sensitive to chamber stirring rate. Oxygen fluxes estimated from interfacial pore water gradients are comparable to those derived from chambers. The California continental slope is an example of this type of region.

Santa Monica Basin represents a second type of region where significant mobile, reduced solutes exist in the pore waters. In this example, ferrous iron is the major solute whereas in many other regions sulfide would be the major contributor. The oxidation of these reduced substances increases the rate at which oxygen is consumed in the sediments perhaps to the point where transport across the diffusive sublayer begins to limit the total flux. In these systems, measured oxygen fluxes will be sensitive to chamber stirring rate. In addition, however, oxidation reactions in the water column may contribute to the oxygen utilization. Thus, to establish total oxygen demand in these systems, it may be necessary to quantify the benthic exchange rate of all of the important oxidants.

Sedimentary Oxygen Demand and Its Effect on Winterkill in Lakes

by

Heinz G. Stefan[1]

Lake Oxygen Budget of Winterkill Lakes

Lake dissolved oxygen (DO) budgets are composed of the following major components:

Sources:	Reaeration at the surface (Ra)
	Photosynthesis by aquatic plants (P)
	Inflow (I)
Sinks:	Sedimentary oxygen demand (SOD)
	Water column oxygen demand (WOD)
	Outflow (O)

Each component can be given in units of g $m^{-2}d^{-1}$. WOD is mainly composed of biochemical oxygen demand (BOD) due to detritus in suspension in the water column and including bacterial respiration, and plant respiration (P). If BOD and P are given in units of g $m^{-3}d^{-1}$ as is often the case, then

$$WOD = (BOD + P)h$$

where h is the mean lake depth. The arithmetic sum of these terms is the net oxygen input to a lake and provides DO enrichment if positive or DO depletion if negative. For an entire well-mixed lake of average depth h this can be expressed as

$$\frac{dC}{dt}h = Ra + P + I - SOD - WOD - O$$

where

C = DO concentration (g/m^3)
t = time

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Lakes are often stratified and a DO budget equation must then be applied to each layer separately. In stratified lakes exchange between layers must be included in the equation, e.g. as a diffusive flux.

In ice-covered lakes, the sources are drastically reduced: ice-covers prevent reaeration and snow on ice screens most of the light necessary for photosynthesis; inflows are often only from groundwater with low DO. As a result it is not uncommon for the DO to decline steadily after an ice-cover has formed. Particularly in very shallow lakes DO may be depleted by February or March. Fish begin to be stressed at different levels of DO depending on species. Winterkill begins to occur when DO falls below 0.2 to 2.5 mg/ℓ depending on fish species. Aeration or unlimited fishing are usually implemented when that happens.

Sedimentary Oxygen Demand

Measured DO depletion in ice-covered lakes is usually attributed to two sinks: WOD and SOD. Particulate organic material in ice-covered shallow lakes, and hence not affected by wind, usually settles out readily. Macrophytes have usually died and also sunk to the bottom. Therefore WOD in such lakes is often small. SOD is directly associated with the biochemical decomposition of organic materials on the lake bottom. In 58 small reservoirs investigated across the U.S., the calculated organic carbon accumulation rate ranged from 26 to 3700 $gCm^{-2}yr^{-1}$ with a mean of 675 ± 739 $gCm^{-2}yr^{-1}$ (Ritchie 1989). The rates were highest in sediments from grassland watersheds. Reservoir sediments are therefore a significant sink for organic carbon. The conversion of organic carbon to mineral inorganic compounds, particularly CO_2, therefore makes the sediments a considerable oxygen sink. If all the above carbon were converted to CO_2, 4.93 $gO_2m^{-2}day^{-1}$ would be required.

Winter oxygen depletion rate (WODR) is

$$WODR = SOD + WOD$$

In lakes WODR has been determined by several investigators. Mathias and Barica (1980) and Ellis and Stefan (1989) arrived at mean values of 0.24 $gO_2m^{-2}d^{-1}$ for a 1.5-m-deep midwestern lake. Previous studies of WODR summarized by Ellis and Stefan (1988) show that for midwestern shallow lakes

$SOD \approx 0.23\ gO_2m^{-2}d^{-1}$ and $WOD \approx 0.01\ hO_2m^{-2}d^{-1}$, where h = lake depth in meters. Other values reported are SOD = 0.142 and 0.20, WOD = 0.062 h and 0.036 h.

In a set of microcosm experiments with quiescent and stirred water columns with Golden Lake, Minnesota, sediments, Dr. H. Runke of Barr Engineering Co. in Bloomington, MN, determined the following BOD and SOD values:

	at 5°C	at 21°C
BOD in water column, mg $O_2\ell^{-1}d^{-1}$	0.12	0.57
SOD static condition, g $O_2m^{-2}d^{-1}$	0.33	1.65
SOD mixed condition, g $O_2m^{-2}d^{-1}$	1.00	4.39

In situ measurements of DO in Island Lake, Minnesota, by Noonan (Ramsey County) gave a WODR of 0.26 g $O_2m^{-2}d^{-1}$. The DO loss in the water column from which this value was derived was 0.18 mg $O_2\ \ell^{-1}d^{-1}$.

The dependence of SOD on other basic physical/biological parameters is of particular interest to this workshop. Available data suggest a dependence of SOD on at least three: temperature, availability of dissolved oxygen, and flow velocity.

Temperature

SOD is the result of bacterial activity and chemical processes by which organic material is decomposed. A dependence on temperature must therefore be expected, and can be expressed through either the Arrhenius equaution or a more empirical relationship of the form $SOD(T) = SOD(T_o)\theta^{T-T_o}$

where T = temperature
T_o = reference temperature
θ = parameter on the order of 1.02 to 1.08

The lower value may be more appropriate at low temperatures.

Availability of oxygen

The rate of oxygen consumption at the sediment surface may become dependent on the rate at which oxygen can be supplied from the water. Obviously when the DO of the overlying water is zero, SOD is also zero. A conceptual model for the transfer of DO from the water to the sediments can be formulated as a diffusion process through a composite boundary layer. This is similar to a surface film reactor model.

The rate of diffusion is $r = k_f \frac{\partial C}{dz}$. The DO concentration gradient $\frac{\partial C}{dz}$ between the sediment surface $z = 0$ and the water column may vary with distance z but will definitely depend on the DO in the water. In field measurements, WODR diminishes typically when DO falls below about 3 mg/ℓ (Belanger 1981; Mathias and Barica 1980).

Velocity

The diffusion coefficient k_f depends on the turbulence level in the boundary layer and, hence, velocity. For flat surfaces in fully developed turbulent and laminar flows, transfer coefficients have been developed as a function of Reynolds number of the flow. Velocity V is a parameter in the Reynolds number $Re = V\delta/\nu$, and controls boundary layer thickness δ. Although near sediment boundary layers in lakes do not have fully established, steady flow, a strong effect of velocity on DO transfer rates must be expected for two reasons.

(1) With velocity, turbulence intensity and k_f increase.

(2) With velocity, boundary layer thickness δ decreases and, hence, the DO gradient $\partial C/dz$ increases.

Velocity effects have been observed directly in field and laboratory experiments. Data by Belanger (1981) and those by Runke given below show this clearly.

Velocity effects also manifest themselves indirectly when lake aeration systems designed for measured WOD values are unable to maintain the expected DO levels. The flow velocities induced near the lake bed by many of these devices are the likely reason for the increased oxygen demand.

Aeration

As a remedy against low oxygen concentrations, various forms of lake aeration techniques are used (Pastorok, Lorenzen, and Ginn 1982). Air bubble plumes and cascade aerators are probably the most common. The former release compressed air at some depth in a lake and the latter withdraw water at some depth and discharge it over a cascade back into the lake. Both create open water in the ice covers of lakes which can be a hazard. Both systems also induce water circulation over the sediment bed at least in a part of the aerated lake. This increases SOD significantly as indicated earlier.

Selective aeration of water layers in the thermocline or the hypolimnion has therefore been studied. Metalimnetic aeration under summer conditions (Stefan et al. 1987) and similarly aeration of the thermocline region in winter lakes has been investigated (Ellis and Stefan 1989). The basic idea behind these designs is to create an oxygenated water layer as a refuge for animals (fish, daphnia) but to minimize oxygen supply to the sediment layer.

Selective aerators are devices which withdraw and discharge water at a low velocity so that the natural stratification is maintained. Between intake and discharge the water is enriched with DO using cascades or enclosed bag-type bubble aerators. Applications are of particular interest in shallow lakes. Selective aerators are designed to discharge at velocities on the order of 1 to 5 cm/s. Typically selective aerators produce an aerated and mixed layer at intermediate depth without destroying the stratification in the lake.

Photosynthesis

Photosynthesis in summer is usually confined to the upper light-receiving layers of a lake. In winter snow covers on ice usually attenuate light penetration and reduce photosynthesis to insignificant levels, compared to WODR. Exceptions do occur, however (Barica, Bigson, and Howard 1983). A very recent case was observed in Island Lake, Minnesota, by Ellis and Stefan (1990b) in the snow-deficient winter of 1989/90. In that case 50 percent of the photosynthetically active radiation (PAR) received from the atmosphere was able to reach the underside of the ice cover. As a result macrophytes started to grow in the shallow lake (2.8 m maximum depth) and mean DO concentrations reached and remained above saturation levels from February 1 to ice-out. DO profiles were nearly uniform with depth except near the underside of the ice cover concentrations were as high near the bed as anywhere else. In this particular situation, photosynthesis near the bed produced more oxygen than SOD could consume. This led to DO supersaturation in the water column.

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Assessment of Sediment-Related Processes in a Central Wisconsin Reservoir

by

Douglas Gunnison[1] and John W. Barko[1]

Background

In 1937 the Wisconsin Valley Improvement Company (WVIC) constructed the 2,760-ha Big Eau Pleine Reservoir by impounding the Big Eau Pleine River. The reservoir was created to assist in providing uniform flows in the Wisconsin River, and has had a subsequent history of major winter fish kills and summer algal blooms (Shaw and Powers Undated). Based on results of previous studies, the winter fish kill problem is believed to result from an oxygen sag which develops periodically under the ice in upper reaches of the reservoir, and then moves downstream as water is withdrawn from the project (Gunnison and Barko 1988).

The US Army Engineer Waterways Experiment Station (WES) was asked to examine results of previous studies and other available data to evaluate earlier recommendations for water quality improvement (Gunnison and Barko 1988). Results of this effort indicated that the reservoir is a sink for total phosphorous, but releases organic matter in the form of biochemical oxygen demand. Insufficient information was available to permit a determination of the environmental factors contributing to dissolved oxygen sag development and propagation. However, additional information related to the dissolved oxygen depletion problem is being obtained from intensive field investigations initiated in 1989. The objective of this initial report is to assess the role of sediment dynamics in dissolved oxygen depletion during the winter in the Big Eau Pleine Reservoir.

Methods and Materials

During May 1989, sediment samples were taken at 37 locations along the length of the reservoir. Multiple samples were taken along transects at river

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miles 0.3, 8.0, 12.0, 16.0, and 17.4. The position of each sampling location and depth were accurately determined for later resampling activities. Two types of samples were taken at each location. These included 5-cm core samples taken to the depth of compacted sand, or to a maximum of about 25 cm (core length).

Core samples were measured for length, and then sectioned vertically into 0- to 5- and then 10-cm strata for determinations of physical characteristics.

Analyses included bulk density and organic matter content; these data were used to characterize patterns of sediment transport and focussing in the reservoir.

To determine the nature of the sediments in intimate contact with the overlying water, several chemical characteristics of the surficial sediments were examined. Composited surficial sediment samples were analyzed for chemical variables using suitable precautions to maintain the anaerobic integrity of the sediments. With interstitial water fractions, Fe, Mn, soluble reactive phosphorus (SRP), ammonium nitrogen (NH_4-N), chemical oxygen demand (COD), and dissolved organic carbon (DOC) concentrations were determined along with conductivity and pH.

Results

Sediment density and organic matter content

Table 1 presents sediment density information obtained from core samples taken at various points along the length of the reservoir. There were four locations where sediments had similar low densities at each of the three depths sampled. These were at river mile 3.0, at river mile 10.0, at river mile 12.0, and at river mile 14.0. Average densities for the entire 0- to 15-cm depth at these locations were 0.42 ± 0.04 g/ml at river mile 3.0, 0.33 ± 0.02 g/ml at river mile 10.0, 0.64 ± 0.04 g/ml at river mile 12.0, and 0.54 ± 0.06 g/ml at river mile 14.0. While there were sporadic incidences of values similar to these at other locations, none of the other areas had deposits of material having low density material homogeneously distributed over the entire 15-cm depth.

Table 2 gives a comparison of sediment organic matter content in core samples from the same locations along the reservoir. There were several

Table 1

Comparison of Density in Upper 15 cm of Sediment Cores Taken Along the Course of the Big Eau Pleine Reservoir*

Sample Location, River Mile	Density, g/ml at Depth Interval		
	0-5 cm	6-10 cm	11-15 cm
0.3	0.94 ± 0.26	1.15 ± 0.12	1.20 ± 0.26
3.0	0.38	0.38	0.49
4.0	0.81	0.91	0.87
8.0	0.74 ± 0.23	0.58 ± 0.02	0.74 ± 0.11
9.0	1.00	1.28	1.23
10.0	0.32	0.30	0.38
11.0	0.67	1.13	1.31
12.0	0.56 ± 0.15	0.68 ± 0.18	0.67 ± 0.12
12.5	1.11	1.05	1.12
13.7	0.93	0.85	1.28
14.0	0.44	0.52	0.66
16.0	1.37 ± 0.18	1.07 ± 0.12	1.01 ± 0.10
17.4	1.06 ± 0.06	1.24 ± 0.14	0.94 ± 0.07

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* Locations where samples were taken across a transect are presented as means ± standard errors. The remaining samples are data obtained from single analyses.

Table 2

Comparison of Organic Matter in Upper 15 cm of Sediment Cores Taken Along the Course of the Big Eau Pleine Reservoir*

Sample Location, River Mile	Organic Matter, Percent, at Depth Interval		
	0-5 cm	6-10 cm	11-15 cm
0.3	5.45 ± 0.86	3.09 ± 1.20	2.83 ± 1.36
3.0	1.45	2.37	2.07
4.0	3.88	3.55	4.07
8.0	9.49 ± 0.48	10.20 ± 0.60	7.92 ± 1.23
9.0	3.05	2.02	2.87
10.0	8.33	9.65	8.59
11.0	5.48	4.04	2.55
12.0	5.82 ± 0.90	5.72 ± 0.93	6.17 ± 0.25
12.5	4.51	3.22	3.61
13.7	0.32	5.41	5.79
14.0	2.67	6.86	6.58
16.0	2.38 ± 0.18	2.69 ± 0.66	3.14 ± 0.67
17.4	2.14 ± 0.46	2.34 ± 0.99	3.04 ± 2.03

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* Locations where samples were taken across a transect are presented as means ± standard errors. The remaining samples are data obtained from single analyses.

locations where organic matter content did not vary over the 0- to 15-cm depth. These were at river miles 3.0, 4,0, 9.0, 10.0, 12.0, 12.5, 16.0, and 17.4. Maximum values of sediment organic matter content occurred at river miles 8.0 and 10.0. Minimum sediment organic matter content occurred at river mile 13.7, but was restricted to the upper 0 to 5 cm. Consistently low sediment organic matter content occurred over the entire 0- to 15-cm depth at river miles 3.0 and 17.4.

Sediment chemistry

Figure 1 depicts NH_4-N, SRP, and DOC levels in sediment interstitial water along the course of the Big Eau Pleine River from 0.3 mile above the dam to mile 17.5, where the uppermost sample was taken. The pattern encountered for NH_4-N and SRP was quite erratic. With the exception of a peak value of 31.7 mg/l achieved at river mile 2, NH_4-N values were less than 20 mg/l over the course of the reservoir length. SRP peaks of 1.2 mg/l and 0.88 mg/l occurred at river miles 8.0 and 12.0, respectively. A peak DOC value of 87.2 ml/l, more than twice the magnitude of concentrations over the first 8 miles, occurred at river mile 10 in a broad-shouldered peak extending between river miles 9 and 14.

Iron, manganese, conductivity, and COD in interstitial waters also demonstrated distinct peaks at the 10.0-mile mark (Figure 2). This was particularly pronounced for interstitial water iron, with a peak value nearly three times the next closest value. Lower-level peaks for each of these constituents occurred between river miles 2 and 7 above the dam.

Discussion

The accumulation of reduced iron and manganese under anaerobic conditions in the interstitial waters of flooded soils and sediments is a well-known phenomenon (Ponnamperuma 1972; Yosida 1975; Brannon, Chen, and Gunnison 1985), and it is assumed that all of the iron and manganese measured in the interstitial waters obtained in this study was in reduced form. The occurrence of a peak value for conductivity in the same areas as peaks for iron and manganese reflects high concentrations of ionized substances in the water. High levels of DOC and COD were found in sediment interstitial water in areas of the reservoir that may receive high inputs of organic matter (Gunnison and Barko 1988). The occurrence of peak values of DOC in combination with reduced

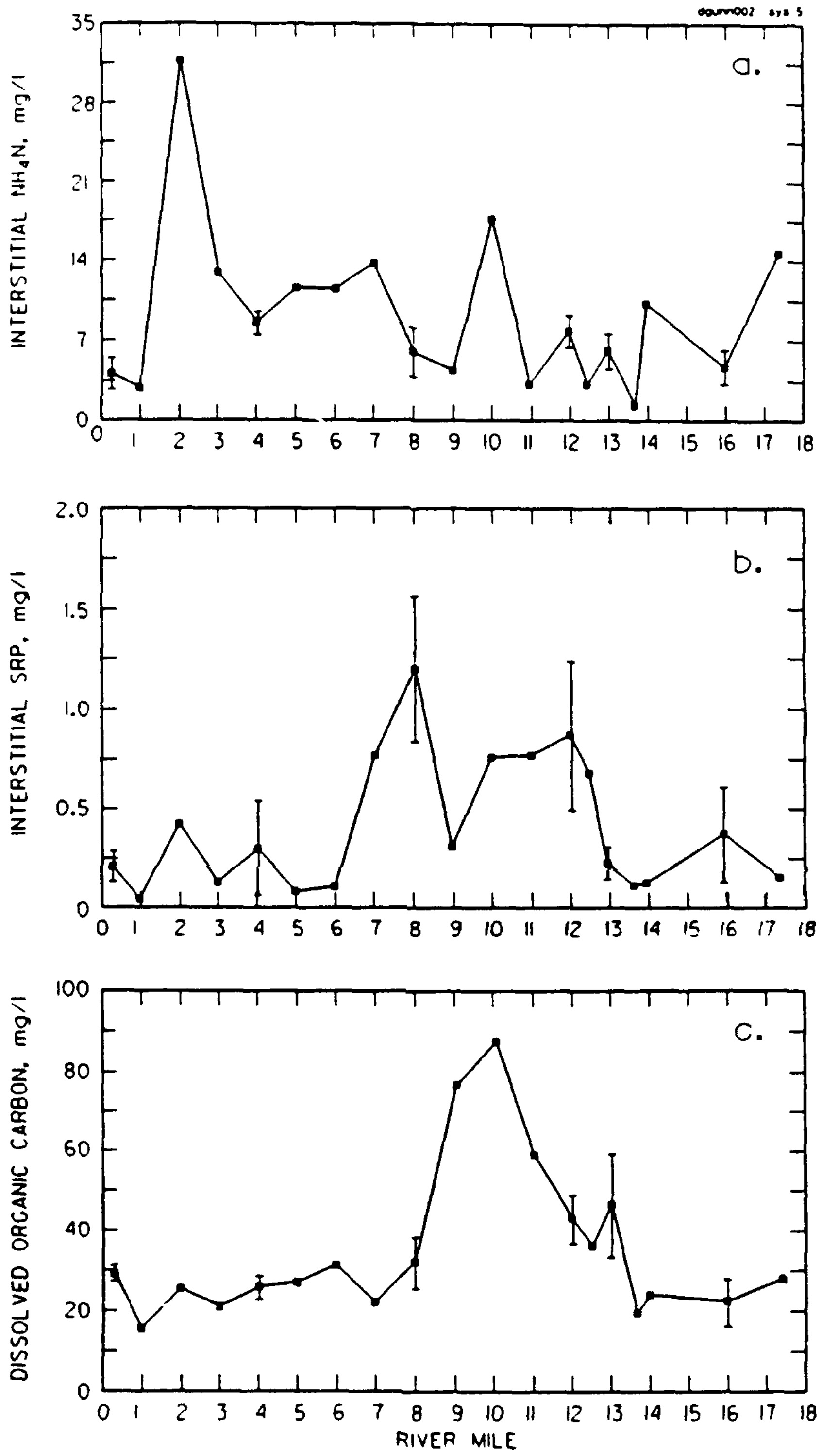

Figure 1. Nutrient levels in interstitial waters of sediment samples taken along the length of the Big Eau Pleine Reservoir: (a) Ammonium-nitrogen (NH_4-N), (b) soluble reactive phosphorus (SRP), and (c) dissolved organic carbon (DOC). Bars represent variation obtained when samples were taken across transects

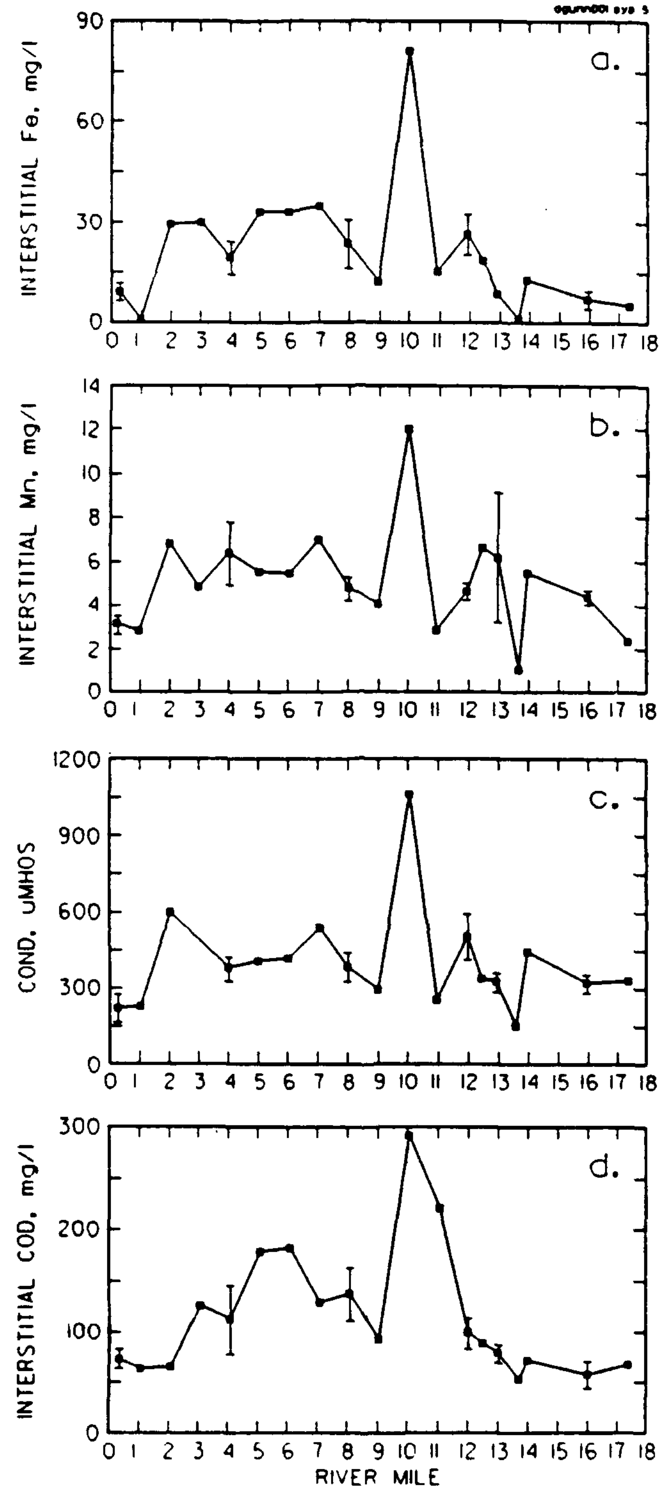

Figure 2. Metal, conductivity, and chemical oxygen demand (COD) levels in interstitial waters of sediment samples taken along the length of the Big Eau Pleine Reservoir: (a) iron, (b) manganese, (c) conductivity, and (d) COD. Bars represent variation obtained when samples were taken across transects

metals in the river mile 10.0 to 12.0 area is important in view of the low density and thus potential erodibility of sediment in this area.

Based on the data obtained, we made the following calculation for the oxygen demand released by potential resuspension of the upper 15 cm of sediment in the river mile 10 reach of the reservoir (this depth is justified by the homogeneity and low density of the sediment in this area).

1. The volume of potentially suspended sediment per m^2 surface area is 150 litres (100 cm x 100 cm x 15 cm = 150,000 cm^3/1000 cm^3/l = 150).

2. Interstitial water content of 150 litres of sediment at a density of 0.32 g/ml is 102 litres (68 percent of sediment volume).

3. The COD of the sediment interstitial water at river mile 10 is 292 mg O_2 per litre. Thus, 292 mg O_2/l x 102 litres = a total COD of 29,784 mg O_2.

4. At 4° C, a litre of water holds 13.1 mg O_2 at saturation. Thus, resuspension of sediment to a depth of 15 cm could completely deoxygenate 2,274 litres of O_2-saturated water.

5. The water depth during winter drawdown at river mile 10 is approximately 4 m (per WVIC), but all of the water is in the main channel at this point. This means that resuspension of a single layer of sediment 1 m^2 in area by 15 cm deep at river mile 10 could remove all of the oxygen from more than one half of the overlying water column. It is important to note that most of the sediment suspended in the main channel could possibly be contributed by material removed from the shallower sides of the main channel, in addition to sediment in the main channel itself.

The findings of this study lend support to the hypothesized explanation of oxygen sag formation in the upper reaches of the Big Eau Pleine River (Gunnison and Barko 1988). Hypothetically, organic matter originating from dairy cattle farms in the upstream area enters the Big Eau Pleine River with spring runoff, and this material, possibly along with algal cells, is deposited as a low-density sediment in the upper reaches of the project. Microbial anaerobic processes, fueled by this organic matter, impart high levels of oxygen-demanding reduced inorganic species (primarily ferrous iron) and easily degraded organic substances (primarily volatile fatty acids and alcohols) within the sediment interstitial waters. This is reflected in the high levels of iron, manganese, and COD in the river mile 10 to 12 area of the Big Eau Pleine River. These materials remain until some process dislodges the sediment. One possible source of disturbance is the scouring actin exerted by ice as it scrapes the sediments during periods in the winter when water is withdrawn from the reservoir. Reduced iron released from sediment has a high immediate oxygen demand, serving to remove oxygen from the water immediately surrounding the disturbed sediments. Reduced organic compounds released at the same time may provide microorganisms in the water with available carbon sources that can be used to support additional oxygen-consuming activities within the oxygen sag.

Sediments in the downstream areas that are deeper and less likely to be disturbed may serve as diffusional sources of reduced chemicals creating an oxygen demand in bottom waters near the dam. This area periodically experiences localized pockets of anoxic water that build from the bottom upward as described in Gunnison and Barko (1988). In particular, the high levels of ammonium-nitrogen present in sediments in the vicinity of river miles 1.0 to 3.0 may contribute specifically to the winter hypolimnetic oxygen demand.

Future Studies

Additional studies will continue in an effort to verify the above scenario. During 1990, one sampling trip will be made in late fall to early winter to determine whether sediments in the area of river miles 10 to 12 have continued to accumulate large levels of oxygen-demanding substances. A second trip will be made in late winter to early spring following drawdown to determine if sediment displacement has occurred. This information will be coupled with detailed information on DO sag formation and movement in 1990.

Acknowledgments

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Sediment Oxygen Demand Measurements Using Benthic Flux Chambers

by

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The Concept of Flux Measurements

Benthic flux chambers work according to a simple principle. Reactions taking place between sediment particles, pore waters, and the overlying water can be monitored by isolating a small volume of bottom water and observing the change in chemistry of this water with time. Benthic flux chambers are instruments that isolate bottom water in contact with the sediment and either monitor the chemistry of this water using sensors or collect subsamples of this water for subsequent chemical determination. In either case, a flux, or the rate of exchange of a substance between the sediment and overlying water, is determined by calculating the rate of change of species concentration within the chamber. It is very important that the flux chamber materials provide neither a source nor sink for the chemical species measured; this is especially important for oxygen flux measurements.

The USC Lander

The Lander used by our geochemistry group was developed in the early 1980's and has successfully operated since 1985. A description of this device and its operation is published (Berelson and Hammond 1986). However, since that time, we have made many new additions to this instrument, both structurally and accessory-wise, and the majority of this paper will focus on the newer aspects of our device.

Frame

The frame of the USC Lander is made of 6061 aluminum square tubing, welded into a triangular base (A in Figure 1), three vertical supports (N) and three struts (K) that angle from the vertical pieces to a center plate (I). A harness (H) connects the Lander to a braided nylon line to which glass floats are attached. Assembled, the frame stands 1.5 m tall, yet it can be

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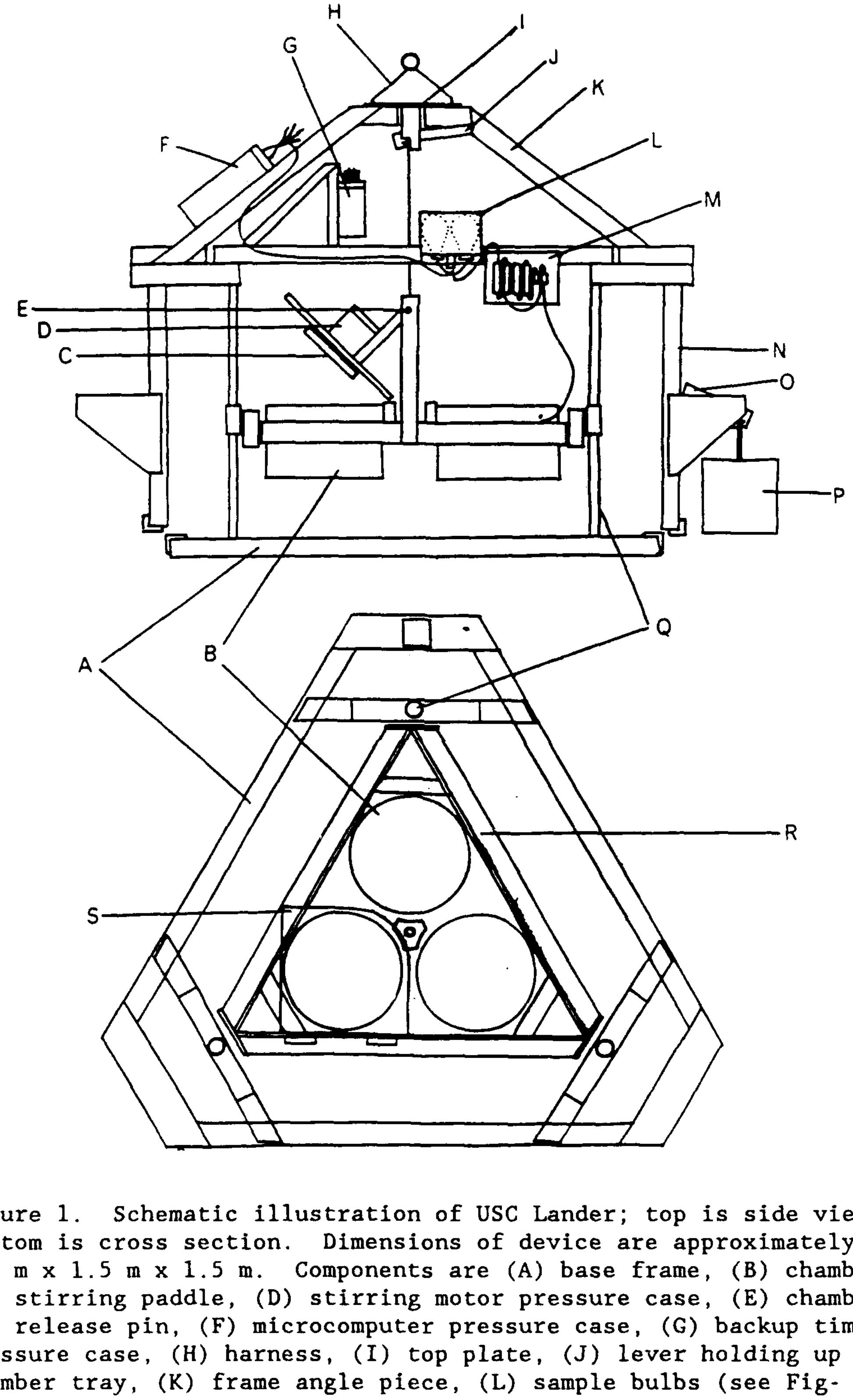

Figure 1. Schematic illustration of USC Lander; top is side view, bottom is cross section. Dimensions of device are approximately 1.5 m x 1.5 m x 1.5 m. Components are (A) base frame, (B) chamber, (C) stirring paddle, (D) stirring motor pressure case, (E) chamber lid release pin, (F) microcomputer pressure case, (G) backup timer pressure case, (H) harness, (I) top plate, (J) lever holding up chamber tray, (K) frame angle piece, (L) sample bulbs (see Figure 2), (M) sample tubes (see Figure 2), (N) frame vertical piece, (O) lever holding ballast weight, (P) ballast weight, (Q) vertical guide tube, (R) chamber tray, and (S) chamber lid

dismantled into units of about 80 cm for easy transport. Fully equipped with pressure cases and sampling arrays (minus the ballast weights), the device weighs about 250 lb in air and about half as much in water.

Chambers

Three cylindrical PVC chambers (B), 12 in. in diameter, 8 in. tall, are mounted inside an aluminum tray (R) which is free to slide vertically on three aluminum guide tubes (Q). The chamber tray is suspended above the base of the Lander frame until the device is located on the sea floor; at this time a lever (J) releases the tray and the chambers imbed partially into the sediment. The chamber tray falls under its own weight and will seat into the sediment so that 3 to 6 in. of chamber are held above the sediment-water interface. Following the implantation of the chambers, a spring-loaded pin (E) releases the chamber lids (S) and an acrylic lid seats to a latex gasket as spring-hinges hold the lids to the top of the chambers. From this moment, the chamber is incubating. Attached to the inside top of the lid is a stirring paddle (C) made of PVC tubing that contains a magnet embedded in resin. This magnet couples to a magnet turned by a small d-c motor located inside a pressure case (D) attached to the chamber lid. As the motor turns the magnet inside the case, the paddle stirs the water inside the chamber.

Water samplers

We draw samples from the chambers using two primary techniques. Approximately 300 ml of chamber water are removed when two vinyl bulbs are allowed to expand (Figure 2). The bulbs are initially filled with de-ionized water and squeezed between two aluminum plates, coupled with spring-hinges. When the plates are allowed to open, the bulbs expand and draw water out of the chamber, through teflon tubing (1/16-in. ID), through a series of glass tubes and eventually into the bulbs. The glass tubes, initially filled with de-ionized water, end up filled with chamber sample water. A second sampler for extracting water from the chambers is a standard syringe (60 ml), loaded with a spring attached to the piston. Water is drawn through glass tubes as the piston is pulled up the syringe barrel. These samplers draw smaller aliquots of chamber water. A short tube (5 in., 1/8 in. ID) permits water from outside the chamber to replace sample water removed. We generally draw five to seven samples from the chamber during the course of an incubation. To date, incubations have lasted between 18 and 120 hr.

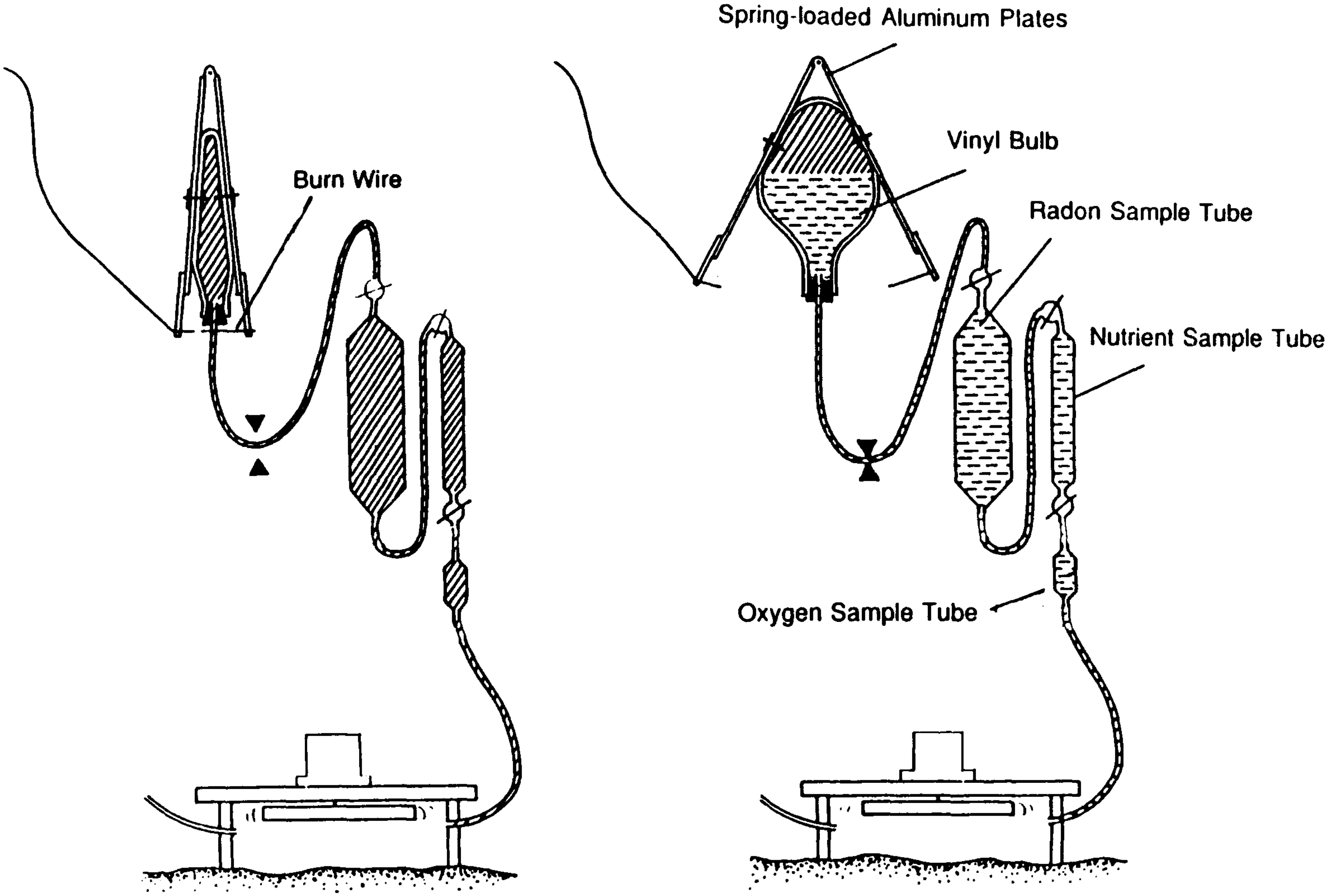

Figure 2. Illustration of chamber sample draw system. Not to scale

Timing and burn wire operation

The brains of our timing device is a Tattletale Data logger (Onset Electronics microcomputer). This computer can be programmed in Basic to keep time and apply voltage for a specified period out of one of twelve specified channels. We use six D-cells to supply the current to burn the wires and run the Onset with 9 volts from a separate source. The batteries and electronics components are packaged inside an aluminum pressure case (17 in. tall, 6 in. OD, 4.5 in. ID) and the signal from the computer is passed through the pressure case end-cap penetrator and a waterproof connector to a burn-wire.

All the mechanical functions necessary to operate the Lander are accomplished by releasing a burn-wire. For example, a burn-wire (nylon coated stainless steel fishing wire, 30- to 90-lb test) is positioned to hold up a lever arm which in turn holds a ring connected to the Lander tray. The lever provides mechanical advantage for holding heavy weights. When this wire releases, the lever arm lets go of the ring and the tray and chambers fall into the sediment. Burning a wire is achieved by applying a voltage between a small part of the wire (exposed by scraping off the nylon coating) and the pressure case (aluminum cylinder which is electrically isolated from the rest of the Lander). Nine volts and about 200 mA applied to the burn wires are sufficient to dissolve a piece of 40-lb test wire, exposed for about 2 mm, in about 2 min. To be sure of achieving a complete reaction, we program the microcomputer to apply this current for 20 min.

Oxygen electrode

The electrode we use is a membrane-covered polarographic electrode operated in a pulsed mode (Lilley, Story, and Raible 1969; Hitchman 1978; Langdon 1984). In this mode of operation, voltage is applied to the electrode periodically, causing oxygen reduction at the cathode and producing a current. The current decreases with time as oxygen in the membrane is consumed, but the amplitude is measured at a precisely known time after the voltage is applied. The output is proportional to the oxygen dissolved in the electrode chamber which is proportional to the concentration in the surrounding water. If the pulses are of short duration and the frequency of pulse generation is long in comparison to the time constant of the sensor (L^2/D where L is the membrane thickness and D is the diffusivity of oxygen in the membrane), the response of the probe is relatively linear. Operation in the pulsed mode greatly reduces the sensitivity to the electrode to the influence of environmental effects near the membrane surface (fouling, turbulence level, etc.) that cause drift in electrodes with continuous sensing.

The oxygen electrode is also controlled by the Tattledale Data logger which turns on the voltage, converts the analog signal from the electrode into a digital signal at a precisely controlled time, and stores the data. The electrode circuitry includes a power supply to apply voltage (1-volt output), a conventional polarographic probe (Yellow Springs Instrument Co.), and conversion of the current generated to a voltage that is transmitted to the Tattletale. The software permits selection of the pulsing frequency, pulse duration, and sampling time. This permits optimizing the electrode performance for different (high and low) oxygen conditions. We are presently field testing and still optimizing our selection of these parameters for different concentration ranges, but we currently use a pulse frequency of 5 min, pulse duration of 8 sec, and take data inputs at 1, 2, 4, and 8 sec. The circuitry and software for this instrument were developed and built by the U.S.C. Geological Sciences Electronics Group (Derek Manov, Michelle Robertson, and John Scott), generally following published descriptions of other designs (Hitchman 1978; Langdon 1984). The Tattletale monitors four electrodes and two thermistors which provide temperature information for electrode calibration.

Pinch plate

The tubing that runs between the syringes, sample tubes, and chambers is routed through a device we call the pinch plate. This device consists of two plates of aluminum connected with spring-hinges. The tubing is routed in between the hinge line of these plates, and the plates are held open by a burn-wire. The tubing that passes between the plates is 1/8-in. ID latex, a very soft and flexible rubber tubing. After all the samples have been taken and before the device is allowed to return to the surface, the wire holding the plates apart is burned and the tubing between the hinges is pinched. This effectively isolates the samples in the sample tubes; no sample water can be pushed out of the tubes and no water can be drawn into the tubes. This is important considering the stresses applied to the sample system during ascent and recovery.

Weight release

The weight release is the most important part of the Lander system because without perfect performance, the Lander remains on the sea floor. The USC Lander carries three lead weights, each weight consisting of two lead bricks (P in Figure 1) which together add up to 60 lb of weight (in air). The weights are hung from an eyebolt from a lever (O) mounted on each corner of the Lander and the weights hang such that the bottom of the lead is at the same elevation as the bottom of the frame. The three levers that hold the lead weights are held in place with stainless steel wire cable that runs to a master lever (not shown in Figure 1). This master lever is held in place with two burn-wires, attached in a U-shape so that if either wire dissolves, the lever will release. One burn-wire leads to the main pressure case and the other burn-wire leads to a secondary, backup pressure case. Each case contains a Tattletale computer and battery packs and is independently programmed. Thus, if one computer or case fails, the backup timer will release the weights and allow the Lander to return to the surface for recovery.

Deployment and recovery

The USC Lander weighs about 300 lb in air without the lead weights, about 480 lb in full deployment mode. Thus, it is necessary to use a ship with an A-frame or crane capable of handling this weight. The flotation line that is attached to the top of the Lander is made of braided nylon (0.7-in. diameter) and is 35 m long. At two positions along this line we have attached steel rings, spaced 1 m apart. These rings are used to couple the line to a flotation package, consisting of two, 17-in.-diameter glass floats (Benthos, Inc.) with hardhats that we have linked together with an aluminum frame. At the top of the float line we have a spar float (17-in. float with aluminum frame) that has a mast (aluminum tubing) with a radar reflector attached. Also mounted on the mast is a xenon flasher and a VHF radio transmitter (both with pressure activated shutoff switches). We also have a small, 10-in. glass float and a 20-ft line attached to the spar float. During a deployment, the floats are streamed off the fantail of the ship while the Lander sits on deck. We pick up the Lander with a winch attached to an expendable line and place the instrument outboard and into the water. When we are satisfied that the Lander will operate successfully (it must pass a preprogrammed test burn), the expendable line is released and the Lander sinks, trailed by the flotation line. The Lander sinks at a rate of about 60 m/min and it weighs about 60 lb on the bottom. When the weights are released, the device becomes about 100 lb buoyant. Release from the sediments upon weight release takes a few minutes.

When the flotation hits the surface, recovery is aided by the flasher and radio transmitter. We first recover the spar float and attach the Lander line to a winch line, then proceed to pull in on the line, decoupling the flotation packages from the line (we use quick-connecting carabiners) as we pull in. Getting the Lander safely on deck usually requires the attachment of two tag lines, and the total recovery operation normally takes 30 min from the time the spar float is grappled.

Mini-Lander

The device we call the "mini-Lander" is pictured schematically in Figure 3. This flux chamber works in the same way as the big Lander, uses many of the same systems that were described above, and is different, mainly, because it is a single chamber unit that has no means of carrying or releasing ballast weights. The chamber (a in Figure 3), stirring paddle (b), and stir motor system (d) are identical to the same parts of the main Lander. The lid (c) is more of a trap-door on the mini-Lander, and is kept open until after the chamber has been emplaced to minimize the effect of a bow wave during emplacement. Samples are drawn with the same bulb (h) and syringe (not shown) systems as used on the big Lander and samples are stored in the same way (i,j,

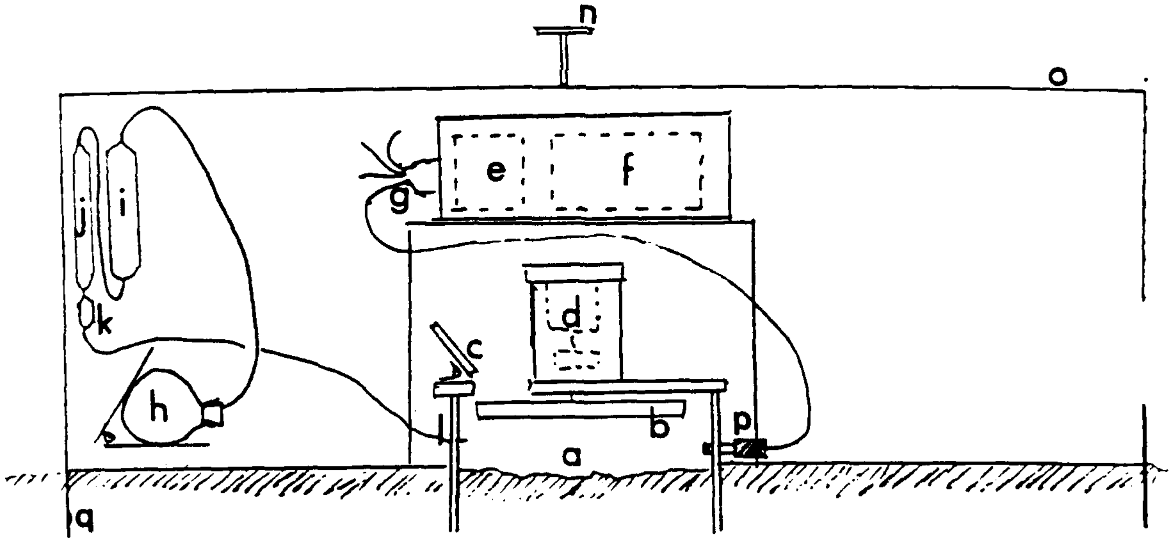

Figure 3. Mini-Lander design. Unit consists of a single cylindrical chamber (a) supported by an aluminum frame (o). Other components include: chamber stirring paddle (b), hinged lid (c), pressure case with magnet-turning motor (d), pressure case with microcomputer and batteries (e,f), burn wire leads and cable (g) to communicate with oxygen electrode (p), sample bulb (h), oxygen (k), nutrient (j) and radon (i) sample tubes, teflon tubing (l), T-handle (n) and struts for unit penetration (q)

and k). We generally draw four to five samples during the course of a deployment. The mini-Lander carries a pressure case loaded with the micro-processor (e) and battery pack (f), and utilizes a pulsed oxygen electrode (p), identical to the big Lander. The frame of the mini-Lander (o) is made of aluminum and the dimensions (1.5 m x 0.5 m x 0.5 m) were designed such that two units could be carried simultaneously within the basket of the submersible *Alvin*. When mini-chambers are deployed by *Alvin*, they are carried by the T-handle (n) pictured in Figure 3. When the device is deployed from a ship, the unit is lowered by hand (or using a small winch) until it touches down. Extensions on the frame (q) assure that the device is not moving horizontally when the chamber enters the sediment. All assembled for deployment, this device weighs about 65 lb in air and about 40 lb in water.

Flux Calibration and Verification Experiments

In this part of this paper we will discuss some of the techniques, experiments, and measurements we have made over the last 5 years that have been useful in verifying the accuracy of data collected with our flux chambers. Many of the topics covered in this short section are explained in greater detail in one of several papers we have published (Berelson and Hammond 1986; Berelson, Hammond, and Johnson 1987; Berelson, Hammond, and Cutter 1990; Berelson et al. 1990). Below, we itemize specific topics concerning flux measurement accuracy and briefly summarize our work to address these points.

Material contamination

Berelson and Hammond (1986) did storage experiments to test if the materials used within the Lander chamber (PVC, acrylic, and nylon) and the materials of the sample containers (teflon, glass, and polypropylene) contaminated water samples for the nutrients and other chemical species measured. Significant quantities of dissolved gases are able to diffuse through teflon, polypropylene, and rubber. As a result, glass tubes were chosen to store samples drawn for analyses of dissolved gases. We have also determined that tygon tubing can contain significant quantities of dissolved oxygen, and our design requires use of small lengths of this tubing to connect glass bulbs. When measuring oxygen fluxes in environments with low oxygen concentrations, a correction must be made for this contamination or the sampling device must sit for 10 to 20 hr in the low-oxygen water to permit the oxygen in the tubing to diffuse away. With the adaptation and use of our oxygen electrode, which is capable of making measurements from inside each chamber every few minutes, discrete oxygen samples will not be necessary.

Our experience since 1985 has also shown that a significant quantity of phosphate is adsorbed to the walls of glass bulbs during storage. We are currently modifying our sample reservoirs to include a plastic tube to store a sample for this analysis. Work is also in progress to determine if our device introduces contamination for trace metals or DOM.

Determination of chamber closure

How do we know that the lids of our chambers seal the chamber securely? We know this is true for at least two reasons. Through spring-loaded syringes, a spike of CsCl is injected into each chamber (about 20 ml of solution with a Cs concentration of 11,000 ppm) during the middle of the incubation. The dilution of this spike is measured in water samples taken subsequently. Since sea water has relatively little Cs, the dilution of a known amount of spike of known concentration accurately measures the volume of the chamber. If the chamber lid were not sealed properly or if the device were not sealed in the sediment, the Cs spike dilution would indicate a volume that is too large. Also, subsequent samples would show a rapid decrease of Cs with time.

A second method of calibrating the efficiency of our chamber seal is by measurements of radon-222 fluxes within the chamber and by independent means (Berelson and Hammond 1986; Berelson, Hammond, and Fuller 1982; Berelson, Hammond, and Johnson 1987; Berelson et al. 1987). The integrated quantity of radon in the water column (standing crop) at a given site provides an estimate of the benthic flux of radon from the sediment at this site. We have measured the standing crop of radon at numerous sites where we have also made Lander deployments and find that there is very good agreement between these two independent flux estimates. The results of these comparative measurements from sites in the southern California borderland are summarized in Figure 4. This agreement indicates that the chambers work as closed incubation systems and measure accurate fluxes.

Disturbance at touchdown

Every free vehicle causes some disturbance when it hits the bottom. Does it disturb the interface so much that *in situ* experiments sensitive to interfacial processes are impaired or invalid? Research with the submersible *Alvin* by Berelson, Reimers, and Hammond (1988) and Berelson, Hammond, and

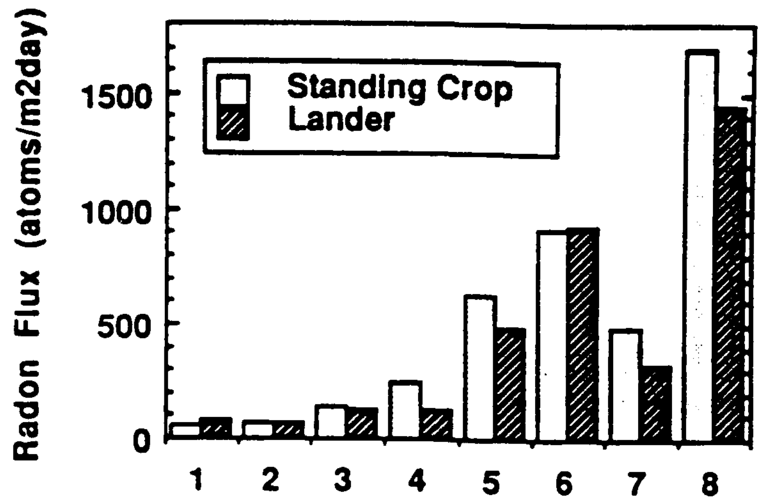

Figure 4. Comparison of radon-222 flux estimates made from water column (standing crop) and Lander measurements. The means of both measurement techniques in different environments lie within 1 standard deviation. The very good agreement in flux estimates from two independent techniques from a variety of environments and depths indicates the ability of our Lander to collect unbiased water samples. Site locations were San Pedro Basin (1), Santa Monica Basin (2), Catalina Basin (3), Tanner Basin (4), San Nicolas Basin (5), San Clemente Basin (6), Equatorial Pacific Site C (7), and Equatorial Pacific Site SC (8)

Giordani (1989) indicates that the answer to this question is *no*. We emplaced the mini-Lander chambers with the submersible in a very careful, meticulous manner so as not to disturb the interface and then compared the fluxes obtained with the big Lander to fluxes obtained with the emplaced chambers. The results (Figure 5) indicate that, within the uncertainty of making these measurements, there was no significant difference between fluxes measured with a free vehicle device and fluxes measured with a carefully placed device. We argue that the agreement in these flux results indicates that the surface reactive layer, if essential in controlling biogeochemical cycling of carbon and nutrients, is not severely disturbed during the free fall process.

Boundary layer effects

An enclosed chamber will always differ, hydrodynamically, from the ambient surroundings. We stir the Lander chambers in an effort to simulate the hydrodynamic conditions near the sea floor. Berelson, Hammond, and Cutter (1990) have discussed the relationship between paddle stirring speed and

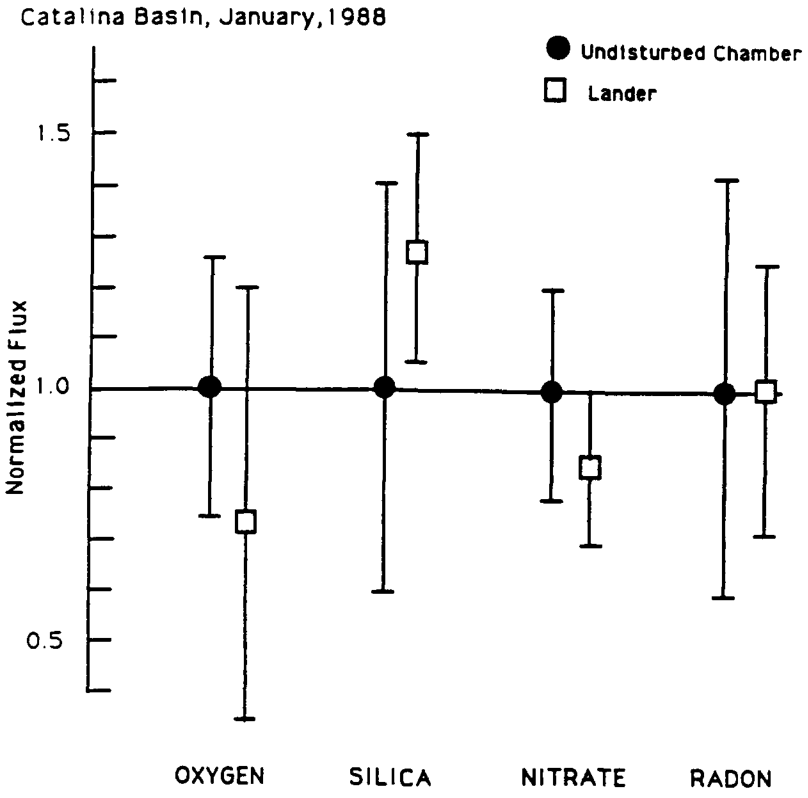

Figure 5. Comparison of fluxes measured with the big Lander, deployed as a free vehicle and the mini-Landers, deployed with the submersible *Alvin* in Catalina Basin. The mini-Landers were deployed with care not to disurb the sediment-water interface. Fluxes are normalized to the flux values obtained in the undisturbed chambers. Within the uncertainty of the measurements, there is no difference between the results from the free fall vehicle and carefully emplaced chambers

benthic boundary layer thickness within Lander chambers (Figure 6). From measurements others have made of natural boundary layer thicknesses in the deep sea (Santschi et al. 1983; Buchholtz Ten-Brink, Gust, and Chavis 1989), we have found paddle stirring speeds that most closely simulate the ambient conditions. The extent to which chamber paddle stirring speed is related to oxygen fluxes in deep sea environments was investigated by examining a summary of all the oxygen flux data for a given site. These data are presented in Figure 7 and we see no systematic relationship between chamber paddle stirring rate and oxygen flux. Although the diffusive boundary layer may play a role in controlling the rate of sediment-water exchange for some species and in

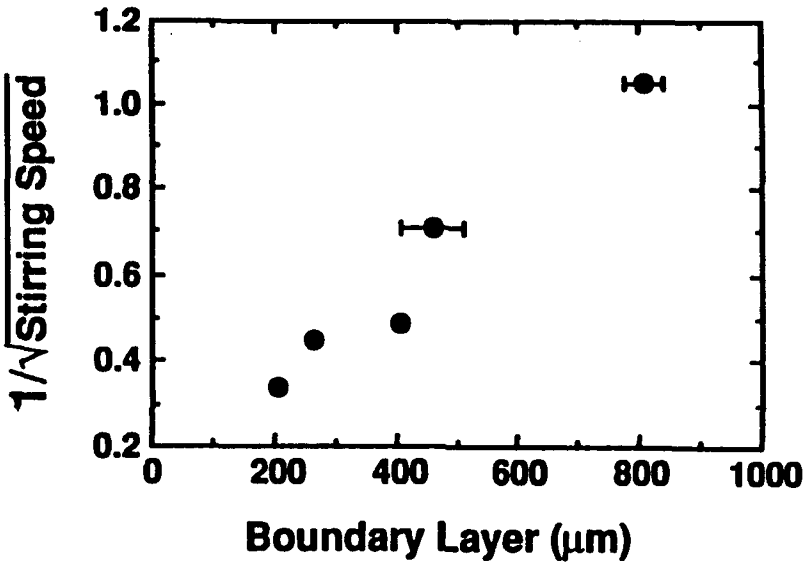

Figure 6. The relationship between diffusive boundary layer thickness measured from dissolution of alabaster plates and chamber paddle stirring speed (in RPM)

some environments, there is not a large effect for the range of stirring speeds we employ and in the environments studied.

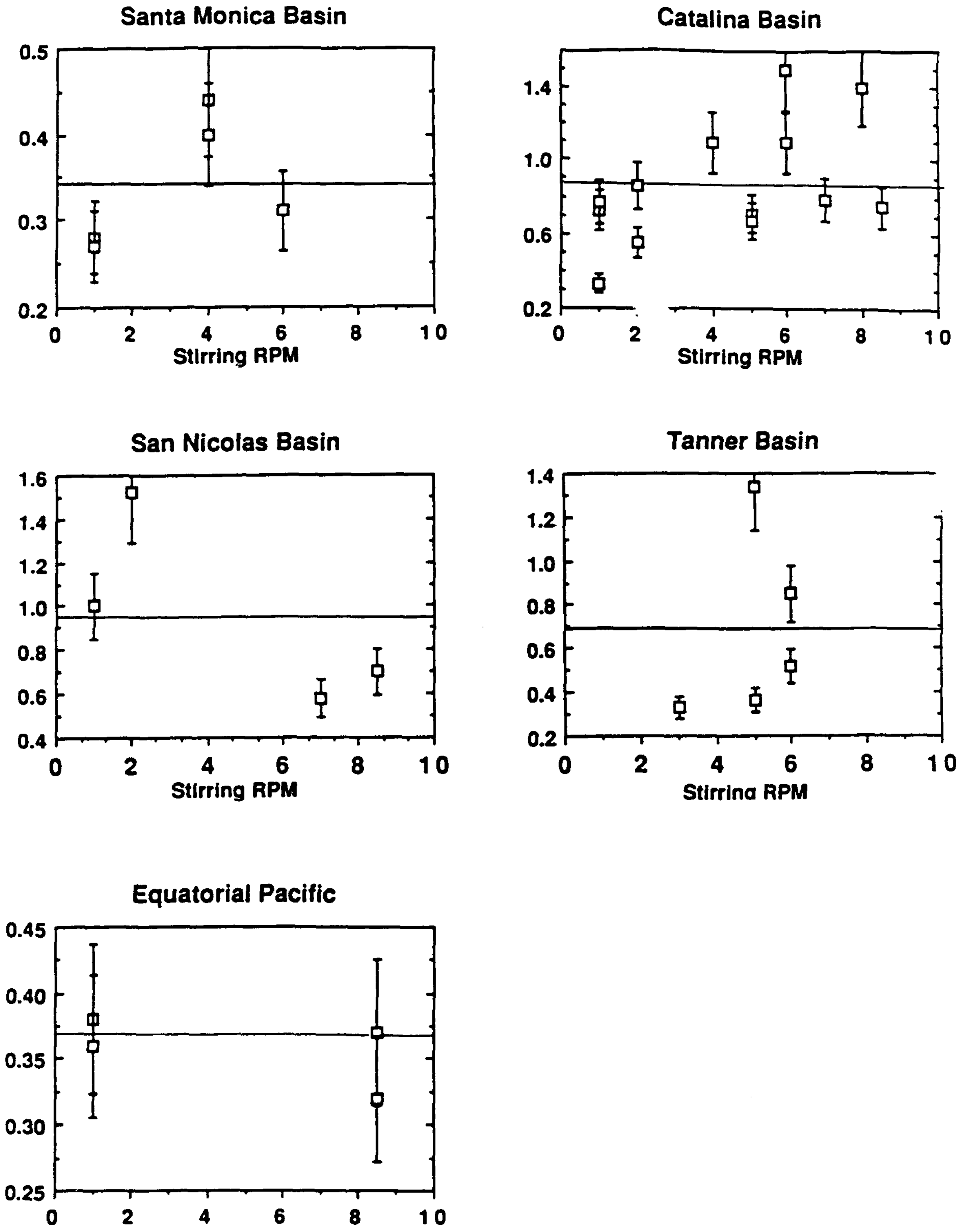

Figure 7. Study of oxygen fluxes from various oceanic sites as a function of chamber paddle stirring speed

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PART III: SUMMARY OF THE SEDIMENT OXYGEN DEMAND PANEL DISCUSSION, 22 AUGUST 1990

Panel Members

Dominic DiToro, HydroQual, Inc.
Robert Gall, Wisconsin Valley Improvement Company
Delbert Hicks, U.S. Environmental Protection Agency
Ray Whittemore, NCASI, Tufts University

Introduction

Dr. Douglas Gunnison of the US Army Corps of Engineers Waterways Experiment Station (USACEWES) outlined for the panel and other participants the current requirements of sediment oxygen demand (SOD) research and the Corps of Engineers (CE) SOD research plan as follows:

Purposes of the Panel discussion:

- Allow organizers and participants the opportunity to pull together the information presented by the speakers for comment and discussion.
- Provide an opportunity for those individuals who face frequent problems with the consequences of SOD to express their concerns and ask questions.
- Provide a forum for WES scientists to present a proposed research plan for critical review. This will determine technical merit and ensure that the direction proposed will provide the required tools to address SOD problems.

Project goal and objectives:

- Develop the means to accurately quantify SOD and its impacts on water quality.
- Determine current state-of-understanding of SOD and SOD processes operative in aquatic environments, identify major weaknesses in knowledge, and recommend and conduct investigations to supply information.
- Develop a predictive model for SOD and the releases of chemical species to water column which are regulated by SOD processes.
- Develop a CE-wide method for measuring SOD.

Current understanding of SOD processes:

- Physical, chemical, and biological processes critical to SOD exertion.
- Present ability to model SOD.
- Techniques available to measure SOD under field and laboratory conditions.

Panel assistance needed:

- Identify current strengths and weaknesses in understanding SOD processes.

- Determine key areas for future investigations
- Ensure that product will address real world concerns.

Process related concerns:

- Type of organic loadings and the rate and magnitude of SOD.
- Effects of aging and burial of organic matter on SOD.
- Organic and reduced inorganic species required:
  - Present in sediment
  - Released from sediment
- Biotic versus abiotic components.
- Mechanisms to describe release of SOD-demanding materials.

Model development related concerns:

- Suitability of Chesapeake Bay Sediment Model (CBSM) as a starting point.
  - Ability to handle freshwater and saltwater sediments.
  - Possible lack of significant SOD components/processes.
- Identified weaknesses in the model:
  - No release of dissolved organic nitrogen.
  - All DOC releases treated as methane.
- Implicit assumption: all dissolved organic releases are negligible.
- Methane, but not reduced iron or manganese, released into anaerobic freshwater.

Study approaches:

- Address both process and model development related issues.
- Conduct laboratory and model development work interactively.
- Formulation of experiments and improvements in model
  - Interpretation of model results.
  - Feedback from model runs.
- Goal:
  - Understand significant processes.
  - Satisfactory representation of processes in model.

Study design:

- Use reservoir or estuary sediment amended with organic matter.
  - Drive SOD processes → baseline SOD loading curves.
  - First cellulose, then other sources.
- Use series of aerobic/anaerobic cycles.
  - Short-term studies - 3- to 5-day cycles.
  - Long-term studies - 30-day cycles.
- Monitor SOD, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Dissolved Inorganic Carbon (DIC), and Dissolved Organic Carbon (DOC), plus:

    - Reduced iron and manganese
    - Various forms of nitrogen, phosphorus, and sulfur
    - Methane and carbon dioxide

- Sacrifice columns for sediment.

Later studies:

- Effects of sediment aging on SOD.
- Effect of periodic sediment resuspension and settling on SOD.
- Products of decomposition contributing to SOD.
- Role of sediment biota and bioturbation in SOD.

SOD measurement:

- Develop field device for SOD measurement.
- Provide SOD data sufficiently accurate for use in the model.
- Need to understand sediment-to-water transfer of reduced products.
- Need to have internal chamber environment simulate surrounding area.
- Should internal water currents be generated?
- Does sediment biota need to be included?
- How many chemical constituents should be measured?

Panel Discussion

Throughout the morning, the four-member panel addressed questions raised by the Corps as well as the other researchers in attendance. An effort was made to reach a general consensus on recommendations to the Corps.

Introduction of panel members:

Delbert Hicks: Mr. Hicks discussed the increasing role that SOD will play in the future as it becomes an indication of nonpoint source pollution and a factor in assessments. Because SOD measurements will become commonplace, it is necessary to develop techniques that can be implemented by a semiskilled individual. It is impossible to send experts out on every SOD measurement and much too costly in terms of time and money.

Robert Gall: Mr. Gall discussed his experience with reservoirs and their various limnological aspects. His main objective as president of the Wisconsin Valley Improvement Company is to ensure a uniform flow through the Wisconsin River using the 21 reservoirs. The Eau Pleine, discussed in Dr. Gunnison's seminar yesterday, is the largest of the reservoirs and contains 25 percent of the water storage capacity in the Wisconsin River reservoir system. The reservoir is unique in that it is located in a predominantly agricultural portion of the state and that there are two controls for the sediment on the river. One is the sediment input, which presumably every reservoir has. The other control is the ability to regulate the drawdown on the reservoir and, therefore, the current that is passing through the reservoir and resuspending the sediment. Drawdowns are presently more restricted than in the past because of the problems they are likely to create with the resuspension of sediment and first kills. Restricting drawdowns causes the uniform flow to be more difficult to maintain. This in turn has a negative effect on the hydropower users. Therefore, it is important to be able to draw the reservoir down as far as possible without fish kills. It is also important to have a clearer understanding of sediment processes.

Ray Whittemore: As a research engineer for the U.S. Pulp and Paper Industry, he has had a long-term interest in water quality and waste load allocation. He favors measurement techniques as the key to accurately determining the role of SOD. He does, however, advocate the use of process models, particularly in the future. Presently, there is a great need for consistent and simplistic approaches to be used in day-to-day measurements.

Dominic DiToro: Dr. DiToro outlined his involvement in measurement of SOD beginning in the mid-1970's. Initially, the SOD model computed the amount of negative dissolved oxygen in the sediment layers while allowing oxygen consumption to continue to a 5-cm depth. In effect the model was computing oxygen equivalents for all the oxidizable carbon. The negative oxygen concentration would then be diffused out. This method was fairly effective because in low-loading situations, SOD can be measured using oxygen equivalents and electron balancing. Then in the mid-1980's, a study on the Milwaukee River showed heavy loading of the sediments with Combined Sewer Outflows (CSOs). Methane was being stripped out of the sediments and, thus, the oxygen equivalent method was no longer valid because a large portion was being lost to the atmosphere. The model then had to be adjusted to account for the production of methane. Finally, the Chesapeake Bay study began, and the model had to adjust for sulfides instead of methane. This model is the starting point for today's discussion.

Discussion:

Q (Gunnison): What are the real questions that need to be answered in the Eau Pleine situation?

R (Gall): A predictive model would be very helpful at this point because we tend to manage the river by hindsight. We draw the river down until we start to see a problem, which is detected by intensive dissolved monitoring at each mile along the river. The oxygen sag can then be traced to determine approximately what is the cutoff point. This does not, however, allow for planning of the all-winter drawdown. Another question to be answered is what is the actual demand of resuspended sediments.

Q (Gunnison): What approaches can the panel suggest to address these problems?

R (Whittemore): To use a model effectively, you first need good data on the inputs.

R (DiToro): You might also want to build a model of the water column coupled with the sediment to see how the system actually works. Ultimately, the model must calculate oxygen in the water column. An SOD measurement model is only one component of a full reservoir eutrophication calculation. State-of-the-art equipment should be used to determine where are the actual technical deficiencies. Use the current state-of-the-art equipment, which provides a reasonable water quality analysis, one that mimics what you see now, and then get a problem analysis done.

R (Snodgrass): You need a model as a framework and as a learning tool.

R (Stefan): You also need a multidimensional sediment transport model to determine at what point the sediment really begins to move.

R (Jacobson): Measure carbon dioxide rather than oxygen, because carbon dioxide is a more sensitive measure of anaerobic metabolism. From this you can determine when and where your sediment is beginning to change.

Q (Garber): Is it true that you have data records for the last 40 years?

R (Gall): We do have records that date back to the mid-1950's.

Q (Garber): Couldn't you then use these data and some of the highway photos to get a good sense of what is happening in the basin and tease out of that what the problem is? Use the time series record concomitantly with a predictive model. How much effort have you put into synthesizing the information you already have?

R (Gall): The information we have isn't as good as you may think. It is monthly as opposed to weekly or daily. Also, it is only data on dissolved oxygen at bridges and dams, not every mile.

Q (Jacobson): Do you have temperature data? Have you looked at the two sets to determine correlations?

R (Gall): In summer there is some correlation. The correlation is not as strong in the winter, as currents interrupt the 4° bottom water. The oxygen sag conditions appear to be well correlated with water level and drawdown, more so than with the time of year.

Q (Dortch): Do you have a feel for the lateral variability of SOD in the Eau Pleine reservoir? The spatial variability needs to be taken into account.

R (Cerco): Don't worry about it. Take cores back to the lab and incubate them to find out the total production of COD that is in the sediments. If it isn't exerted in the sediments, it will be exerted in the water column or converted to methane.

Point by Hicks: One measurement method is not going to fill the bill. You will first need a suite of methods. Then take those and narrow it down to the ones that fit the situation.

Q (DiToro): What's wrong with the Chesapeake Bay model? It runs tests in triplicate and accounts for most all inputs. The same drill is also used effectively in the Long Island Sound. What is wrong with that as the standard? But then how does it account for stirring rates?

R (Garber): Variable stirring rates do not alter the response as long as there is consistency in the measurements. The real question is whether or not the rates make sense--you can't burn more carbon than is present.

Q (Berelson): How do you ensure that the Bay cores don't get oxidized?

R (DiToro): They are assessed on board the ship, very carefully.

Point by Snodgrass: The real goal, as Del Hicks pointed out, is to be able to have semiskilled workers doing the work in the field. The method shouldn't be so complicated that experts are needed to carry it out. You need a method that can be carried into backwater swamps with highly organic sediments. We also need to agree on a standard method or methods to be used because many techniques will be developed by different agencies.

Suggestion by Cerco: We need to find an effective technique that can be applied by anyone out of tech school, whereby cores are collected, brought back to the lab, and incubated anoxically for a long time, and then measured for COD export. This process has been shown to be foolproof and consistent, and, ultimately, it tells you the total oxygen demand that is created by those sediments.

Q (Gunnison): Is this appropriate to use as a standard or at least as a starting point?

R (Berelson): You might get consistent measurements, but you wouldn't get an accurate picture of what is going on in this system.

R (Jacobson): I disagree. There are publications that show the correlation is very good between the flux core and incubations. It is not a difficult thing as long as care is taken with the measurements.

Point by Farris: By using a number of technicians to take the measurements, you tend to get variations among the technicians.

Point by Jacobson: Examine each technician's data separately and then examine them together to see the big picture. You should be able to calibrate the highly sensitive measurements.

Q (Dortch): What technique would you use to get a snapshot of the SOD in a large waterway, for example, the Ohio River?

R (DiToro): Either the Chesapeake Bay model for fine sediments or Del Hicks' model for coarser sediments. Also, make some measurements of microelectrodes. There are only three ways to solve this problem: yank cores, build a chamber or dome, or get the microelectrodes. And someone in this room knows how to take these measurements.

Suggestion by Gunnison: Test chambers against cores against microelectrodes, consistently use a three-pronged approach.

Suggestion by Vigil: We used the flux chambers, the jar incubation method, and then used microelectrodes. On top of that, we did a model. All of the data were surprisingly close. However, it does not work well for phosphorus in aerobic systems or for ammonia as it will be over-predicting for whole core incubations. It depends on the system.

Counter by DiToro: The model requires whole core incubations because it is based on diagenetic production functions, and those are only directly accessible by whole core incubations. You have to know how much is being produced in the sediment itself. There are three pieces to the problem:

- What is the flux of organic matter that settles to the sediment?
- What are the kinetics of decomposition of particulate organic matter in the sediment?
- What happens to those anaerobically produced substances as they diffuse up into the aerobic layer and then diffuse out?

Sediment traps measure the first, whole core incubations measure the second, and flux measurements measure the third. They are distinct, independent things.

Suggestion by Garber: We need to establish spatial and temporal scales and work to define the nature of the problem. This needs to be a whole system approach.

Q (Gunnison): Why are we modeling in the first place? The Corps' purpose is to be able to manage our system and minimize the environmental impacts of what we are doing. Are we justified in trying to get just one model, or do we need to do this on a site-specific basis.

R (Dortch): We should try to create a model that is applicable to more than one situation until we find we can't.

Q (Gunnison): Is the Chesapeake Bay model a suitable way to approach the problem of SOD, or should we be trying to expand the Chesapeake Bay system?

R (Hicks): You need to define what type of water bodies you want to deal with.

Q (Gall): Have we only looked at the Chesapeake model because it is the only one around?

R (Garber): No, but because it is the current state-of-the-art and because it appears to be the best. We are using it as a starting point and not all of it. It does do a fair job of modeling the actual sediments.

Q (Cerco): We have made the assumption that we have an accurate assessment of the chemical makeup and workings of the sediment. Is this how they really function?

R (Berelson): Test the model using three approaches. First, does the model produce water column concentrations that are what you measured for the same time series; second, does that model predict pore water concentrations that are consistent with what you measured; and third, does the model take into account solid phase concentrations?

R (DiToro): The model is fairly accurate using these three tests, especially with respect to the first two. The fluxes are measured effectively, but we do not know the correct phosphorus solid phase to look at yet.

Q (Jacobson): How predictive is the model?

R (Berelson): It overpredicts silica and ammonia because you use a transfer coefficient that measures oxygen, which has very different absorptive and diffusive qualities than those of silica or ammonia.

R (DiToro): The model does take into account, though, that ammonia reacts differently than oxygen.

Q (Berelson): Does the model take into account spatial and temporal variability?

R (DiToro): Yes. The model has built into it a diagenetic decomposition code and then spends the majority of the time trying to determine what the anaerobic reproduced substances do. Do they oxidize in the aerobic layer and at what rate? At what rate do they diffuse from the aerobic layer to the overlying water? At what rate do they form solid phase material?

Q (Gunnison): You say it will work for the Chesapeake Bay. But will it work in other places?

R (DiToro): Yes, it seems to work in the Long Island Sound.

Q (Gunnison): But what if you try to apply it to freshwater?

R (DiToro): I wouldn't. It doesn't completely close the electron balance. It doesn't make an intelligent decision on whether or not to use methane, and it needs a better understanding of the transition from marine to freshwater.

Q (Berelson): What runs this model? Do you need to know the input of organic matter on a seasonal basis?

R (DiToro): Yes, in its predictive mode.

Q (Berelson): Do you need to know the net fluxes of ammonia and silica, et cetera, on a seasonal basis to calibrate it?

R (DiToro): Yes.

Q (Jacobson): How does it deal with resuspension?

R (DiToro): It explicitly does not. It is a bedded sediment model.

Q (Jacobson: Would your model then be transferrable to another setting by adding a resuspension component?

R (DiToro): Yes, but obviously you would have to make some modifications. Currently, it only thinks about the world in two layers. You might, however, need a multiple-layer model.

Q (Farris): What about biological communities?

R (DiToro): The key is to get particle mixing built correctly. The model has a particle mixing velocity that mixes between layer one and layer two. The velocity is specified as a function of temperature whose theta comes from the subduction velocities versus temperature data that exist in the benthic biological world. Further, there is a lot of information that says that solid phase mixing is proportional to benthic biomass. We have oxidizable labile carbon, instead of having benthic biomass. Therefore, we build in the proportion of labile carbon to particle mixing. The third thing that is built into it is an oxygen stress mechanism. Initially, when the oxygen got low, the mixing turned off and turned on again when the oxygen level increased. That does not, however, match the fluxes during aerobic times of year after the anaerobic periods. What the stress function now does, is as stress builds up with decreasing levels of oxygen, that is pegged at its minimum for the rest of the year independent of reoxygenation. Therefore, if the sediment or overlying waters become anaerobic, or almost so, the benthos are killed or they are put into nonactive mode and they only get reinitialized in the next year. To that extent the biology is built in. That is it.

Q (Farris): Does it account for differences in various communities?

R (DiToro): No, it doesn't know what the community is. All it knows is how much carbon is in the sediment, which serves as the effective particle mixing intensity, and it takes into account the degree of oxygen depletion in the overlying waters which kills off the benthos.

Point by Jacobson: These details may be beyond the scope of this model. To get that type of model on a smaller scale, you might need only change things like bioturbation diffusive flux, for instance.

Q (Berelson): You have got a good model, but do you take into account solid phase variable terms?

R (DiToro): They are taken into account, but they are not pyritized.

Q (Berelson): Your model would be much improved if it took into account the burial of silica, phosphate, and sulfur. Do you agree?

R (DiToro): Yes. Here is how it works now. We have bay-wide estimates of sedimentation velocities that are measured by a number of techniques. All of these measurements were put together, and we then made bay-wide estimates of burial velocities to the order of magnitude one to two tenths per year. Therefore, we know what that number is from independent estimates. The trick to burying things right is to get the solid phase compositions right, but it doesn't matter for ammonia or nitrate. Our computation for oxygen equivalents of sulfide is slightly higher than the acid volatile sulfide, but lower than total reducible sulfides. Thus, there is a problem there. We should have some pyrite kinetics in there. With regard to phosphorus, we don't know what the active inorganic solid phase phosphorus pools are that are interacting with pore waters. For phosphorus, we look at the organic phosphorus. For inorganic phosphorus, we just plot what we compute the phase looks like and plot that against oxalic acid extractable phosphorus and total inorganic phosphorus. With regard to silica, we have biogenic silica pretty well modeled.

Q (Berelson): What about calcium carbonate? It can have a great impact on the system as it affects the carbon balance.

R (DiToro): The oxygen has been consumed. After carbon becomes inorganic, it no longer needs to be taken into account. Seasonality turns out to be the hard part. The amount of nitrogen that is in the sediments that gets denitrified and then goes away needs to be taken into account. That is the big deal. Currently, the model nitrifies and denitrifies 40 percent of total deposited nitrogen. Sixty percent is recycled.

Q (Jacobson): How accurately can you predict when a system goes from a system that loses nitrogen to the environment to one that loses ammonia?

R (DiToro): We hope we are doing a fairly accurate job of predicting it already. That is the critical nutrient cycle that is controlling half of the eutrophication cycle.

Q (Jacobson): Does the model indicate when you move from the oxic to the anoxic?

R (DiToro): Yes, absolutely. That is a critical part of the model, but the transition from salt to fresh water is not done well. It makes no attempt to do iron and manganese which is necessary in freshwater systems. It also does nothing about Dissolved Organic Carbon (DOC), Dissolved Organic Nitrogen (DON), and Dissolved Organic Phosphorus (DOP) fluxes. There is plenty of room for improvement.

Q (Gunnison): We have proposed to take this model and start playing with it in freshwater and marine situations. Is this an appropriate way to get started?

R (DiToro): The modification it would take to make it do methane and sulfur in a consistent way is not a moonshot. Given that the modification is made, then it would be interesting to see the two major electron acceptor systems working across a gradient. The iron and manganese are second-order problems with fully anaerobic hypolimnions. That is when you need it. Ultimately, the best model would have all the modifications of all the electron acceptors built into the model. The methane system would, however, be first priority.

Q (Berelson): What about building in resuspension?

R (DiToro): Yes, that is an important issue. We have effectively ignored it and gotten away with it. In tidal scrub areas, however, it will be an important consideration.

Recommendations for Further Research

The following ten recommendations were discussed by the group as potential ways to improve existing models.

1. Conduct a side-by-side comparison of measurement methods for marine and fresh water.
   - Nutrients.
   - Oxygen.
   - Organics and pesticides.

Point by Dortch: More research is required on the exchange between the sediment and overlying water. A good boundary layer model is needed.

2. Study mechanisms of sediment/water interface exchange, specifically, need to determine:
   - Role of surface flows.
   - Effect of stirring during sampling.
   - Particles at interface.
   - Boundary layer thickness.
   - Thickness of aerobic layer (use microelectrodes) as it determines the kinetics of nitrate and ammonia fluxes.
   - Consider passive boundary production at steady state as it is important in reactions and as a measure of the oxygen profile.
3. Critically review and compare existing SOD data bases.
   - Account for variability - solid quantitative analysis.
   - Estimate loads to sediment - loading drives sediment.
   - Temperature correlations/correction.
4. Look at loadings relative to SOD exerted.
5. Make experiments more process based.
   - Ports.
   - Plug experiments.
6. Add provisions to monitor pore water.
7. Experiments should track key components.
   - Loading.
   - Sediment/particle dilution.
   - Temperature.
8. Concentrate majority of effort in the field. Use lab for monitoring, examining specific questions, and for testing the accuracy of measuring techniques.
9. Examine benthic community interactions.
10. Use alternative data sources - take advantage of existing data.

PART IV: DISCUSSION

SOD Measurement Techniques

Two themes run through this workshop and through the SOD work unit: (1) measurement of SOD and (2) modeling of SOD. Vigil's paper summarizes the various measurement techniques that are available. With one exception, the techniques rely on incubating sediments in contact with water. Sediment-water fluxes of oxygen and other materials are inferred from concentration changes in the water. The exception is a technique in which microelectrodes are employed to measure concentration gradients in the first several millimeters of water immediately overlying the sediments. Sediment-water fluxes are calculated through employment of measured gradients in a diffusion equation.

One goal of this work unit is the development of a standard SOD measurement technique for use throughout the Corps of Engineers. For maximum utility, the technique must be easy to employ, reliable, require minimum equipment, and demand minimum training and skills on the part of the technicians conducting the measurement. Probe measurement techniques appear to be incompatible with these requirements. Special-purpose probes are required for the measurement of individual ions and experience with the care and treatment of the probes is a must. Moreover, a means must be at hand to precisely lower the probe through the first several millimeters of water overlying the sediment.

The remaining techniques are divided between *in situ* techniques in which an enclosure is installed at the sediment-water interface, and *in vitro* techniques in which sediments are removed to a laboratory for analysis. The advantage of *in situ* techniques is that sediments remain undisturbed by the careful installation of the measurement device. Temperature, activity of benthic fauna, and other sediment properties are unquestionably similar inside and outside the incubator. This advantage is weighed against the disadvantages of *in situ* measurement techniques. The greatest of these is that dissolved oxygen (DO) in the water trapped in the device declines during the measurement. The lower DO cannot only force a decline in SOD but also alter the sediment-water flux of materials which are dependent on the DO concentration of the overlying water. The most accurate flux measurements are of lengthy duration yet this duration, in oxic water, is limited to the period in which DO inside the device remains reasonably similar to ambient DO.

Otherwise, the *in situ* device must be periodically reaerated. Additional disadvantages include ensuring a perfect seal between internal and external environments, and the general difficulties encountered in deploying, operating, and recovering the device in waters of great depth. Whittemore, Hicks, Jahnke, and Berelson describe devices that overcome the disadvantages of *in situ* measurements. The elaborate devices and techniques required, however, indicate that *in situ* measures do not comply with the ideals of ease of application and minimum required equipment suggested for this project.

The primary advantage of *in vitro* measurements is that once a core is collected, a successful SOD or sediment-water nutrient flux measurement is ensured. A counter to this advantage is that the similarity of the measured flux, removed from its environment, to the *in situ* flux must be verified.

Replacement or reaeration of the overlying water and other manipulations of the sediment-water enclosure are readily performed in the laboratory. The laboratory also offers the advantage that the environment can be controlled and measurements can be conducted under standard conditions (temperature, DO concentration, water circulation) that are beyond control in the natural environment. No one measurement technique offers all advantages nor can any method be ruled out; however, the relative ease of *in vitro* measurements, as well as the potential for standardization, renders laboratory measurements the rational starting point for investigation of techniques in this work unit.

SOD Processes and SOD Modeling

The framework presented by DiToro at the workshop provides an excellent conceptualization of the origin and characteristics of SOD in the freshwater environment. A key feature of the model is the distinction of diagenesis from SOD. Within the context of SOD, diagenesis may be defined as the total biogeochemical processes occurring in sediment that produce oxygen-demanding materials. SOD is the fraction of the total oxygen demand present in sediment that is exerted at the sediment-water interface. The balance of the diagenentic oxygen demand is released to the water column or buried in deep inert sediments.

Some of these materials, such as reduced iron and sulfide, can, within a short period after their formation, exert a strong immediate oxygen demand that is manifested through a rapid chemical oxidation occurring in the presence of dissolved oxygen. Other materials, such as reduced manganese, require somewhat longer to chemically oxidize in the presence of dissolved oxygen, although both reduced iron and manganese may also be oxidized microbiologically. Still other materials of diagenetic origin, including organic compounds such as volatile fatty acids and alcohols, must be combined with oxygen through the process of microbial metabolism (see the paper by Jacobson). As indicated in the paper by Vigil, we know a fair amount about various aspects of SOD processes active in sediment, but many aspects of sediment diagenesis are not understood. This is particularly true of the composition, structure, and mechanisms of formation of geopolymers and the fate of dissolved organic matter and its effect on solute fluxes.

A second feature of the model is an explicit accounting of the role of nitrogen in both the exertion and analysis of SOD. Nitrification, the microbiological oxidation of ammonium to nitrite and nitrate within the sediments, contributes to SOD, while sediment denitrification decreases the amount of dissolved oxygen required to meet diagenetic demand. Ammonium release under anoxic conditions provides a first approximation to total sediment diagenesis. As a consequence of the intimate association of the nitrogen cycle and SOD, any study of SOD must include the study of nitrogen.

The framework presented by DiToro has since has been expanded to cover both freshwater and saltwater environments and to allow analysis of transient conditions (HydoQual 1991). Still, some shortcomings remain in the analysis. Primary among these is the identification of methane as the sole reduced species produced by carbon diagensis in fresh water. Incorporation of sediment iron and manganese release into the model appears to be a worthwhile improvement in view of the detrimental role these reduced species play in determining reservoir water quality. A second shortcoming is the identification of ammonium as the sole nitrogenous species produced by organic matter decay. Partitioning of nitrogen into dissolved organic and ammonium fractions may be worthwhile, especially if nitrogen release is employed as an indicator of total diagensis.

What Does Modeling Say About Measurement?

The model partitions oxygen demand created by the sediments into three fractions. One fraction is oxidized at the sediment-water interface and is identified as SOD. A second fraction escapes into the water column and may be oxidized in the immediate vicinity or far from the sediment origin. A third fraction escapes to the atmosphere and is never oxidized in the aquatic system. Partitioning of the total oxygen demand into these fractions depends, in part, upon the supply of dissolved oxygen to the sediment-water interface. Implicit in the model and explicit in DiToro's abstract is the need to measure total sediment diagensis as well as SOD. Measurement of SOD alone can result in underestimation of the effects of sediment on dissolved oxygen in overlying water. A simplistic example of a potential pitfall is the measurement of SOD when DO is depressed substantially below saturation. In this situation, SOD is depressed by the limited supply of DO to the sediment-water interface and a large fraction of diagenetic oxygen demand is exported to the water column. An increase in DO to near saturation levels would induce an apparent increase in SOD due to the enhanced availability of oxygen to the sediments. Measurement of total diagensis as well as SOD would, in this situation, indicate no change in diagenesis, but rather a switch from methane export to SOD exertion as a function of available oxygen.

Presentations by Whittemore and Stefan indicated that the supply of oxygen to the sediments is determined not only by the concentration in the overlying water, but also by the motion of the water. Stefan related this phenomenon to the effect of turbulence on the thickness of the diffusional sublayer that exists at the sediment-water interface. (More detailed analyses may be found in Whittemore (1986) and Boudreau and Guinasso (1982.) The fundamental problem in SOD measurement, both *in situ* and *in vitro*, is ensuring that turbulence within the measurement device (and the transfer of oxygen to the sediment-water interface) is similar to turbulence in the ambient environment. Jahnke described the experiments that preceded specification of the mixing device for his flux chamber, but doubts that exact matching of internal and external mixing conditions can be attained. The problem of mixing presents another powerful argument for measurement of total diagenesis. Total diagenesis is not affected by mixing; only the fraction of diagensis exerted at the sediment-water interface is mixing-induced.

Insights provided by the model coupled with presentations at the workshop provide the framework for an ideal SOD measurement. First, total diagenesis should be measured. Whole-core incubation, as outlined by Vigil, under anoxic conditions for a period sufficiently long for steady-state COD release to be attained is a suggested methodology. Next, SOD should be measured under constant, repeatable conditions of dissolved oxygen concentration and mixing. This reference SOD is a representation of ambient SOD when ambient conditions resemble DO and mixing employed in the measurement. A closer approximation can be obtained by employing the sediment model and a diffusional sublayer model to compute the fraction of total diagensis exerted at the sediment-water interface when ambient conditions differ from the reference values.

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