

USEFULNESS OF SEDIMENT OXYGEN DEMAND
AS A TOOL FOR IMPOUNDMENT
MANAGEMENT

by

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ABSTRACT

Sediment erosion and transport have a significant effect on water quality in agricultural watersheds. In the midwest there are many man-made impoundments which experience severe sediment-related problems. Sediment Oxygen Demand (SOD) measurements have great practical utility for the management of sediment-impacted lakes for which sediment dredging or aeration/destratification schemes represent viable rehabilitation schemes.

The report summarizes a fifteen-month study of the phenomenon of SOD in two shallow Illinois impoundments. Both lakes have served as public water supplies and experienced significant water quality problems associated with sediment accumulation or seasonal anoxia. The aims of the investigation were to identify the principal components of the SOD and to develop an optimized SOD procedure. Briefly, batch respirometric measurements of SOD were found to be most diagnostic of oxygen depletion due to sediment resuspension or disturbance. As such, the bulk of the demand could be identified as chemical, and associated with sediment solids rather than due to reduced soluble species in sediment pore waters. Sulfide minerals contributed to the SOD in nearly all cases. An improved method for the determination of acid-soluble sulfide was developed to permit correlation of sulfide levels with sulfidic SOD.

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*sediment-water interfaces/mud/lake sediments
*oxygen sag/aeration/anaerobic conditions/water pollution effects
*sulfides/hydrogen sulfide/mineralogy

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EXECUTIVE SUMMARY

Observations of the kinetics and fractionation of sediment oxygen demand (SOD) are reported on six cores from two shallow, freshwater lakes. These measurements were made by batch respirometry on discrete sub-cores which were handled to minimize aerial oxidation. The kinetics of oxygen uptake were measured for periods ranging from one to twenty-four hours. Four parallel sediment samples were processed to differentiate oxygen uptake arising from chemical, biological and sulfidic origins. The SOD values ranged from 0.05 to 5.24 mg·g⁻¹ wet sediment and the major portion of the oxygen demand resulted from chemical reactions. Reduced soluble species in sediment pore waters were calculated to account for less than 10% of the total SOD. Approximately twenty-eight percent of the SOD was due to the reaction of sulfide minerals. The remainder of the demand resulted from the oxidation of organic matter and reduced metallic minerals associated with surfaces. Bulk sediment parameters (percent volatile solids, organic carbon and acid-soluble sulfide) showed significant correlations with corresponding SOD fractions. Total SOD rates were adequately described by an apparent first order rate equation. Rates were found to be significantly greater in the upper 20 cm of sediment than they were in deeper samples. The relationships between sediment composition, SOD magnitude and oxygen uptake rates provide valuable insights for engineering applications of the results to dredging operations.

INTRODUCTION

Sediment oxygen demand (SOD) results from various chemical or biochemical reactions as well as biological respiration in sediment/water systems. Its magnitude generally requires the inclusion of SOD in models of the oxygen balance of lakes or streams. However, reported values of sediment oxygen demand range widely and much of the observed variation seems to arise from the unique character of each site and methodological differences. Bowman and Delfino (1980), reviewing past in-situ and laboratory SOD techniques, discussed the interpretive problems which stem from varying contributions of biological or chemical demand. They presented an optimized laboratory batch method in order to improve the precision of reported results. Their choice of a laboratory method was made in the interest of improved control over experimental variables, such as: agitation, temperature, initial dissolved oxygen concentration and light. These authors further noted that the bulk of reported SOD values had been obtained on dredged samples and that additional work on undisturbed cores was needed to obtain information on benthic oxygen demand.

In practice, however, the collection and handling of sediment samples is difficult. The selective nature of sediment core sampling would likely introduce bias into measurement of biological respiration, which under certain conditions, can be a major portion of total SOD. Spotty populations of benthic macroinvertebrates may be missed entirely. Hunter, et al. (1973) have reported up to sixfold increases in the oxygen demand of stream deposits related to the abundance of tubificid worms. Apart from the respiratory demand of benthic macroinvertebrates,

their burrowing activity exposes effectively greater masses of the sediment system to oxic waters.

Also, the unavoidable disturbance of the upper portion of sediment cores is known to disrupt microbial processes sensitive to oxygen levels (Hall, et al., 1972; Herron, et al., 1978). Dredged samples must be very carefully collected so as to minimize contact with air and consequent oxidation of reduced substances. If SOD rates are rapid, the introduction of bias is very likely for such samples. Schnoor, et al. (1979) have reported a 20% decrease in measured oxygen demand after short-term (1-2 days) storage of dredged sediment in plastic bags. Eighty percent of this loss could be attributed to sulfide oxidation. Despite the 35% reduction in SOD after nine days of storage, these workers reported no significant decrease in bulk sediment parameters frequently correlated with oxygen demand: (e.g.) chemical oxygen demand, total volatile solids. Improper handling of sediment samples may then result in significant underestimation of chemical SOD though the resultant measurements might correlate well with data on sediment composition.

Belanger (1981) has reported benthic oxygen uptake rates for diver-collected cores and dredged sediments in a flowing reactor apparatus. The oxygen demand data correlated poorly with bulk sediment parameters. Results were found to be strong functions of flow rate and dissolved oxygen concentrations. He further cited limitations of the core uptake methods: the length of experimental runs, insufficient "acclimation times" and inability to approximate natural flow conditions. Thus, even carefully handled, sediment core data require careful interpretation.

The significance of SOD studies seems to be heavily dependent on methodology. Though laboratory results are more precise, the actual

processes giving rise to observed oxygen demand remain in doubt. Benthic oxygen demand measurements made in-situ or in flowing laboratory systems on large undisturbed samples are ideally representative of natural sediment/water systems. When the aim of a study is the determination of actual benthic demand, in-situ methods seem to be the obvious choice (Mathis and Butts, 1981). Batch reactor measurements may underestimate the long-term in-situ demand, however they provide a means to separate respiratory processes from chemical or microbial demands and clearly show the effects of artificial aeration on lake sediment systems (Wang, 1980 and 1981). When the sediment is disturbed or resuspended in the environment, it appears that batch SOD studies are more useful for engineering applications in lake management projects.

Further study of sediment oxygen demand is needed to assess the impacts of commercial dredging operations or wind, construction, and barge-induced sediment disturbances. The fates and mobility of sediment-associated trace elements, nutrients, or organic compounds can be drastically affected by changes in oxygen concentration and redox potential (Lee, et al., 1976). These observations have led to disagreements over the usefulness of the Standard Elutriate Test (U.S.A.E., WES-1976) and to the recognition of the need for reliable methods for prediction of oxygen levels in receiving waters or transported dredge spoil (Schnoor, et al., 1979).

This project was initiated to investigate the usefulness of the SOD parameter as a tool for lake management. The systematic study of SOD, oxygen uptake rates and the specific sources of oxygen demand were the main goals.

MATERIALS AND METHODS

The design of the SOD fractionation experiments was that reported by Wang (1980) with modifications to insure sample integrity as reported by Schubel, et al. (1978). Briefly, oxygen uptake was measured as a function of time in four thermostatted (23-25°C) stirred batch reactors (300 mL BOD bottles) filled with oxygen-saturated deionized water. Three reactors were treated with appropriate inhibitors (1% phenol, 3 mM zinc acetate and 1% phenol/3 mM zinc acetate) to permit determination of biological, chemical and sulfidic oxygen demand fractions relative to a control. All runs were made in the absence of light. Oxygen electrode (Yellow Springs Instruments) measurements were made at twelve minute intervals in each reactor using an automatic sequencing switch. All electrometric oxygen determinations were calibrated and corrected by using the azide-modified Winkler titration. Sediment additions were made using cut-off 5 mL polyethylene syringes with rubber caps which were weighed before and after each handling. These syringes allowed the collection, storage and handling of horizontal sub-cores from pre-drilled, polycarbonate, gravity-core liners. Sub-sampling was accomplished in a N₂-filled glove box within 24 hours of core collection.

Sampling was performed during 1980-1981 in two shallow freshwater lakes in Illinois: Lake Eureka and Lake Paradise. L. Eureka was constructed 40 years ago, while L. Paradise is over 70 years old. These lakes have mean depths less than 4 m, with maximum depths of 6-7 m. The lakes' areas represent less than 2% of the watersheds which are over 80% cultivated in row crops or pasture.

Net sedimentation rates in these lakes range from 0.5 to 1.5 cm·yr⁻¹ in the deeper areas where coring took place. Rapid sediment accumulation rates have severely reduced storage capacity in these reservoirs and shortened their lifetimes for public water supply. Both of these water supply impoundments undergo periods of seasonal anoxia and have severe sediment-associated water quality problems, such as taste and odor (IEPA, 1979 and Lin & Evans, 1981).

Determinations of bulk sediment parameters, total trace metals, nutrients and reduced species in sediment or pore waters were made using the analytical methods referenced in Table 1. Analysis of parallel sub-cores for acid soluble sulfide were performed by a modification of the H₂S evolution/iodometric titration method described by Black (1965). Pore waters were obtained by centrifugation of whole sediments and transfers were made under nitrogen. Analytical results on sediment samples from cores have been paired with parallel SOD samples on the basis of moisture content and wet density. This permitted the comparison of observed SOD's with those calculated from analytical data. Similarly, pore water concentrations of the reduced chemical species: NO₂⁻, Fe(II), Mn(II), HS⁻/S⁼, NH₄⁺, CH₄ and dissolved organic carbon (DOC) were converted to a whole sediment basis via wet density and percent moisture determinations at each depth. The stoichiometric oxygen requirement for each species was calculated, presuming complete oxidation to: NO₃⁻, Fe₂O₃, MnO₂, SO₄⁼, NO₃⁻ and CO₂, respectively. The oxidation reactions are shown below:

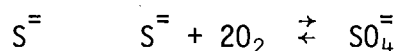
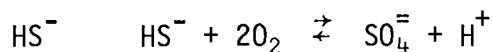
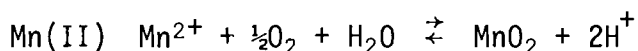
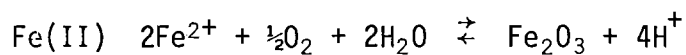
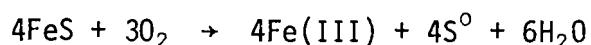


Table 1

<i>Parameter</i>	<i>Method of Analysis</i>	<i>Reference</i>
<u>Pore H₂O</u>		
Ammonia	Indophenol Blue Spectrometry	Strickland & Parsons, 1972
Dissolved Organic Carbon	Glass-Fiber Filtration, Persulfate Digestion CO ₂ Infrared	Oceanography International, Inc.
Ferrous Iron	Ferrozine Method	Stookey, 1970
Methane	Modified Multiple Phase Equilibration Method Flame Ionization Gas Chromatography	McAuliffe, 1971
Nitrate	Chromotropic Acid Method	A.P.H.A., 1975
Nitrite	Azo-Dye Formation	U.S.E.P.A., 1979
Sulfide	Phenylendiamine Method	Cline, 1969
Trace Metals (Mn, Cu, Cd, Pb, Zn)	Filtration-Atomic Absorption Spectrometry	U.S.E.P.A., 1979
<u>Whole Sediment</u>		
Moisture	Gravimetry, 60°C	A.P.H.A., 1975
Organic Carbon	Wet Digestion - CO ₂ Infrared	Anderson, 1980
Volatile Solids	Gravimetry (Difference), 550°C	A.P.H.A., 1975
Total Metals (Fe, Mn, Al, Cu, Cd, Pb, Zn)	HNO ₃ /HClO ₄ Digestion Atomic Absorption Spectrometry	U.S.E.P.A., 1979

The oxidation of NO_2^- , NH_4^+ , CH_4 and DOC was presumed to occur by biological (or biochemical) processes. The remaining soluble reduced species were categorized as chemically oxidizable.

The SOD due to acid soluble sulfides was calculated on the basis of the following oxidative/dissolution reaction:



— assuming that ferrous sulfide was the principal mineral phase present in this fraction. It should be noted, however, that the acid soluble sulfides in freshwater sediments are quite complex (Nriagu, 1968) and that in addition to ferrous sulfides the Mn, Zn, Cd and Pb minerals may also be present.

Kinetic parameters for the SOD were determined on selected samples assuming an apparent first order rate dependency by the linearization method reported by Thomas (1950). Rate constants for sulfidic demand were estimated by initial slope determinations from plots of oxygen uptake versus time.

RESULTS AND DISCUSSION

Batch SOD Results

Sediment oxygen demand, analytical and kinetic determinations were made on sediments collected from each of the lakes throughout the study period. Final oxygen concentrations were always greater than $3.0 \text{ mg}\cdot\text{L}^{-1}$ which is the minimal value reported to have no effect on the magnitude of the SOD (Fillos and Mollof, 1972; Pamatmat, et al., 1973). The batch SOD results are tabulated in Table 2a and 2b for multiple depths in each core in units of $\text{mg}\cdot\text{O}_2\cdot\text{g}^{-1}$ wet sediment. On any single sample, duplicate SOD determinations were found to be reproducible

Table 2a. L. Paradise Sediment Oxygen Demand Observations

Core No. (Date)	Depth Interval (cm)	1-Hour SOD				Final SOD						
		Total	Biological	Chemical	Sulfidic	Total	Biological	Chemical	Sulfidic			
mg·g ⁻¹												
LP-1 (7/7/80)	0-5	5.24	4.02	1.22	0.82	0.40	2.77	<0.05	2.31	1.85	0.96	
	6-10	2.33	0.30	2.03	1.81	0.22	3.33	0.14	2.66	2.13	0.53	
	11-15	2.27	<0.05	2.17	1.87	0.40	2.39		-	Not Available	-	
	16-20	2.00	<0.05	2.00	1.8	0.20						
	21-25	2.24	0.18	2.06	1.60	0.46						
	26-30	1.03	0.05	0.98	0.83	0.15						
	31-35	1.00	0.08	0.92	0.65	0.27						
	36+	0.95	0.08	0.87	0.63	0.24						
	LP-7 (5/26/81)	0-4	0.68	0.06	0.62	0.50	0.12	1.12	0.13	0.99	0.72	0.27
		5-8	0.50	<0.05	0.50	0.39	0.11	1.15	0.14	1.01	0.79	0.22
9-12		0.60	<0.05	0.60	0.45	0.15	1.21	<0.05	1.21	1.06	0.15	
13-16		0.72	<0.05	0.72	0.49	0.22	1.21	0.19	1.02	0.88	0.14	
17-20		0.60	<0.05	0.60	0.45	0.15	1.17	<0.05	1.17	1.13	0.04	
21-24		0.53	<0.05	0.53	0.42	0.11	1.12	0.30	0.82	0.82	<0.05	
25-28		0.41	0.12	0.29	0.29	<0.05	0.94	0.27	0.67	0.67	<0.05	
29-35		0.05	<0.05	0.05	0.05	<0.05	0.82	0.03	0.79	0.79	<0.05	
LP-16 (8/20/81)		0-4	0.54	<0.05	0.54	0.35	0.19	1.03	<0.05	1.03	0.68	0.35
		9-12	0.61	<0.05	0.61	0.34	0.27	0.76	<0.05	0.76	0.66	0.10
	17-20	0.66	<0.05	0.66	0.40	0.26	1.01	<0.05	1.01	0.83	0.18	
	25-28	0.74	<0.05	0.74	0.34	0.40	0.98	<0.05	0.98	0.86	0.12	
	33-36	0.13	<0.05	0.13	0.05	0.08	0.39	<0.05	0.39	0.33	0.06	
	37-45	0.97	<0.05	0.97	0.64	0.33	1.20	<0.05	1.20	1.03	0.17	
	46-54	0.81	<0.05	0.81	0.51	0.30	1.20	<0.05	1.20	0.88	0.32	

— = data unavailable
 All values in mg·g⁻¹ wet sediment

Table 2b. L. Eureka Sediment Oxygen Demand Observations

Core No. (Date)	Depth Interval (cm)	1-Hour SOD			Final SOD						
		Total	Biological	Chemical	Total	Biological	Chemical				
		mg·g ⁻¹									
		Total	Biological	Chemical	Total	Biological	Chemical				
		Sulfide									
LE-1 (10/6/80)	0-4	0.78	0.12	0.66	0.61	0.05	0.27	0.94	0.63	0.31	
	5-8	0.98	<0.05	0.98	0.60	0.38	0.47	1.05	0.74	0.31	
	9-12	0.95	0.24	0.71	0.66	0.05	1.68	0.67	0.67	<0.05	
	13-16	1.36	<0.05	1.36	0.99	0.37					
	17-20	1.05	0.07	0.98	0.86	0.12	1.70	0.45	1.25	0.15	
	21-24	1.44	<0.05	1.44	0.73	0.71					
	25-32	0.92	<0.05	0.92	0.53	0.39	1.72	0.25	1.47	1.25	
	33-36	0.77	0.14	0.63	0.58	0.05	1.22	0.22	1.00	0.76	
	37-40	0.86	<0.05	0.86	0.51	0.35	1.50	0.50	1.00	0.77	
	41-44	0.99	<0.05	0.99	0.79	0.20	1.80	0.09	1.71	1.71	
	45-48	0.35	<0.05	0.35	0.28	0.07	0.71	<0.05	0.71	0.62	
	49-52	0.98	<0.05	0.98	0.57	0.41					
	53-55	1.02	<0.05	1.02	0.36	0.66					
	LE-7 (4/2/81)	0-4	0.36	<0.05	0.36	0.36	0.05	1.07	<0.05	1.07	0.52
		5-8	0.90	<0.05	0.90	0.67	0.23	1.80	<0.05	1.80	1.28
9-12		1.26	<0.05	1.26	0.81	0.45	1.80	<0.05	1.80	1.20	
13-16		0.34	<0.05	0.34	0.29	0.05	0.89	<0.05	0.89	0.29	
17-20		0.88	<0.05	0.88	0.65	0.23	1.68	<0.05	1.68	0.59	
21-24		0.61	<0.05	0.61	0.55	0.06	1.29	<0.05	1.29	0.41	
25-28		0.63	<0.05	0.63	0.11	0.52	0.81	<0.05	0.81	0.44	
0-4		0.61	<0.05	0.61	0.52	0.09	1.35	0.09	1.26	0.72	
LE-10 (7/21/81)	5-8	0.90	<0.05	0.90	0.50	0.40					
	9-12	0.85	<0.05	0.85	0.70	0.15					
	13-16	0.54	<0.05	0.54	0.54	<0.05					
	17-20	0.70	<0.05	0.70	0.57	0.13	1.43	0.05	1.38	1.14	
	21-24	1.13	<0.05	1.13	0.67	0.46					
	25-28	0.96	<0.05	0.96	0.67	0.29	1.29	<0.05	1.29	1.14	
	29-32	0.78	<0.05	0.78	0.45	0.33					
	33-35	0.94	<0.05	0.94	0.75	0.19	0.94	<0.05	0.94	0.23	
	36-39	0.68	<0.05	0.68	0.56	0.12	0.66	<0.05	0.66	0.57	
	40-42	0.85	<0.05	0.85	0.80	0.05	1.17	<0.05	1.17	0.91	
	43-46	--	--	--	--	--	1.08	<0.05	1.08	1.03	
	47-50	--	--	--	--	--					

within $\pm 5\%$ relative standard deviation. The minimum detectable level at this precision was $0.05 \text{ mg}\cdot\text{g}^{-1}$. The total SOD value agreed with the sum of the chemical and biological fractions within $\pm 10\%$ in the range 0.5 to $1.5 \text{ mg}\cdot\text{g}^{-1}$.

Although the oxygen electrodes gave quite consistent results during the SOD runs, the final dissolved oxygen levels were about 30% lower than those determined by Winkler titration. The average error was somewhat higher in the long-term runs. Linear corrections were applied over the duration of each run. The inhibitors were not a source of systematic error in this regard. Electrode poisoning or a buildup of organic substances may explain the impaired response.

Several aspects of the 1-hour data set should be recognized at the outset. Chemical (phenol inhibited) SOD was the dominant fraction in over 90% of the samples. Biological SOD was observed in scattered instances and over half of these were encountered in sub-cores from the upper 20 cm. No significant difference between fresh, refrigerated or frozen samples was observed. Since the sediments were generally reduced (high Fe(II), NH_4^+ , CH_4 , NO_2^- and $\text{HS}^-/\text{S}^{2-}$) it follows that one hour of exposure to oxic conditions would be insufficient for the acclimation of populations of aerobic microorganisms. This observation is supported by the results of Belanger (1981) and Schnoor, et al. (1979). An increase in biological demand was observed in the 15-24 hour runs for samples which showed detectable short-term biological demand.

The major portion of the total SOD consisted of a rapid demand during the initial 30 minutes of each run. Thus, 1-hour SOD's averaged 59% of the corresponding final values. It should be obvious that the rapid initial demand was the consequence of chemical oxidation reactions.

The chemical SOD was further divided into sulfidic demand (phenol inhibited minus phenol/zinc acetate inhibited) and chemical-sulfide contributions. These sub-fractions accounted for roughly one-third and two-thirds of the chemical demand, respectively. The chemical-sulfide demand probably represents the oxidation of organic matter and reduced iron or manganese minerals. The average contributions of these sub-fractions agrees remarkably well with those previously reported by Wang (1980) on related samples.

With the exception of core LP-1, the SOD data in Table 2 does not show an obvious trend with depth. The SOD values from the upper 20 cm of all cores are not statistically different from those in the deeper sections. This observation essentially agrees with conclusions of Bowman and Delfino (1980). One might expect an increase in SOD if the concentration of reactive reduced substances increases with depth. This relation has been inferred in several studies reporting such trends (Schnoor, et al., 1969; Ogunrombi and Dobbins, 1970; and Reynolds, et al., 1973). Whether or not an SOD trend is observed with depth in a sediment depends largely on the vertical distributions of reduced substances. These distributions are a function of the water body, sediment source and the environment of deposition. Therefore one would not expect a simple correlation to hold in a variety of freshwater environments.

Correlation of SOD Results with Sediment Composition

The foregoing discussion dealt with the relative magnitude of batch SOD results and the contribution of various fractions to the total oxygen demand. Comparison of the SOD data with the chemical composition of the sediment and sediment pore waters demonstrates the usefulness of the

fractionation scheme. Further, it serves to identify the actual species exerting the oxygen demand. The comparison was facilitated by the very low biological demand observed in these lake sediment cores.

The bulk of the observed SOD was associated with the solid portion of the sediment. Table 3 contains the concentration ranges of reduced chemical species in the sediments which are labile to either chemical or biological oxidation. The diffusion of the soluble reduced species from the sediments into overlying waters contributes to oxygen depletion in the hypolimnia of stratified lakes. Whether or not these species contribute to short-term measurements of sediment oxygen demand depends on their stoichiometric oxygen requirement and the rates at which the oxidation processes occur. The tabulated concentration of reduced species: particularly, iron (II), manganese (II), nitrite, sulfide, and methane are indicative of reducing conditions in the sediments. The total calculated stoichiometric-oxygen requirement of the chemically labile species was insufficient to account for more than 0.1% of observed oxygen demand. This consideration was conservative since it presumed rapid, quantitative reaction.

The "biologically" labile reduced species: NO_2^- , NH_4^+ , CH_4 and DOC required more thorough consideration. Nitrite was present at levels too low to materially contribute to the observed oxygen demand. The total calculated oxygen requirements for the remaining species averaged 18 and 10% of the 1-hour and long-term SOD's, respectively. Further, the calculated oxygen demand of these soluble species exceeded the average observed biological demand in all cases. The actual rates of NH_4^+ , CH_4 or DOC oxidation in the batch SOD experiments remain unknown. These rates would be expected to be slower than those reported for

Table 3. Concentrations of Reduced Chemical Species in Lake Sediments

	<u>L. Paradise</u>		<u>L. Eureka</u>	
	<u>Range (N)</u>	<u>Average (± 1 S.D.)</u>	<u>Range (N)</u>	<u>Average (± 1 S.D.)</u>
<u>Constituents Labile to Chemical Oxidation</u>				
<u>Pore Water</u>				
HS ⁻ /S ²⁻	<0.01-0.25 (5)	0.17 (± 0.07)	<0.01-0.25 (32)	0.07 (± 0.07)
Fe(II)	0.06-4.24 (16)	1.15 (± 1.2)	<0.01-4.80 (22)	0.75 (± 1.3)
Mn(II)	2.71-11.2 (16)	5.22 (± 2.4)	<0.01-7.26 (11)	5.17 (± 2.0)
<u>Whole Sediment</u>				
Acid-Soluble Sulfide (mg·g ⁻¹ wet wt.)	0.15-0.87 (15)	0.50 (± 0.20)	0.16-2.75 (26)	1.08 (± 0.56)
<u>Constituents Labile to Biological or Biochemical Oxidation</u>				
<u>Pore Water</u>				
NO ₂ ⁻	<0.01-1.85 (17)	0.96 (± 0.78)	<0.01-0.08 (15)	0.28 (± 0.25)
NH ₄ ⁺	0.04-106 (18)	30.1 (± 38)	<0.04-27.0 (29)	12.3 (± 9.8)
CH ₄	<0.01-136 (41)	40.2 (± 34)	<0.01-110 (23)	46.6 (± 26)
DOC	9.0-61.0 (17)	27.1 (± 13)	8.0-38.6 (21)	24.8 (± 5.3)
<u>Other Oxidizable Constituents</u>				
<u>Whole Sediment</u>				
Organic Carbon (% wet wt.)	0.29-2.46 (23)	1.22 (± 0.73)	0.66-1.96 (31)	1.11 (± 0.40)

All pore water species reported in mg·L⁻¹.

natural lacustrine environments, at similar oxygen levels, with standing populations of appropriate microorganisms. Table 4 contains selected values for reported rates of nitrification, methane oxidation and dissolved organic carbon uptake, together with the average pore water concentrations of the reduced species, (Table 3), transformed to their equivalent concentration in the batch reactor. These rates were used to calculate the percent utilization of each presumed substrate and the percent of the average total and biological SOD's for 1-hour and long-term runs.

Table 4

<i>Substrate</i>	<i>Average Batch Reactor Concentration $\mu\text{g}\cdot\text{L}^{-1}$</i>	<i>Oxidation Rate $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}$</i>	<i>Estimated Percent Utilization</i>		<i>Reference</i>
			<i>1-hour</i>	<i>24-hour</i>	
NH_4^+	45	1	2	48	(a)
CH_4	22	16	1	22	(b)
DOC*	39	10	23	100	(c)
Total Oxygen Demand ($\text{mg}\cdot\text{g}^{-1}$)			0.01	0.08	
Percent of Average Total SOD (1-hour, $0.96 \text{ mg}\cdot\text{g}^{-1}$; Final $1.33 \text{ mg}\cdot\text{g}^{-1}$)			1.0	8.3	
Percent of Average Biological SOD (1-hour, $0.04 \text{ mg}\cdot\text{g}^{-1}$; Final $0.12 \text{ mg}\cdot\text{g}^{-1}$)			26	67	

- (a) Brezonik (1972)
 (b) Reeburgh and Heggie (1977)
 (c) Allen (1969); *Rate corresponds to glucose or acetate utilization with low heterotrophic bacterial populations.

These conservative values for oxygen uptake rates yielded very low estimated oxygen demands as percentages of the total SOD. The estimates were, however, of the order of magnitude of the average observed biological demand. Therefore, biological oxidation of reduced species in the pore water may contribute a small fraction of the total SOD in mixed sediment/water systems. The frequency of observed biological SOD was too low to allow significant correlations with percent volatile solids or percent organic carbon for these systems.

The major portion of the total SOD resided with the chemical fraction. Since the calculated chemical oxygen demand of the pore water species was less than 0.1% of the total SOD, sediment solids must provide the bulk of the rapid chemical demand. The chemical demand sub-fractions: sulfidic and chemical-sulfide averaged 27 and 67% of the total SOD. The measured sulfidic demand was generally lower than calculated values based on levels of acid soluble sulfide (Table 3). The results for each sample are shown in Table 5.

The observed sulfide demands have been expressed as percentages of values calculated from measured levels of acid soluble sulfide. Sediments from both lakes obviously contained significant portions of oxidizable solid sulfides. On the average, Lake Paradise sediments contained about half the total sulfide levels of Lake Eureka sediments (Table 3). This is principally due to the fact that sulfur inputs to L. Eureka are greater due to the frequent use of copper sulfate algicide over the past 30-40 years. There was some indication from the first hour results that Lake Paradise sediments had a slightly greater proportion of readily oxidizable sulfide minerals. This observation may be related to the particle size

Table 5. L. Paradise Calculated Sulfidic Oxygen Demand Results

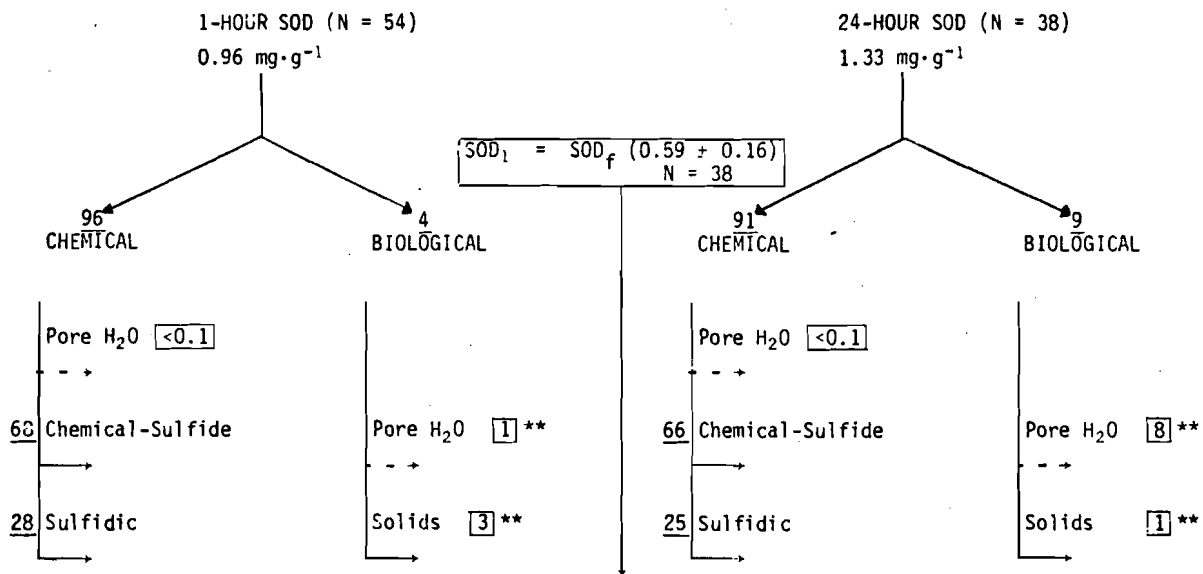
Core No. (Date)	Depth Interval (cm)	Acid Reactive Sulfide mg·g ⁻¹	Calc'd. "FeS" mg·g ⁻¹	SOD' _S mg·g ⁻¹	$\frac{SOD'_S}{SOD_S}$ 1 hr	$\frac{SOD'_S}{SOD_S}$ final
LP-7 (5/26/81)	0-4	0.79	2.19	0.59	20	46
	5-8	0.86	2.39	0.65	17	34
	13-16	0.56	1.56	0.42	52	33
	17-20	0.48	1.33	0.36	42	11
	21-24	0.49	1.36	0.37	30	<14
	25-28	0.46	1.28	0.35	<15	<14
	29-35	0.70	1.94	0.54	<10	<10
LP-16 (8/20/81)	0-4	0.52	1.44	0.39	46	90
	9-12	0.64	1.78	0.48	56	21
	17-20	0.39	1.08	0.29	90	62
	25-28	0.27	0.75	0.20	200	60
				Maximum Average*	52%	30%
LE-1 (10/6/80)	0-4	1.19	3.31	0.89	6	35
	5-8	1.45	4.03	1.09	35	28
	9-12	1.57	4.36	1.18	4	<4
	13-16	1.12	3.11	0.84	44	--
	17-20	0.82	2.28	0.62	19	24
	25-32	0.32	0.89	0.24	163	92
	33-36	0.17	0.47	0.12	42	200
	37-40	0.98	2.72	0.74	47	31
	41-44	0.62	1.72	0.47	43	<11
	45-48	0.34	0.94	0.26	27	35
LE-4 (4/2/81)	0-4	0.78	2.17	0.59	<10	93
	5-8	1.33	3.69	1.00	23	52
	9-12	1.16	3.22	0.87	52	69
	13-16	0.91	2.53	0.68	7	91
	17-20	1.16	3.22	0.87	26	125
	21-24	0.88	2.44	0.66	79	133
LE-10 (7/21/81)	0-4	0.78	2.17	0.59	15	92
	21-24	1.53	4.25	1.15	40	21
	29-32	0.70	1.94	0.53	62	28
				Maximum Average*	34%	65%

— = Data unavailable
 All values are mg·g⁻¹ wet sediment
 * = Includes minimum values when little or no sulfide demand was detected.
 SOD'_S = Calculated maximum sulfidic oxygen demand
 SOD_S = Measured sulfidic oxygen demand

or the nature of the sulfide minerals present. The 24-hour sulfide SOD's showed a weak correlation with the calculated values ($r = 0.40$ at the 0.05 level, $N = 28$). However, only about 16% of the variance in measured values could be explained by the analytical data. It is therefore very likely that the bulk of the scatter in the data arises from differences in the oxidative reactivity of various chemical forms of sulfide and their distributions within the sediment column.

Figure 1 consists of a schematic summary of the SOD fractionation results. The average percentage of the total 1 or 24-hour SOD is noted next to each fraction or sub-fraction (pore water or solid). The contribution of each observed fraction to the whole was remarkably constant over the two periods of SOD runs. The bulk of the oxygen demand was: rapid, chemical, and associated with the solids. Roughly, one-third of the chemical SOD could be attributed to the oxidation of sulfide minerals. Schubel, et al. (1978) were successful in accounting for 36% of the observed oxygen demand of estuarine sediments on the basis of sulfide oxidation. Since 91 percent or more of the average total SOD was chemical, it is unsurprising that many investigators observe some correlation between observed demand and bulk sediment parameters, such as chemical oxygen demand, volatile solids or percent organic carbon (Rolley and Owens, 1967; Schnoor, et al. 1979; Leutheuser, 1981).

In this study, statistically significant linear correlations (0.01 level, $N = 54$) were found between the 1-hour total SOD observations and sediment volatile solids ($r = 0.49$) and percent organic carbon ($r = 0.54$) (See Table 6). These correlations improved substantially relative to the 24-hour SOD's. The chemical SOD's were also correlated with these bulk sediment parameters but not as strongly as were the totals. The subfractions



X% Observed value or calculated by difference between observed values

* Calculated from analytical data (Fe(II), Mn(II), HS⁻/S²⁻)

** Estimated from analytical data (NO₂⁻, NH₄⁺, CH₄, DOC) and conservative rates of biological oxidation processes.

Figure 1. Summary of Batch SOD Fractionations on Freshwater Sediments
(all values expressed in percent of total SOD)

of the chemical SOD: chemical-sulfide and sulfide were not as strongly correlated with the presumed components of their demand as might have been expected. For example, the chemical-sulfide subfraction, presumably composed of reduced iron or manganese minerals and organic carbon, showed no correlation whatsoever with analytical data for total iron. The calculated sulfidic SOD's did correlate well with those measured over the 24-hour periods. The difficulty in correlating total oxygen demand measurements and bulk sediment parameters may be attributed to interactions between individual factors (Pamatmat, et al., 1973) or differences in the reactivity and chemical nature of bulk parameters in different locations.

An example of the latter source of variability is the effect of the aging and mineralization of organic carbon in sediments. The percent organic carbon content of a sediment column decreases very slightly over a period of years to decades. Organic carbon in an older lower section of a core may be considered less reactive than that in more recent accumulations since it has served as a substrate for microbial activity for a longer time. Leutheuser (1981) noted that higher levels of organic carbon do not necessarily support higher short-term oxygen demands, since "old" carbon may react more slowly than "young" carbon. Such an effect should be most evident in SOD measurements made on successively deeper (older) sections of uniformly accumulated sediment cores.

Marine geochemists have routinely applied a correction for the unreactive or residual organic carbon in studies of carbon mineralization during sediment diagenesis (Berner, 1972; Murray, et al., 1978). The measured organic carbon contents of sediment samples are corrected by subtracting the average value observed in the deepest section from

each succeeding younger section. It has the effect of removing the refractory or unreactive carbon from the total.

This organic carbon correction was made on the sediments in the present study to yield values of reactive or labile organic carbon. The correlations of these corrected values with the total SOD's and chemical-sulfide fractions showed a moderate improvement (See Table 6). Similar corrections could be applied to other presumed contributors to rapid sediment oxygen demand when the mineralogy and reactivity towards oxygen are better understood.

This approach must be taken cautiously in freshwater environments. Even in large lakes, a combination of physical factors, such as mixing, sediment resuspension or transport, can override chemical and biological controls on net sedimentary processes. Periods of seasonal anoxia, coupled with the physical factors noted above, may cause horizontal variations in lake sediment composition which exceed the vertical gradients of selected chemical species within the sediment column. Therefore, progressively lower redox potentials or increases in the concentration of reduced substances with depth need not translate into increased SOD's. The rates of these processes are the controlling factors.

Kinetics of Sediment Oxygen Demand

The results of batch respirometric SOD measurements and their relation to specific fractions of sediment water systems established that more than half of the SOD occurred in the first hour of observation. The bulk of this observed rapid demand resulted from chemical oxidation processes involving the sediment solids. In Figures 2a and 2b,

Table 6. Selected Correlations of Bulk Sediment Parameters with SOD Observations

y	x	r	Level of Significance	N
<u>1-Hour Results</u>				
Total SOD ₁	% Organic C	$y = 0.72 (x) + 0.13$	0.54	54
Total SOD ₁	% Volatile Solids	$y = 0.16 (x) + 0.13$	0.49	54
SOD ₁ Chem.-S	% Organic C	$y = 0.37 (x) + 0.20$	0.55	54
Total SOD ₁	% Labile Organic C	$y = 0.84 (x) + 0.45$	0.56	54
SOD ₁ Chem.-S	% Labile Organic C	$y = 0.42 (x) + 0.38$	0.54	54
<u>24-Hour Results</u>				
Total SOD _f	% Organic C	$y = 0.62 (x) + 0.60$	0.64	39
Total SOD _f	% Volatile Solids	$y = 0.13 (x) + 0.62$	0.47	39
SOD _f Chem.-S	% Organic C	$y = 0.26 (x) + 0.56$	0.37	38
Total SOD _f	% Labile Organic C	$y = 0.75 (x) + 0.83$	0.68	39
SOD _f Chem.-S	% Labile Organic C	$y = 0.34 (x) + 0.64$	0.41	38
SOD _f Sulfidic	SOD Calculated Sulfidic	$y = 0.34 (x) + 0.09$	0.40	28

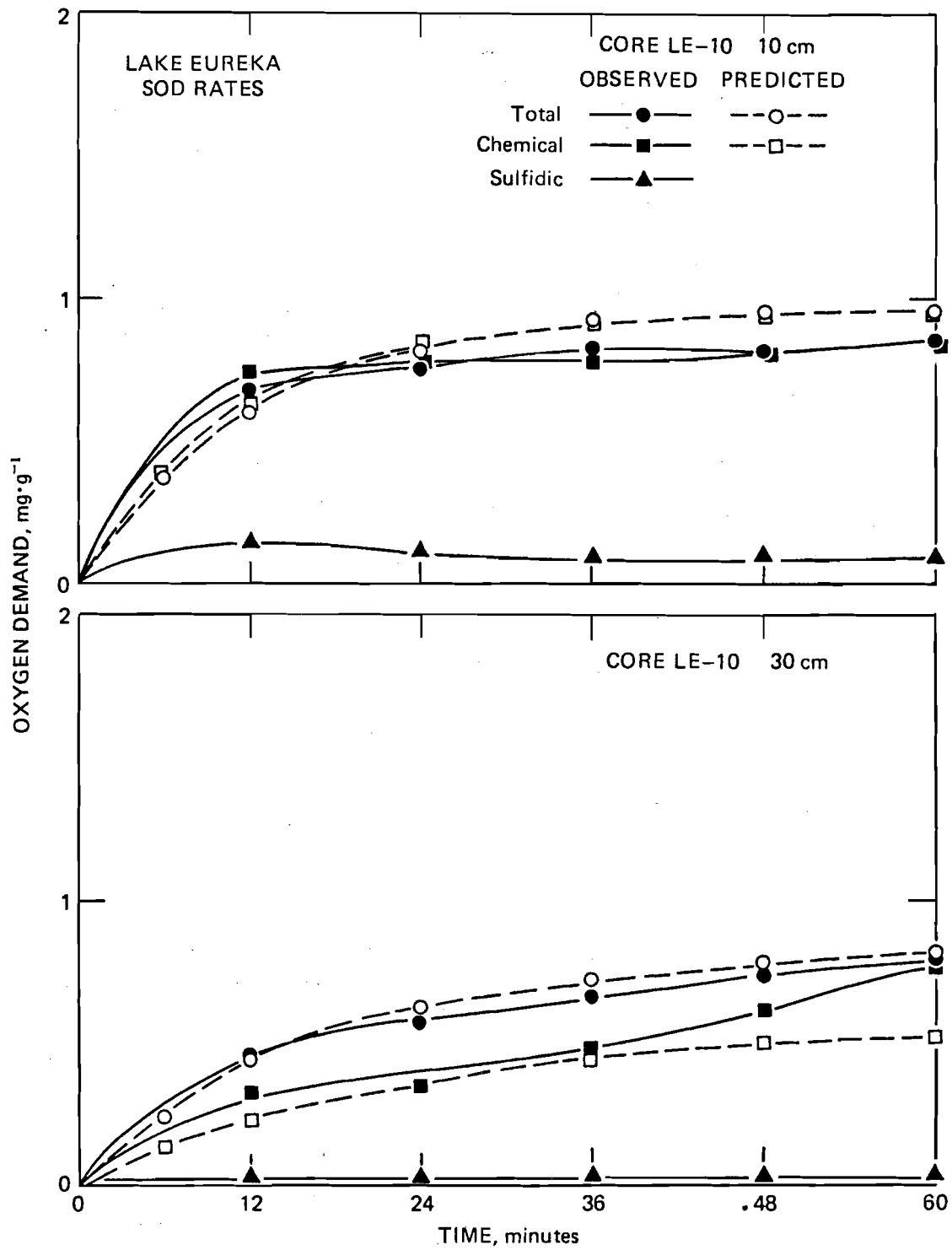


Figure 2a. *L. Paradise* SOD Rates

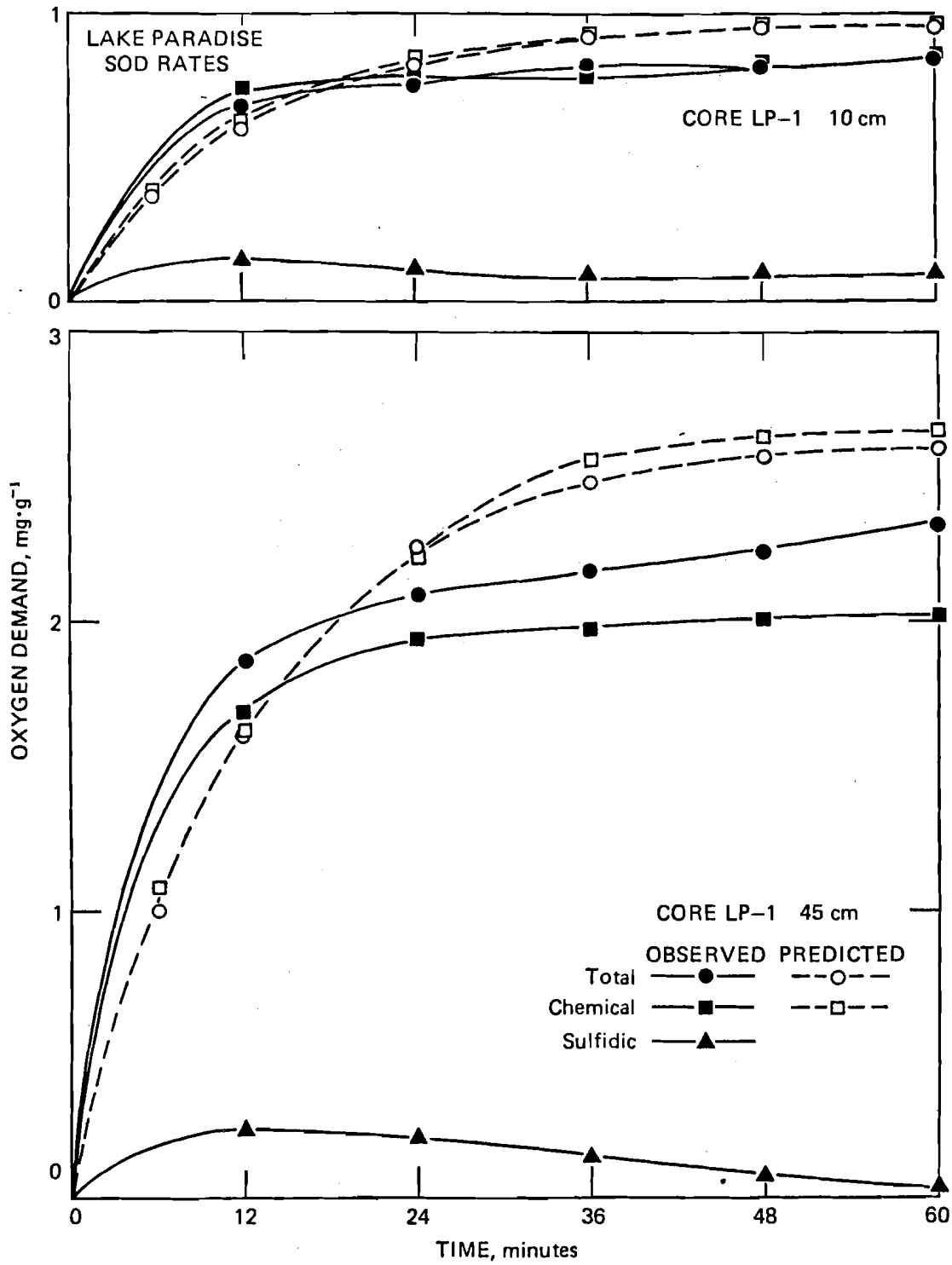


Figure 2b. L. Eureka SOD Rates

the variations of oxygen demand as a function of time are presented for representative SOD runs on sediments included in this study. The plots show clearly the rapid demand which occurs in the initial ten to fifteen minutes. This phenomenon has been observed for similarly handled sediments in short-term batch SOD studies (Schubel, et al., 1978; Schnoor, et al., 1979; Leutheuser, 1981). These observations point out the loss of detailed kinetic information in batch studies in which oxygen uptake has been measured initially and at one-hour intervals (Wang, 1981). The major fraction of the demand, chemical SOD, closely tracked the total. This supports the assignment of the bulk of SOD to chemical reactions involving dissolved oxygen. Sulfide demand rates leveled off early in the experimental runs; and, in the case of shallow samples, the uptake rates actually decreased.

It was assumed that the oxygen uptake rates could be approximated by a first order rate process. The integrated form of the rate equation was:

$$SOD_t = SOD_u (1 - 10^{-kt})$$

where SOD_t denotes the SOD at time t (min), k is the apparent rate constant and SOD_u is the ultimate demand (Brezonik, 1972). Apparent rate constants were determined using the linearization technique developed by Thomas (1950), and a simple linear regression to determine the slope and intercept values. Due to the number of complex, contributing heterogenous (surface-solution) reactions, it is most unlikely that a single rate expression of integral order could adequately fit the data. Various theoretical considerations have been offered to improve the fit of experimental SOD data, including two-step first order reactions and

surface oxidation product inhibited reactions of higher order (Wang, 1981). Methodological differences and the heterogeneity of sediment particles make systematic comparison of SOD kinetic observations very difficult. Since the greater portion of SOD due to sediment resuspension or dredge spoil discharge is exerted within a relatively short time-frame, future mechanistic work should be directed towards the initial reaction period and the products of the oxidation reactions. Particular attention should be paid to the experimental conditions of: light, temperature and sediment loading. The choice of kinetic models was one of convenience and no information on the actual mechanism may be inferred.

Oxygen uptake curves predicted from the apparent first order rate equation are included in Figures 2a and 2b. Within experimental error, the model adequately described the rate dependency for the first hour of reaction. The ultimate or total SOD values calculated by the linearization technique were about 20% higher than the observed one-hour SOD's.

Practical Application of Batch SOD Results

The agreement between the first order rate model and observed SOD rates allows the construction of some empirical guidelines for hydraulic dredging operations or estimates of the impact of dredge spoil discharge to water bodies. Faced with time, mixing and flow constraints, the engineer interested in minimizing "oxygen sag" in dredge pipelines and/or receiving waters must consider both the magnitude and rate of the SOD. Schnoor, et al. (1979) have presented a promising method which involves estimation of the total SOD from its empirical correlation with analytical data on volatile solids. Then a high, medium or low SOD rate was selected to provide boundary conditions for the prediction of the oxygen content of dredge discharges.

Open-water disposal operations will require a somewhat more involved comparison of mixing and available ambient dissolved oxygen with the total oxygen demand within a known period.

Consideration of the range of values for total SOD and reported rates of oxygen uptake provides a measure of the sensitivity of one's prediction to each input in such calculations. Figure 3 depicts the results of a series of calculations of the maximum hydraulic detention time which will insure an oxic effluent for a 10% (v/v) slurry of hydraulically dredged sediments with $8.0 \text{ mg}\cdot\text{O}_2\cdot\text{L}^{-1}$ water. These are conditions frequently encountered in dredging operations conducted in shallow lakes. The calculations were performed over the range of reported first order rate constants for sediments of varying SOD. The results show that at high SOD rates the magnitude of the SOD has a minimal effect on the maximum detention time. At the lower end of the rate range, the input value for the total SOD has an increasingly dominant effect on these times. The figure shows that if the dredge slurry is handled for three to four minutes, the bulk of the initial "oxygen sag" will have been exerted for high SOD sediments ($>1 \text{ mg}\cdot\text{g}^{-1}$), regardless of the SOD rate.

This approach has been applied to a hydraulic dredging operation in Lake Paradise, Mattoon, Illinois. Using average total SOD values and the empirical rate constants, it was possible to predict the oxygen content of the dredge slurry for various lengths of pipeline. In this particular case, the minimum distance (time at a constant pumping rate) to the available dewatering area was so great that total oxygen depletion during pipeline transport was predicted. The design of the dewatering area was therefore modified to provide adequate reaeration in the settling

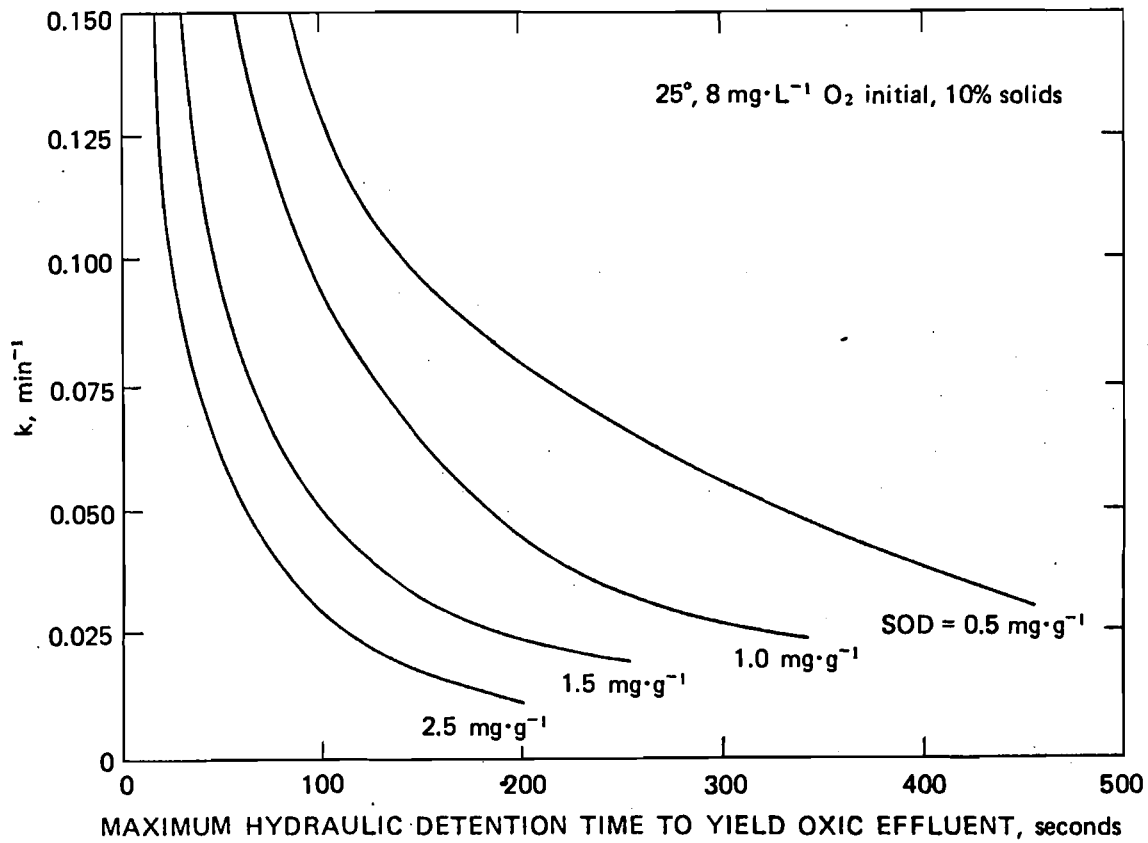


Figure 3. Variation of Maximum Hydraulic Retention Time with Total SOD and Oxygen Uptake Rates

ponds (Lembke, et al., 1982). In this way the release of reduced chemical constituents to receiving waters was minimized.

Application of these general guidelines should be made prudently. SOD determinations are reproducible, straightforward, and relatively inexpensive to make. Reasonable approximations can be made by correlating a small number of empirical determinations with analytical data on sediment composition, such as organic carbon, volatile solids or acid soluble sulfide. A working range of reasonable operating conditions can be established by presuming first order kinetics and a range of rate constants.

CONCLUSIONS

Batch respirometric studies of the sediment oxygen demand of lake sediments have established several points of interest in SOD methodology and interpretation. The batch method is most applicable to situations in which sediment resuspension or transport of a dredged slurry is anticipated.

The bulk of the SOD in short-term batch studies is rapid, chemical and associated with sediment solids. Minimal biological demand was observed in scattered cases. This contribution increased somewhat during longer experimental runs. Less than 10% of the total SOD can be attributed to reduced chemical species in sediment pore waters. Some biological demand may occur due to the oxidation or utilization of ammonia, methane and dissolved organic carbon.

Oxygen uptake rates were rapid, and nearly 60% of the long-term SOD was observed in the first hour of reaction. The SOD rates and one-hour SOD's could be described by an apparent first order reaction.

The calculated rate constants in shallow sediments (<20 cm) were significantly greater than those for deeper samples. Reasonable estimates of the SOD rate and magnitude in situations of sediment disturbance or resuspension can be made with a minimum number of observations.

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