MODELLING SEDIMENT OXYGEN DEMAND IN LAKES

By

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ABSTRACT

Field and laboratory investigations were carried out to explore sediment oxygen demand (SOD) and its component parts. An *in situ* measurement device was built, tested and applied in Hamilton Harbour. Techniques were developed to measure SOD and oxygen uptake by chemical oxidation (CSOD). Sediment samples were taken from Hamilton Harbour and seven other lakes in Northern Ontario and Cape Breton Island. All samples were analyzed for organic content and selected samples were placed in laboratory columns. Experiments were conducted in which oxygen uptake was measured within the columns under controlled conditions. Sediment oxygen demand was fractioned into portions attributable to chemical oxidation, biological respiration and direct macroinvertebrate respiration.

Models were selected to describe the dependence of each portion of SOD on oxygen concentration and temperature. Where possible, mechanistic explanations are presented for the models selected. Results indicate that the chemical portion of SOD is dependent on oxygen concentration in the manner of a first-order reaction and that it responds to temperature change in

a manner typical of a mixed bacterial community. At high oxygen concentrations, anaerobic metabolic activity is found to be the limiting factor in CSOD. Bacterial and macroinvertebrate oxygen uptake are dependent on oxygen concentration at low concentrations, following a Monod kinetic form. These fractions respond to temperature in the same fashion as the chemical portion. Macroinvertebrates contribute a large part of the direct respiration as well as having a profound effect on the total community respiration.

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1. INTRODUCTION

The muddy bottom of lakes, rivers and estuaries is recognized as a region of intense biological activity. It is a complex ecosystem unto itself and the study of this zone can reveal much about the general balance of life in aquatic systems.

Organic and inorganic material settles to the sediment surface and comprises a matrix inhabited by organisms competing for food and space. The dominant life form is usually the heterotrophic bacteria which oxidizes the organic material in order to derive the stored chemical energy within. The relatively more bioresistant material is buried by the continuous 'rain' of fresh material, until it lies beneath the extent of penetration of oxygen. Deep within the sediment, anaerobic heterotrophs continue the decay process. A measure of the ecological balance of a system is the degree of organic material accumulation and oxidation. In eutrophic bodies of water, organic material accumulates quickly despite high rates of decay. Organisms are limited in this environment by

space alone. In more pristine environments, readily decomposable material does not accumulate and the bacterial community is in a constant state of competition for oxidizable organic matter.

The rate of oxygen uptake at the sediment-water interface, sediment oxygen demand (SOD) otherwise called total sediment oxygen demand (TSOD), is of prime concern in studies of the oxygen dynamics of a natural water body. TSOD may be divided into two fractions: the biological sediment oxygen demand (BSOD), the oxygen uptake by aerobic organisms, and the chemical sediment oxygen demand (CSOD), the direct oxygen uptake by purely chemical reactions. The latter fraction is defined operationally in this study as the chemical oxidation of reduced by-products of anaerobic decomposition processes.

The objectives of this study are two-fold. Firstly, SOD is measured *in situ*. In so doing, the techniques of applying such measurements are tested and assessed. The results of these measurements are used to determine the degree of spatial and temporal variability of SOD in lakes of Southern Ontario, Northern Ontario and one lake on Cape Breton Island, Nova Scotia. The measurements also provide an independent set of data to compare with laboratory measurements

from the second part of the study. Secondly, SOD is characterized by fractioning the total rate into its component parts: CSOD, BSOD and macroinvertebrate oxygen uptake (MSOD). The effects of oxygen concentration and temperature on these rates are examined and modelled. The techniques involved in measuring TSOD, BSOD, CSOD and MSOD are evaluated and recommendations for standardization are made.

2. LITERATURE REVIEW

2.1. Introduction

The purpose of this chapter is to summarize existing information concerning SOD and to clarify the methodologies used in this study. The following sections deal specifically with *in situ* and laboratory measurements of SOD, sediment chemistry and structure, the temperature and dissolved oxygen effect on sediment activity, the macroinvertebrate community and the mechanisms of sediment oxidation.

2.2. *In situ* Measurements of SOD

Many attempts have been made to measure SOD directly using devices which have been developed for this purpose. In this study, the equipment and techniques employed were designed to obtain a first approximation of oxygen utilization by sediments in an undisturbed state. Crook and Bella (1970), Smith *et al.* (1972), Smith *et al.* (1973), James (1974), Pamatmat and Banse (1969), National Council for the Paper Industry for Air and Stream Improvement (NCASI)

(1978), and Polak and Haffner (1978) conducted *in situ* measurements in rivers, lakes, estuaries and the sea.

In the studies of Crook and Bella (1970), James (1974) and the NCASI (1978), *in situ* chambers were used to isolate a portion of the substrate from the mainstream of flowing waters and to observe the rate of oxygen utilization by the sediment. Drawings of Crook and Bella and James' tunnel-like devices are reproduced in Figures 1 and 2, respectively. The system used in the NCASI study is similar to that of James. The units of James and the NCASI employ a flange to seal the tunnel into the sediment. Crook and Bella's device is 5.64 metres in length, sealed at both ends and equipped with a variable speed pump to provide an artificial current within. Water samples can be withdrawn at any time interval and the rate of oxygen loss from the water can then be calculated.

The device used by James is longer (30 metres) and when aligned with the flow allows water to pass through at the natural velocity. The time of water passage through the tunnel is accurately measured; then the dissolved oxygen is measured by a probe or chemical analyses as it enters and leaves. In each study, consistent results were achieved. The authors

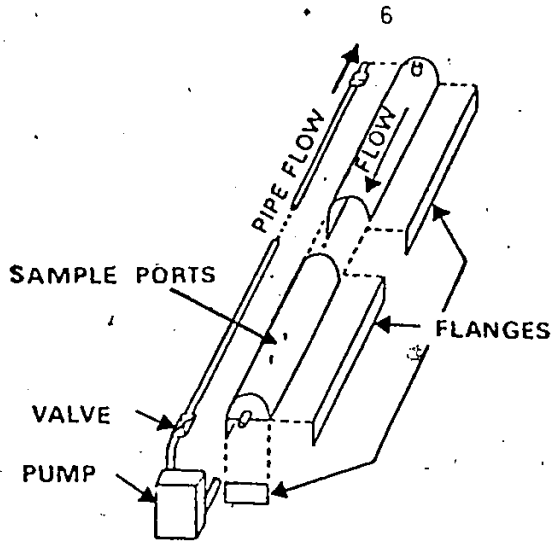


Figure 1. Closed recirculating respirometer (from James, 1970)

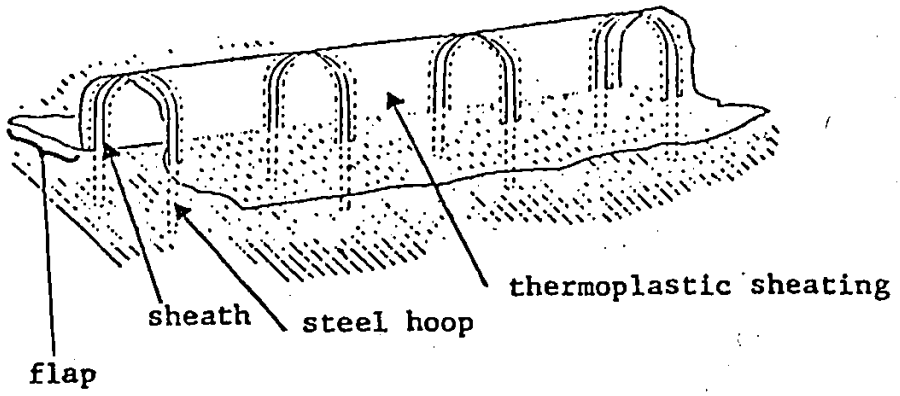


Figure 2. Open tunnel respirometer (from James, 1970)

did note, however, that their techniques are limited to shallow, slow moving stream sections.

James (1974) also tested a respirometer, a device in which the effects of biological respiration can be contained and observed (see Fig. 3). This device differs in shape from the instrument of Crook and Bella (1970) but is similar in operation. A variable speed pump is used to create an artificial current over the sediment. Working in the sediments of an Oregon estuary, Crook and Bella applied linear velocities of 0.12 to 0.24 m/sec to the trapped water. A gradual increase in SOD rate from 1.4 to 2.1 grams O_2/m^2-day was observed. It was concluded that a direct relationship exists between oxygen uptake rate and water velocity over the sediments in this velocity range. This respirometer can be used in deep water. In the NCASI study, a correlation was developed between water velocity and SOD over the velocity range 0-0.4 ft/sec. At some sites, almost a two-fold increase in SOD was observed as velocity was doubled.

Smith *et al.* (1972), Smith *et al.* (1973), Pamatmat and Banse (1969), Smith and Teal (1973), NCASI (1978) and Polak and Haffner (1978) used respirometers of their own design in deep non-flowing locations.

Smith's chamber is typical and is reproduced in Figure 4. This instrument is fitted with a mixer, a dissolved oxygen probe and meter, a recording unit and a power source. The mixer circulates the trapped water past the probe eliminating stagnant areas within the chamber and providing a gentle movement of water over the sediment. Smith used divers to place his instrument when in deep, non-wadeable waters. He also conducted experiments in deep sea conditions in which the instruments were lowered by cable to a depth of 1850 metres. His measurements continued for a period from 2 to 72 hours, depending on the rate of sediment oxygen demand.

Most researchers have provided their devices with a system for injecting solutions of metabolic poisons into the trapped water. Smith and Teal (1973) used formalin after several hours of normal operation. When formalin was added to the chamber in the sea at a depth of 1850 metres, the uptake of oxygen ceased. They concluded that SOD at that location was totally due to the direct uptake of oxygen by the biological community.

Smith *et al.* (1972) and Smith *et al.* (1973) measured SOD in the sea near Bermuda and the sewage outfall near Wood's Hole, Ma. At these locations, a

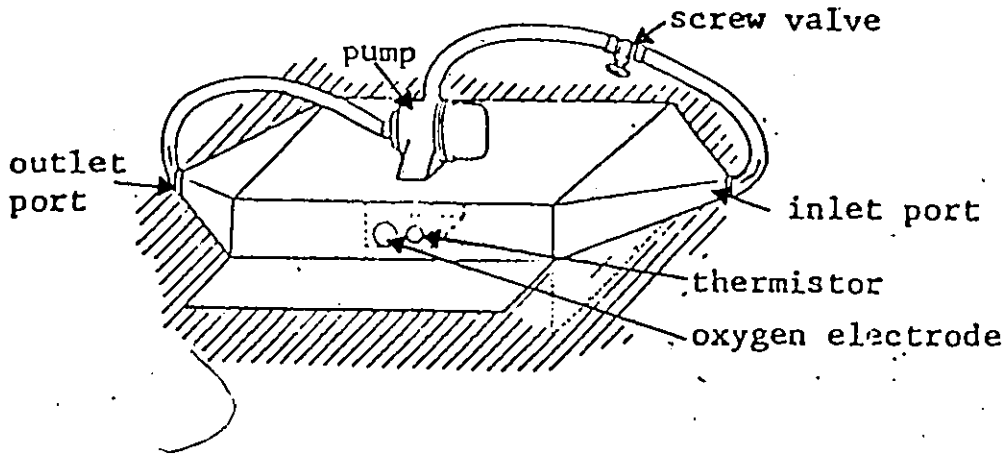


Figure 3. Closed recirculating respirometer (from James, 1973)

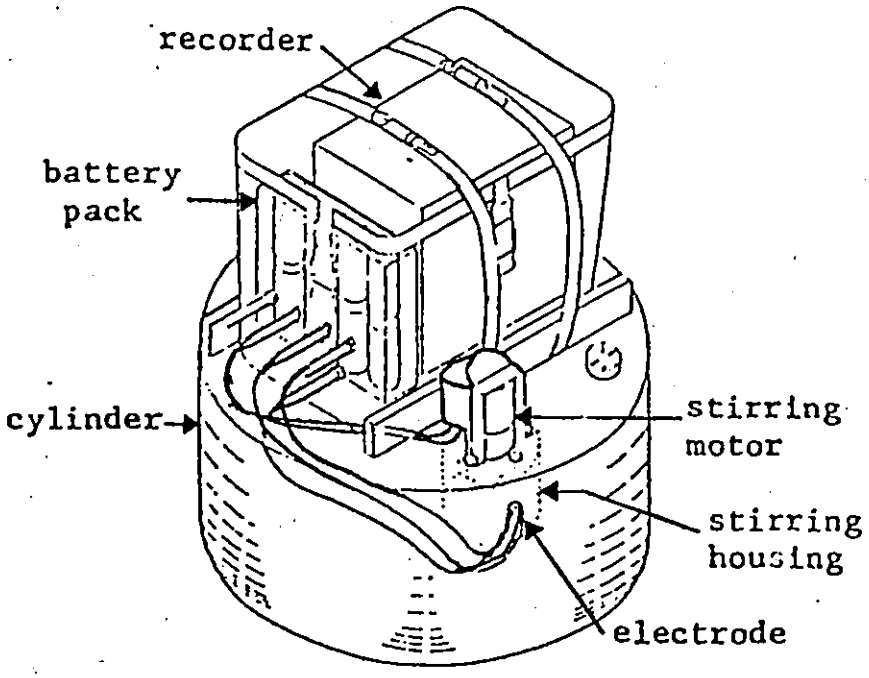


Figure 4. Oxygen demand chamber (from Smith *et al.*, 1972)

solution of penicillin and streptomycin was added to the chamber as a metabolic inhibitor. The inhibitors were added in equal parts and the final concentration was 50 mg/ℓ of each. Hargrave (1969a) reported that this solution will stop bacterial activity yet will not effect the macroinvertebrate community. Smith's measurements consisted of three phases: one conducted under normal conditions; one in which streptomycin and penicillin were added; and a final stage in which formalin was added. In this way, the SOD rate could be partitioned into the contributions from bacteria, macroinvertebrates, and non-biological reactions.

A summary of SOD rates reported by several authors appears in Table 1. Initial temperature and oxygen concentrations are included, when available. Note that some of the measurements were made in laboratories on sediment cores overlain with water. Certain observations are relevant. The chemical portion of the rate, when measured, was found to constitute a significant portion of the total rate in most cases. In fact, Pamatmat (1971) found that the SOD rate could totally consist of chemical uptake in some locations. There is a large range reported in the rates (0.024 gm/m^2-day in the East Tropical Pacific

Table 1

Measured SOD Values from Literature

The following symbols are used when more than one measurement method is used: C - cores; CH - chambers; T - tunnel; S - *in situ*

Author	Location	Oxygen concentration mg/ℓ	Temperature °C	SOD gm/m²/day		Breakdown into % as CSOD
Granéli (1978) (cores)	Lake Hinnasjön	saturation	various	0.368	yearly average	52
	Lake Trummen	saturation	various	0.744		31
	Lake Växjösjön	saturation	various	0.587		13
	Lake Vombsjön	saturation	various	0.920		17
	Lake Södra Bergundasjön					
Hayes and MacAulay (1959) (cores)	Lakes: Bluff	saturation	11 ± 1.5	0.188		90 (approximately)
	Punchbowl	saturation	11 ± 1.5	0.408		42 (approximately)
	Silver	saturation	11 ± 1.5	0.201		85 (approximately)
	Boar's Back	saturation	11 ± 1.5	0.348		49 (approximately)
	Jesse	saturation	11 ± 1.5	0.317		54 (approximately)
	Tedford	saturation	11 ± 1.5	0.460		37 (approximately)
	Blackbrook	saturation	11 ± 1.5	0.290		59 (approximately)
	Copper	saturation	11 ± 1.5	0.309		55 (approximately)
	Grand	saturation	11 ± 1.5	0.264		64 (approximately)
	Lily	saturation	11 ± 1.5	0.399		42 (approximately)
	Sutherland	saturation	11 ± 1.5	0.198		86 (approximately)
	Crecy	saturation	11 ± 1.5	0.149		100 (approximately)
	Gibson	saturation	11 ± 1.5	0.379		45 (approximately)
	Kerr	saturation	11 ± 1.5	0.165		100 (approximately)

	Montague	saturation	11 ± 1.5	1.063		16
	Southport	saturation	11 ± 1.5	0.895		19
Pamatmat (1971) (cores)	Puget Sound, 180 m	5.0	9	0.230		50-69
	Puget Sound, 23 m	7.9	7	0.295		-
	Puget Sound, 23 m	6.5	7	0.235		-
	N.E. Pacific, 2750 m	3.4	7	0.057		-
	N.E. Pacific, 146 m	2.8	7	0.230		31-49
	N.E. Pacific, 105 m	3.1	7	0.101		87-112
	N.E. Pacific, 146 m	3.4	7	0.117		66-73
	E. Trop. Pacific, 275 m	1.1	15	0.130		71-77
	E. Trop. Pacific, 85 m	1.4	15	0.317		48-101
	E. Trop. Pacific, 2820 m	2.4	15	0.142		66-81
	E. Trop. Pacific, 2900 m	2.4	15	0.055		85-106
	E. Trop. Pacific, 1325 m	1.6	15	0.024		42-62
Edberg (1976) (cores)	Lakes: Uttran	saturation	10 and 4	0.54	0.50	-
	Malmsjön	saturation	10 and 4	0.54	0.45	-
	Sillen	saturation	10 and 4	0.44	0.34	-
	Djulösjön	saturation	10 and 4	0.50	0.54	-
	Boren	saturation	10 and 4	0.43	0.27	-
	Ryssbysjön	saturation	10 and 4	0.48	0.49	-
	Södra Bergundasjön	saturation	10 and 4	0.60	0.42	-
	Norra Bergundasjön	saturation	10 and 4	0.41	0.45	-
	Ramsjön	saturation	10 and 4	0.47	0.50	-
	Kyrkviken	saturation	10 and 4	0.47	0.47	-
	Molkomsjön	saturation	10 and 4	0.24	0.17	-
	Gåran	saturation	10 and 4	0.53	0.41	-
	Glaningen	saturation	10 and 4	0.60	0.45	-
	Näsbysjön	saturation	10 and 4	0.38	0.32	-

Crook and Bella (1970) *In situ*	Parker slough with macro.	0-6	14-16	4.8-8.5	-
	Parker slough without macro.	0-5	20-22	1.4-2.1	-
Smith *et al.* (1972) *In situ*	Bermuda, April	4.7-5.4	19	0.707	0
	Bermuda, May	4.7-5.4	23.1	0.918	0
	Bermuda, April	4.7-5.4	19	0.649	0
	Bermuda, May	4.7-5.4	23.1	0.836	0
Smith *et al.* (1972) *In situ*	Wood's Hole	-	-	2.33	-
	Buzzard's Bay	-	-	1.86	-
Smith and Teal (1973) *In situ*	New England in the sea at 1850 m	7.15	4.5	0.017	0
James (1974)	Streams: Cunsey Beck: T, CH, C	-	-	5.3, 3.8, 3.6	-
	Moorsburn: T, CH, C	-	-	38.2, 27.1, 22.1	-
	River Anker: T, C	-	-	10.1, 5.3	-
James (1974)	Lakes: Lea Harston, CH	-	-	3.6	-
	Esthwaite Water: CH, C	-	-	9.6, 9.4	-
	Blelham Tarn: CH, C	-	-	8.4, 5.3	-
	Loch Leven: CH, C	-	-	3.1, 1.7	-
Edberg and Hofsten (1973)	Baltic Sea: Askö 1: S	-	15	2.5	-
	Askö 1: S	-	15	1.1	-
	Askö 2: S	-	16	1.2	-
	Edeboviken 1: S,C	-	13, 10	3.0, 0.71	-

	Edeboviken 2: S,C	-	15, 10	0.92, 0.40	-
	Karlholm 1: S	-	15	0.93	-
	Karlholm 2: S	-	17	1.3	-
	Karlholm 3: S	-	17	1.7	-
Lakes:	Ekoln: S,C	-	18, 13	2.6, 0.6-1.2	-
	Erken 1: S,C	-	4, 10	0.43, 0.32-0.36	-
	Erken 2: S	-	14	0.5	-
	Norrviken 1: S,C	-	5, 10	1.8, 1.1	-
	Norrviken 2: S,C	-	7, 10	2.4, 1.5	-
	Ramsen: S,C	-	17, 10	2.3, 0.21-1.08	-
Streams:	Arbogaån 1: S,C	-	2, 5	1.44, 0.26-1.2	-
	Arbogaån 1: S	-	10	0.68	-
	Arbogaån 2: S,C,	-	0, 10	0.31, 0.31-0.61	-
	Arbogaån 3: S	-	9	0.84	-
	Arbogaån 3: S,C	-	2, 5	1.4, 0.42-0.63	-
NCASI (1978)	New England stream	-	22-27	10-13	-
In situ	D/S of Kraft Mill	-	25.7	2.2-4.5	-
	North New England stream	-	22.5	4.9-16.9	-
	Estuary of Chesapeake Bay	-	27	7.3-33.2	-
Polak and Haffner (1978)	Hamilton Harbour, Stn. 252	9.7	10.8	3.41	67
	Hamilton Harbour, Stn. 252	9.4	11.9	2.82	74
In situ	Hamilton Harbour, Stn. 270	7.2	15.3	2.64	84
	Hamilton Harbour, Stn. 270	0.19	14.0	0.59	7
	Hamilton Harbour, Stn. 270	3.5	16.0	1.45	65
	Hamilton Harbour, Stn. 270	3.6	14.8	1.71	42
	Hamilton Harbour, Stn. 270	0.8	15.1	1.11	70
	Hamilton Harbour, Stn. 270	4.8	14.7	2.08	52
	Hamilton Harbour, Stn. 270	0.8	14.2	0.72	
	Hamilton Harbour, Stn. 270	3.0	13.3	1.77	74

to 38.16 gm/m^2-day in an English stream). Crook and Bella (1970) observed a large contribution to the total rate from worms. They observed SOD rates at locations with worms to be about four times that without them. Other authors referenced here, with the exception of James and the NCASI study, reported SOD rates in the range of 0.1 to 3.4 gm/m^2-day while James (1974) observed extremely high values in English streams and lakes (1.68 to 38.16 gm/m^2-day).

Several authors noted high SOD rates after initial placement of their respirometers. The rate eventually decreased to some steady value. One possible explanation for this phenomenon is that during placement the sediment is disturbed by the chamber's edges resulting in some resuspension of sediment.

In situ measurement techniques are used extensively and under varying conditions of temperature, depth, oxygen concentration and substrate type. The devices employed are similar in design and purpose. However, operational techniques have not been standardized. There is, as yet, some question as to the proper duration of tests and the minimum relative change in oxygen that should be observed in a measurement. Little information is available on the spatial

and temporal variability, or indeed, repeatability of measurements that one might observe in a particular water body. The use of metabolic inhibitors is common yet various poisons are used and their effects on the sediment community can be quite different. Respirometer design and size is highly variable but usually reflects the conditions encountered in the field, the handling facilities and the sediment characteristics.

While some authors have successfully compared SOD rates measured *in situ* with laboratory measurements, there is, as yet, no real independent assessment of the value of this method. The literature does not contain a discussion of possible errors or problems associated with *in situ* measurements.

2.3. Laboratory SOD Measurements

Direct measurements of SOD have been made on sediments in laboratories under controlled conditions. Laboratory procedures involve monitoring the oxygen loss from the water overlying either disturbed sediment in a respirometer or an undisturbed sediment core in a coring tube. The operational techniques, observations and conclusions resulting from both methodologies are reviewed in this section.

Mixing schemes within laboratory respirometers are recognized as an important parameter and thus have been a topic of study. Crook and Bella (1970) compared *in situ* SOD measurements made in a Toledo estuary with earlier measurements made on cores in a laboratory. Their laboratory measurements compared favourably with core measurements that were made with no mixing but were about half of the rate of laboratory measurements made with plunger-type mixing. James (1974) assessed the mixing in three devices. He found no effect on SOD rates from low-mixing speeds in a stirred core-type respirometer. However, mixing was positively related to SOD rate using the *in situ* device illustrated in Figure 3. He concluded that when overlying water velocity exceeds 0.4 m/sec the sediment becomes resuspended, thus increasing surface area and SOD rate. Edwards and Rolley (1965) observed a similar relationship between mixing and SOD rate. They concluded, as James later did, that when mixing exceeds the velocity required to cause resuspension of material the SOD rate increases. Pamatmat (1971) found mixing to be important with some sediments and attempted to simulate natural mixing conditions in his experiments. The 1978 NCASI field study employed tunnel and chamber type respirometers.

While variability was high in measured SOD values at the same site, it was evident from the results that SOD was a linear function of velocity in the 0-0.4 ft/sec range. Resuspension of bottom material was eliminated as the cause of increased rates in this study.

Hayes and MacAuley (1959) examined three methods of sediment handling and preparation and their effects on measured SOD rates in the laboratory. The sediment samples were taken and prepared in the following structure: 1) in an intact condition; 2) in a disturbed condition and allowed to settle; and 3) in a disturbed condition and settled by centrifuging. Despite the differences in preparation the SOD rates were similar. Hayes and MacAuley were able to conclude that after disturbance sediment systems return to a near-natural state with respect to the vertical stratification of chemical and biological characteristics.

Granéli (1978) investigated the ability of sediment samples to acclimatize to different temperatures. Various Swedish lakes were sampled for SOD laboratory measurements. The samples were taken at regular time intervals and incubated at the *in situ* temperature. Similar rates were measured on the incubated samples

as on another set of samples collected at the same sites at the same time. The second set of samples were allowed to acclimatize to the same temperatures as the first set. Similarly, Rolley and Owens (1967) obtained almost identical rates when they measured SOD on sediments taken from the same river site during winter and summer and allowed to acclimatize to the same temperature.

Pamatmat (1971) conducted experiments to determine the variability of SOD rates with depth in the sediment matrix. He measured the SOD rate in an intact core, then removed the top few centimetres of material and measured the rate exerted by the remaining sediment. An initial higher rate was observed in the second case. However, after a few hours, this rate decreased to the rate measured in the undisturbed case. Pamatmat partially credited the initial elevated SOD rate to a sudden and short-lived release of reduced metal ions which had been buried under the oxidized zone of the sediments. These results also illustrate that a degree of vertical homogeneity exists in the upper zone of sediments with respect to their oxidizability.

In all laboratory studies conducted at conditions dissimilar to the natural condition, a time

lapse was allowed so that the sample could acclimatize to the new condition. Edberg and Hofsten (1973) allowed their disturbed cores to acclimatize in their laboratory for long periods of time and observed time-dependent changes over 20 days. During this time period, SOD rates continued to increase and reached a steady value after 20 days. They explained that this phenomenon was due to the re-establishment of bacterial and macro-invertebrate populations to near-natural conditions and numbers.

Pamatmat (1971) avoided acclimatization uncertainty by on-shipboard measurements. Shortly after retrieval, SOD rates were measured on undisturbed cores at *in situ* temperatures. Only the first few hours of measurement were used to determine the SOD rate.

Several different poisons have been used in sediment respiration studies in laboratories. Edberg and Hofsten (1973) used potassium cyanide (KCN), an inhibitor of cytochrome oxidase, to measure the SOD rate which remains after the aerobic organisms are inhibited. Pamatmat (1971) used formaldehyde (2.5 to 5.0% by weight) to kill all organisms and thereby determine oxygen uptake by purely chemical processes in sediments. Granéli (1978) poisoned sediments with 1000 mg/ℓ of mercuric chloride (HgCl) to completely

halt biological activity. There is a discrepancy between the approach used by Edberg and Hofsten and that used by Pamatmat and Granéli regarding the activity of the anaerobic bacterial community. In the long term, Edberg and Hofsten's method results in a higher oxygen uptake rate for the same sample. The reason is that the by-products of anaerobiosis are still being produced and consequently still contribute to oxygen consumption by chemical oxidation. It is highly questionable whether a significant difference would result during the short time scale of an SOD measurement.

Liu and Strachan (1977) tested various poisons in a laboratory experiment in which sediment samples were placed in Warburg respirometers and treated with m-Cresol, KCN or sodium azide. After an initial uninhibited period, during which bacteria in the sediment were allowed to respire normally, the poisons were added. The m-Cresol was the most effective in almost immediately reducing respiration. The KCN concentration applied (0.2 ml of 0.1 M solution for 3 grams of dry sediment) was nearly 100% effective after one hour. The sodium azide produced only minor inhibition during the course of the experiment.

In their study, Edberg and Hofsten (1973) confirmed that oxygen transfer through the plexiglass walls of their core respirometer was negligible and any error resulting from this process could be ignored.

Laboratory measurement methods have been tested with special emphasis on mixing schemes, sample handling, incubation temperatures, acclimatization times and metabolic poisons. The concensus is that mixing should simulate natural conditions without causing resuspension. Sample handling and preparation techniques vary from one study to the next; however, evidence suggests that if samples are allowed sufficient time to acclimatize, they will return to a condition similar to the natural condition. In addition, if samples are subjected to temperatures differing from those at the time of sample collection, an acclimatization period of several days should be allowed. Various poisons have been used to inhibit components of the total SOD rate. Care must be exercised in interpreting the results of these measurements and in comparing the results from studies in which different poisons were used.

As yet, it is difficult to compare the merits of *in situ* and laboratory measurements. No independent

assessment technique exists. Laboratory methods offer the investigator more flexibility and the facility to make more precise visual and chemical observations. However, measurements made *in situ* are less subject to disturbance and resultant errors. More work of a comparative nature is required, not only to evaluate these techniques, but to establish the best operational procedures.

2.4. Sediment Characteristics

Sediment composition and structure are investigated in order to address two questions: what is the importance of sediment-water interfacial reactions to the chemical dynamics of the whole water body, and what descriptive knowledge of long-term trends can be obtained by studying sediments? Despite the large temporal and spatial variability usually encountered in the chemical properties of a water body, surface sediment characteristics often reflect the prevailing condition. Conversely, deeper sediments are investigated to obtain information about historical patterns. In this section, literature pertaining to descriptive sedimentology is reviewed with emphasis placed on sediment chemical and biological structure.

Several researchers have studied sediment properties at various depths within the matrix. Vanderpost (1972) dated various strata within sediment cores from Lake Ontario. This investigation revealed that the top 10 to 12 centimetres of sediment were deposited during the past 120 years. Despite this time span, chemical properties were homogeneous throughout the profile with the exception of the thin top layer. Bacterial populations, sorted into fundamental divisions, were also shown to be similar throughout the various zones. The thin top layer (2-3 cm) contained higher aerobic bacterial densities and had a higher organic content.

Shapiro *et al.* (1971) investigated the sediments of Lake Washington and noted evidence of recent changes to the water body which was reflected by the sediment. In 1963, sewage inputs to this lake were eliminated. This action resulted in a dramatic improvement in water quality which was observed in the following years. In 1968 and 1970, significantly higher sediment phosphorous concentrations were found at a depth of 4 cm. These concentrations were similar to surface values measured in 1958-59. The higher phosphorous concentrations, indicative of pre-1963 conditions, were

buried by fresh sediments which reflected the new, cleaner water quality conditions.

Researchers have found that the surface sediments are generally richer in organic content and support more intense bacterial activity than deeper sediments. In a Quebec Lake, Cooper *et al.* (1953) observed a decrease in the organic content of the sediment below the surface layer of sediment. Mortimer (1942), Sorokin (1975) and Vanderpost (1972) observed a strong relationship between aerobic bacterial populations and the eH profile in the sediment column.

The sediments are a zone of intense activity. The interstitial water of the sediments reflects this activity with high chemical ion concentrations. Weiler (1973) found elevated concentrations of soluble reactive phosphorus, nitrate, silica, iron and manganese in the interstitial water of Lake Ontario surficial sediments. Gardner and Lee (1965) measured extremely high buffering capacity in eutrophic Lake Mendota sediments. Alkalinity as $CaCO_3$ was measured at 260,000 mg/ℓ while iron and sulphides were in the range of 17,000 to 23,000 mg/ℓ and 1,400 to 3,300 mg/ℓ, respectively. Bruskill *et al.* (1971) while studying six oligotrophic lakes in the Experimental Lakes Area

(ELA) of Northern Ontario, found that major ions were present in interstitial water, in concentrations that were 1.5 to 5 times higher than those in the overlying water. Sorokin and Donato (1975) measured sulphide reduction rates in the sediments of subalpine lakes as high as 18.2 mg/ℓ-day. These extremely high rates were found in eutrophic lakes with sediment sulphide concentrations ranging from 500 to 1,500 mg/ℓ.

The results of investigations indicate that the sediment matrix and interstitial water is a zone of concentrated chemical and biological activity. These high concentrations of major ions impart a high buffering capacity to the sediments.

Many researchers have investigated the so-called "mixed zone" at the surface of sediments. This zone usually includes only the top few centimetres of the sediment compartment and displays chemical and biological conditions quite different from the deeper sediment strata. Mortimer (1941) used redox potential to delineate this mixed and oxidizing zone from the lower reduced zones thereby implying that these zones can be differentiated by their chemical potential. Hargrave (1972a) found that an eH value of +100 millivolts corresponds to the deeper extent of this zone. He

was able to measure oxidized zones as deep as 3 cm in sandy material while silty sediments displayed about 2 to 3 mm of mixed zone. Viner (1976) measured the depth of the mixed zone to be 10 cm in the sediments of Lake George, Uganda.

Gorham (1958) studied the formation and breakdown of the oxidized zone. In this study, the lower extent of the zone was defined as the depth at which colour change occurred from a brown-orange to black. The brown-orange colour is indicative of iron oxidation. Iron does not oxidize below this zone. Oxidized zones were found to extend from 6 to 38 mm into the sediment of a eutrophic English lake. Gorham took sediment cores during an anoxic period and could find no apparent oxidized microzone. The water overlying the cores was aerated yet still no microzone developed. However, after the samples were disturbed and allowed to resettle, a distinct mixed zone appeared. After 2 months the zone had extended its depth to 14 mm. Gorham concluded that in similar lake types, the mixing which accompanies fall turnover is essential to the establishment of the mixed microzone. He noted that it is possible for wind mixing to cause this zone to overturn several times in one year and that worms, when present in the

sediments, could extend the depth of the zone by their tunneling action.

The organic fraction and the nature of the organic fraction of sediments has been the object of several studies. Kemp (1976) studied Lake Erie sediment and characterized the organic fraction. This study showed that 96% of Lake Erie's organic sediment is autochthonous. This organic material was found to consist of 24 to 41% kerogen material (non-degradeable matter), 7 to 9% humic material, 12 to 28% fulvic material and 58 to 71% humins. Humic, fulvic and humin materials are bioresistant. In a study by Kemp and Lewis (1968), an estimated 95% of the organic material in Lake Erie decomposed on settling and did not reach the lake bottom. The material which did reach the bottom was the most bioresistant.

Gorham *et al.* (1974) confirmed the observation made by Kemp and Lewis (1968). In England's Ethwaite Water, a small eutrophic lake with a mean depth of only 6.3 metres, sediment traps were set at the thermocline and at the lake bottom to compare sedimentation rate and sediment composition. Very little decomposition occurred in the hypolimnion since 94% of the mass settling out of the epilimnion reached the sediment

surface. Chlorophyll derivatives were highly concentrated in the surface sediments to a depth of 0.5 cm and decreased quickly to less than 1/3 of the surface concentration at a 3 cm depth. Two deeper lakes were studied and a more even distribution of chlorophyll derivatives (with depth into the sediments) was observed. It was concluded that because of Esthwaite Water's shallow hypolimnion, autochthonous material was accumulating on the sediment surface, whereas in deeper lakes decomposition in the hypolimnetic waters reduced the sediment load at the sediment surface.

The sediment compartment acts as a trap or 'sink' for bioresistant organic material. Jewel and McCarty (1971) found that 40% of algal material is relatively bioresistant. This bioresistant material is primarily skeletal detritus. Bordovskiy (1965) suggested that this is basically all that remains of settling phytoplankton at the sediment surface of deep lakes.

Correlations between various sediment characteristics have been reported by several researchers and are relevant to this review. Rolley and Owens (1967) were able to correlate loss on ignition, humic acid, kjeldahl nitrogen, organic carbon and permanganate

value and achieve correlation coefficients greater than 0.875. A regression relationship was also established between permanganate value (P.V.) and humic acid (H.A.) as follows:

$$P.V. = 1.76\ (H.A.) + 1.23 \qquad (1)$$

Other correlations are listed here as ratios.

$$\frac{\text{Organic carbon (\% of dry weight)}}{\text{Carbohydrates}} = 2.0/1.0 \qquad (2)$$

(Gerchakov and Hatcher, 1972)

$$\frac{\text{Organic carbon (\% of dry weight)}}{\text{Loss on ignition}} = 0.47/1.0 \qquad (3)$$

(Dean and Gorham, 1976)

$$\frac{\text{Organic carbon (\% of dry weight)}}{\text{Nitrogen}} = 8.2/1.0 \qquad (4)$$

(Kemp and Mudrochova, 1972)

Pamatmat and Banse (1969) were also able to show an inverse relationship between organic matter (as a percentage of dry weight) and particle size.

In summary, the available literature describes the sediments as a highly concentrated, strongly buffered deposit which can be studied in two parts. The upper zone is mixed and, under oxic conditions, displays positive eH values. This layer is dominated

by oxidative chemical reactions and is populated primarily by an aerobic bacterial community. This zone often displays the brownish-orange colour indicative of the fully oxidized state of iron.

Below the oxidized zone is a perpetual zone of chemical reduction. Redox potential, measured as eH, is negative and bacterial communities are dominated by anaerobes. This zone is not effected by wind or macroinvertebrate mixing. Decomposition occurs at a slower rate as the organic fraction in this zone is much more bioresistant than in the surface sediments. Reduced chemical species diffuse upward through interstitial water to the oxidized zone. The reduced zone is often quite homogeneous throughout its depth yet close investigation of chemical properties in the strata can often reveal long term historical patterns and past water quality trends.

2.5. Organic Carbon and SOD

Once it had become apparent that SOD was largely a result of heterotrophic organisms degrading organic deposits, many researchers attempted to relate the kinetics of SOD to the organic properties of the substrate. This line of research aimed at answering the

questions regarding the large variability in oxygen uptake rates of sediments observed in various water bodies. Unfortunately, the problem could not be resolved. For example, Hargrave (1969b) found no significant correlation between SOD and total organic matter, protein and carbohydrate content of the sediments in Marion Lake, B.C. Specific measures of organic content were not reported but allochtonous organic inputs were high in the incoming stream. In 1939, Anderson was unable to show a correlation between the organic content of undisturbed sediment and the SOD. A wide range of organic contents of sediments were used in this study. Kato (1956) found a positive correlation between CSOD and organic carbon content of stirred sediments after poisoning with toluene. Edwards and Rolley (1965) studied river muds with organic carbon contents of 4 to 13% by weight and found no relationship with SOD. They did note that permanganate value (a measure of readily oxidizable matter) was strongly related to organic carbon. Edberg and Hofsten (1973) reported similar results but felt that the quality (biodegradability) of the organics is important. One lake in their study had a low SOD and a largely wood fibre type of sediment. Another lake

had a high SOD, a sediment of low organic content and a thin layer of algae at the surface. Pamatmat and Banse (1969) found no seasonal changes in organic carbon or nitrogen in Puget Sound sediment despite changes in SOD. They concluded that a large portion of the organics were non-living and refractory when SOD was low.

Rolley and Owens (1967) elaborated on the work of Edwards and Rolley (1965), analyzing sediments for permanganate value, loss on ignition, humic acid, organic carbon and kjeldahl nitrogen. They found strong correlations between the various parameters but no correlation with SOD.

Lui *et al.* (1973) used the manometric technique to measure the effects of carbohydrate content on the uptake of oxygen by sediments. They measured carbohydrate content at different depths in sediment cores and found that it decreased quickly with depth from 5% at the surface to 1.5% at 2 cm and 0.6% at 20 cm. This suggests that carbohydrates are gradually depleted in older sediments. Manometric uptake rates for the different depth slices showed a definite positive relationship between carbohydrate concentration, below 1.5% and oxygen uptake rate. In the San Diego Trough,

Smith (1974) measured SOD of 0.082 gm/m^2-day in sediments with an organic content of 1 to 3% by weight. However, Smith noted that Smith and Teal (1973) had obtained values of 0.017 gm/m^2-day in similar depths where organic content was 0.5%. These reports suggest that there might be a relationship between SOD and an organic parameter when organic content is low. Unfortunately, no one has attempted to characterize the thin top layer of sediment. In sediments with low organic content, this thin top layer is likely to display higher than average organic content and related biological activity. However, Pamatmat and Banse (1969) studied the top 0.5 cm of sediment in Puget Sound in winter and found the lowest organic content at one station was 1.14%. This station also had the lowest SOD. The same results were not observed in summer.

While several studies indicate that no obvious relationship exists between SOD rates and organic content of the sediment, common sense and some research on sediments with low organic content tends to indicate that there is such a relationship. Perhaps the best measure of organic content, or at least readily oxidizable organic content, has as yet not been found.

2.6. Temperature Effects

Relationships between sediment oxidation rates and temperature have been widely observed. The consensus is that there is a strong positive temperature relationship in the mesophilic temperature range (10 to 30°C).

Arrhenius' law has been used to describe the temperature effects of many elementary reactions:

$$k \propto e^{-E/RT} \qquad (5)$$

(Levenspiel, 1972)

where: k = rate constant

E = activation energy

R = ideal gas law constant

T = absolute temperature

This relationship adequately describes the behaviour of physical and chemical reactions over a broad range of temperatures. However, in systems involving simultaneous, highly complex reactions the use of one value of E may be inappropriate. Empirical models derived from that of Arrhenius are often used in these situations.

Researchers in biological waste treatment processes have achieved some success using empirical temperature models to describe rates in transient

temperature systems. Their work concentrates on a narrow range of temperatures (0 to 30°C) which most frequently occur in natural and man-made environments. The term, Q_{10} has been adapted by them as a parameter of comparison. It is a quotient or factor which indicates the relative rate change observed as temperature is increased by 10C°. Q_{10} is specific to each reaction, or set of reactions, and each 10C° temperature range. A typical Q_{10} for an elementary chemical reaction might be 1.5 while biological systems can display a Q_{10} as high as 4.0, (i.e., rate (20°C) = 4 x rate (10°C)).

A summary of Q_{10} values extracted from the work of various authors for different systems including some with macroinvertebrates is reproduced in Table 2. Generally, values are high. There is, however, a large variation at each temperature range indicating either inconsistency in measurement technique and/or actual variations in sediment community and the community's response to temperature. Both reasons have some validity. Table 3 is a summary of Table 2 Q_{10} values reported as means. Variability of Q_{10}'s, reported as variance, is high yet a similarity exists between Q_{10}'s in all temperature ranges. No clear

Table 2

Temperature Quotients, Q_{1_0} for SOD from Literature

Author	Water body or system studied	Temperature range °C	Q_{1_0}
Smith, Burns and Teal (1972)	Castle Harbour, Bermuda-1, Total	19.0-23.1	3.17
	Castle Harbour, Bermuda-1, Bacteria	19.0-23.1	2.59
	Castle Harbour, Bermuda-2, Total	19.0-23.1	3.14
	Castle Harbour, Bermuda-2, Bacteria	19.0-23.1	2.69
Granéli (1978)	Lake Hinnasjon	5.0-10.0	2.4
	Lake Trummen	5.0-10.0	2.2
	Lake Växjösjön	5.0-10.0	1.2
	Lake Vombsjön	5.0-10.0	2.0
	Lake Södra Bergundasjön	5.0-10.0	3.0
	Lake Hinnasjon	10.0-15.0	1.7
	Lake Trummen	10.0-15.0	1.6
	Lake Växjösjön	10.0-15.0	1.1
	Lake Vombsjön	10.0-15.0	1.5
	Lake Södra Bergundasjön	10.0-15.0	1.9
	Lake Hinnasjon	15.0-20.0	1.5
	Lake Trummen	15.0-20.0	1.4
	Lake Växjösjön	15.0-20.0	1.1
	Lake Vombsjön	15.0-20.0	1.3
	Lake Södra Bergundasjön	15.0-20.0	1.6
Hanes and Irvine (1968)	River sediments	15.0-20.0	3.2-4.0
	River sediments	20.0-25.0	3.0-3.8

Hargrave (1969b)	Marion Lake, B.C. - sediments	5.0-10.0	4.4
	Marion Lake, B.C. - sediments	10.0-15.0	3.2
	Marion Lake, B.C. - sediments	15.0-20.0	2.6
Edwards and Rolley (1965)	River Ivel	10.0-15.0	2.5
	River Hiz	10.0-15.0	2.8
	River Ivel	15.0-20.0	2.8
	River Hiz	15.0-20.0	3.0
Edberg and Hofsten (1973)	19 Lakes	5.0-15.0	3.4
	19 Lakes	10.0-20.0	2.1
	19 Lakes	15.0-25.0	1.5
Otsuki and Hanya (1972b)	Anaerobic decomposition of algae (first days of batch)	20.0-30.0	2.0
Brinkhurst, Chua and Kaushik (1972)	3 species of oligochaetes	5.0-15.0	1.5
	In sand and water	10.0-20.0	2.1
Duff and Teal (1965)	Nova Scotia salt marsh mud, low tide	10.0-20.0	1.0
	Nova Scotia salt marsh mud, high tide	10.0-20.0	2.2
	Nova Scotia salt marsh mud, low tide	2.0-10.0	1.9
	Nova Scotia salt marsh mud, high tide	2.0-10.0	4.1
	Nova Scotia salt marsh mud, low tide	10.0-20.0	2.3
	Nova Scotia salt marsh mud, high tide	10.0-20.0	2.7
	Nova Scotia salt marsh mud, low tide	2.0-10.0	3.2
	Nova Scotia salt marsh mud, high tide	2.0-10.0	3.6
	Georgia salt marsh mud, low tide	10.0-20.0	1.7
	Georgia salt marsh mud, high tide	10.0-20.0	1.9
	Georgia salt marsh mud, low tide	2.0-10.0	1.3
	Georgia salt marsh mud, high tide	2.0-10.0	4.8

Table 3

Summary of Literature Q_{10} Values

According to Temperature Range

Temperature range, °C	Mean Q_{10}	Variance
5-10	2.79	1.33, n = 14
10-15	2.06	0.41, n = 17
15-20	2.03	0.52, n = 18
20-30	3.10	0.70, n = 6

standard method exists for sampling or measuring SOD.

One difference exists in the method used by researchers to allow their samples to acclimatize to temperature change (see section 2.3). Duff and Teal (1965), Edwards and Rolley (1965), Otsuki and Hanya (1972a,b), Edberg and Hofsten (1973), Hanes and Irvine (1968) and Granéli (1978) conducted experiments with sediment samples in which they varied temperatures from the *in situ* temperature in order to assess temperature change effects. Brinkhurst *et al.* (1972) did work on temperature variation effects on macro-invertebrates. Hargrave (1969) and Pamatmat *et al.* (1973) recorded O_2 uptake rates on cores at various *in situ* temperatures. Edberg and Hofsten (1973) and Smith *et al.* (1972) measured uptake rates *in situ* with respirometers. These four studies involved well acclimatized communities and yet their results are widely different in terms of temperature effects. This suggests that actual community response is a variable. Duff and Teal (1965) confirmed this theory with their work on two different sediment communities. One community was in a Georgia salt marsh and normally experiences large seasonal temperature changes. The

other community was in a Nova Scotia salt marsh and does not experience large temperature fluctuations. Low Q_{10}'s were observed in the Georgia marsh community and high Q_{10}'s in the Nova Scotia community. It was concluded that the Georgia salt marsh community adjusted better to fluctuating temperatures than the Nova Scotia community. Therefore, the temperature change dynamics of a system should be considered when assessing temperature effects.

The summary of Q_{10} values in Table 3 does not indicate any clear correlations between Q_{10} and temperature yet some researchers have noted such trends in their work. Hargrave (1969) found Q_{10} to decrease with increasing temperatures. The evidence suggested that one should expect higher increases in the respiration of individual microorganisms in response to a temperature increase in the spring as opposed to the late summer. Duff and Teal (1965) concluded that increases in both population and activity accompany temperature increases but that more stable systems display a larger increase in activity than do acclimatized communities. Hargrave's contention is that the similarities which exist between different communities' response to temperature change can be explained by the oxygen supply rate.

Oxygen uptake rate is limited by oxygen supply or diffusion rate and it is this rate which changes with temperature in all cases. Edberg and Hofsten (1973) concluded that Q_{10} values were lower at high temperatures because the community experiences a change in dominant species to a species which reacts more moderately to temperature change (in the new temperature range). The new temperature range is closer to the optimum for the new dominant species. Q_{10} values less than 1.0 have not been reported. This suggests that all systems studied were observed below the collective optimum temperature of the community.

Pamatmat *et al.* (1973) found that Q_{10}'s for chemical oxidation were lower than those for total oxidation but above Q_{10} for purely chemical or physical reaction. This indicates that chemical oxidation is, to some extent, limited by biological activity. However, Pamatmat concludes that chemical oxidation is ultimately controlled by oxygen diffusion. Therefore, a linear relationship is used to describe the response of chemical oxidation to temperature change.

Two facts are clear from the literature regarding temperature change effects on oxygen uptake in sediments. Firstly, temperature effects are substantial

and must be taken into account in sediment oxidation studies. Secondly, a great deal of uncertainty exists as to the cause of these responses.

2.7. Oxygen Concentration Effects

The uptake rates of dissolved oxygen by benthic communities is used indirectly as a measure of metabolic activity or sediment oxidation rate and directly as part of the total hypolimnetic oxygen demand. Researchers have, therefore, been interested in the effect that oxygen depletion near the sediment-water interface has on SOD.

Hargrave (1969b), Edwards and Rolley (1965), Edberg and Hofsten (1973), Pamatmat (1971), Edberg (1976), Pamatmat *et al.* (1973), Polak and Haffner (1978), Abernathy and Bungay (1972), Knowles *et al.* (1962), and Berg *et al.* (1962) have all found a correlation between oxygen concentration and SOD. Hargrave, measured SOD rates in undisturbed cores at 15°C. His plot of SOD versus dissolved oxygen (see Fig. 5), shows a sudden decrease in SOD rate at oxygen concentrations below 2.0 mg/ℓ. The data is somewhat sparse in the lower oxygen range, however, linear regression was used on the data with some success.

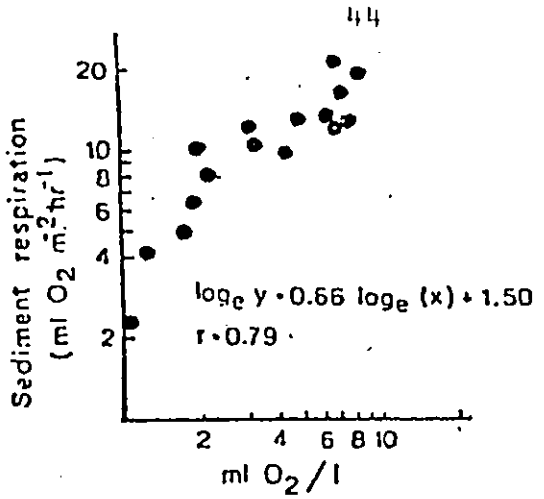


Figure 5. Sediment respiration at 15°C in Marion Lake, B.C. versus oxygen concentration (from Hargrave, 1969b)

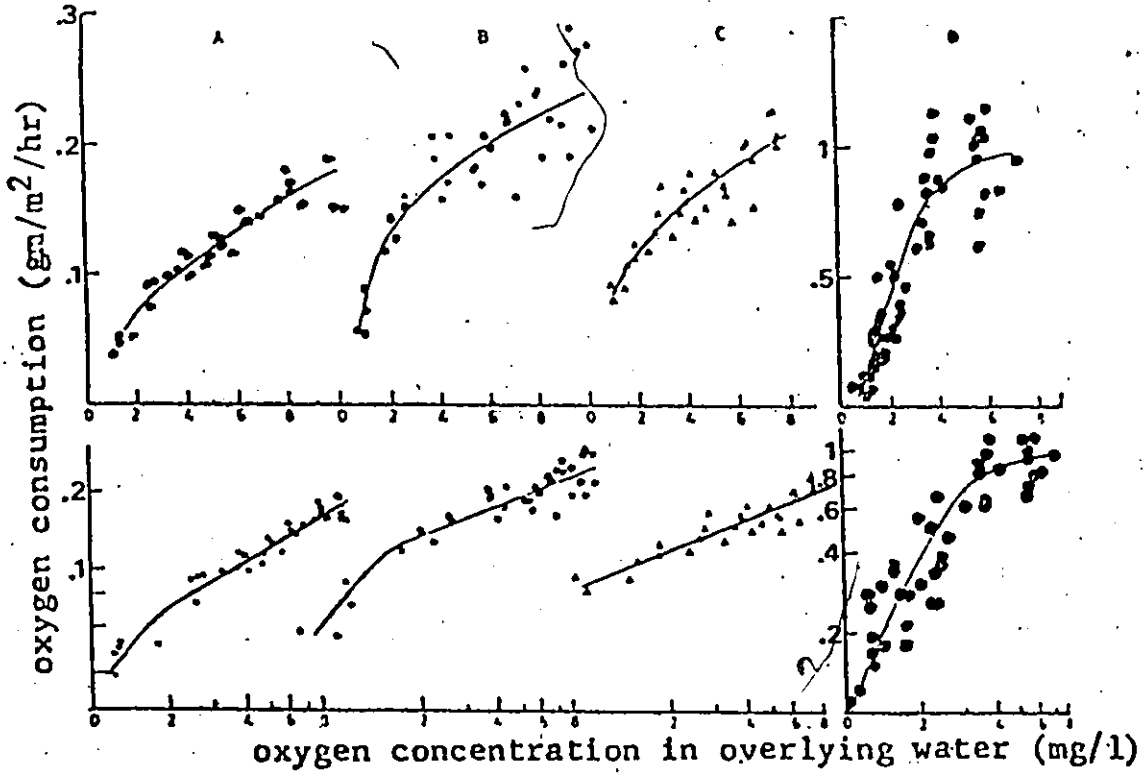


Figure 6. Oxygen consumption rate of mud cores at 20°C from four rivers versus oxygen concentration (from Edwards and Rolley, 1965)

Edwards and Rolley (1965) used intact cores and observed a similar trend (see Fig. 6). A logarithmic transformation of their rate versus concentration data yields a breakpoint around 1.5 to 2.0 mg/ℓ of dissolved oxygen. The model,

$$SOD = a \cdot [D.O.]^b \qquad (6)$$

where a and b are constants, was used to fit data with some success. This model type was also used by Crank (1956) to describe a system wherein simultaneous reaction and diffusion occur.

Pamatmat's (1971) data is plotted in Figure 7 as sediment oxygen demand as well as its component parts, respiration and chemical oxidation. The respiration rate in this case also 'breaks' at about 1 to 1.5 mg/ℓ of oxygen. The chemical oxidation curve appears to change from first order at higher oxygen concentrations to less than first order at lower oxygen concentrations.

Edberg and Hofsten (1973) used the model:

$$SOD = b + 2 \cdot [D.O.] \cdot t \qquad (7)$$

where t is time and b is a constant, to describe the loss of oxygen in a sediment-water reactor. The shape

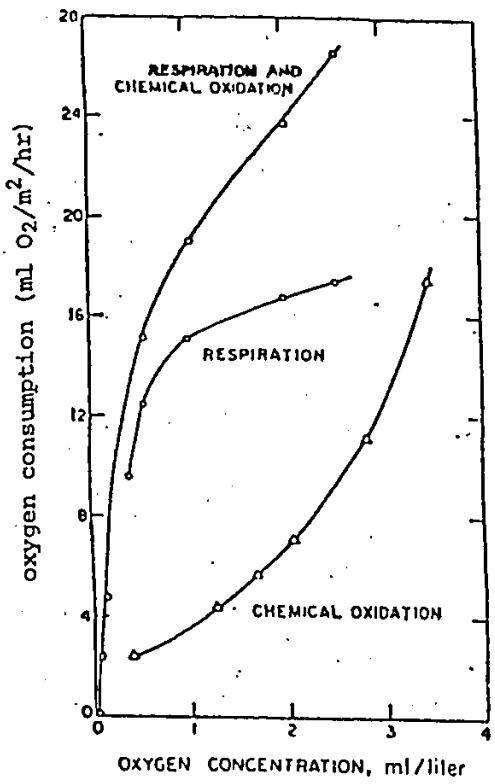


Figure 7. Component parts and total oxygen uptake (from Pamatmat, 1971). *In situ* measurements at 74 m in Puget Sound

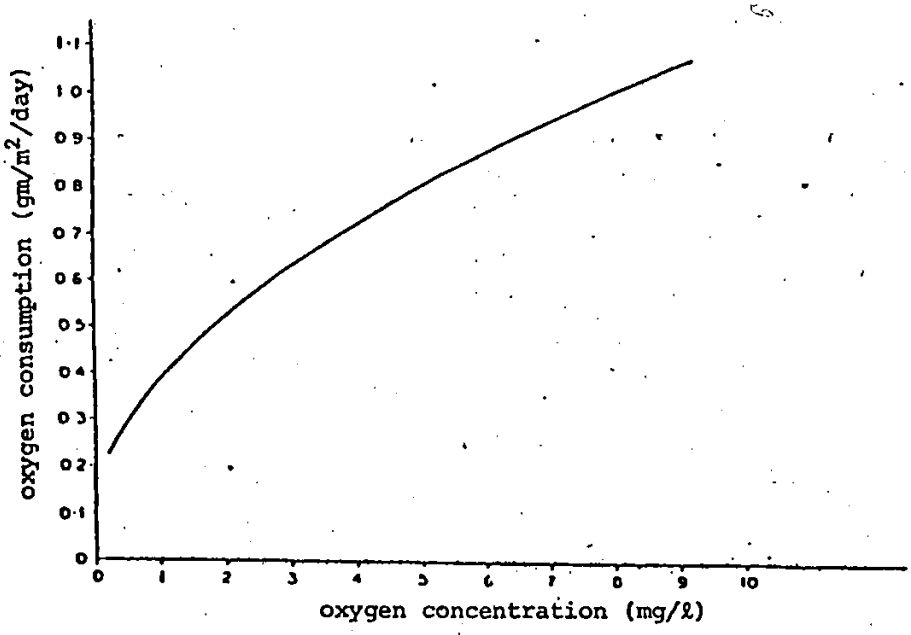


Figure 8. Oxygen consumption versus oxygen concentration (from Edberg and Hofsten, 1973)

of this model (see Fig. 8) illustrates, once again, that at lower O_2 concentrations SOD is definitely dependent upon O_2 concentration.

In a later paper, Edberg (1976) compared a straight line fit of SOD versus dissolved oxygen to the form used by Edwards and Rolley (1965), Owens *et al.* (1969) and Crank (1956) in equation (6). His straight line is a first order relationship with computer selected constants and appears as follows:

$$k(c) = k(11) \cdot (0.22 + 0.0707 \cdot c) \qquad (8)$$

where k(c) is the SOD in gm/m^2-day at an oxygen concentration c and k(11) is the SOD at 11 mg/ℓ of dissolved oxygen (see Fig. 9). Because of the large scatter of data in both, neither model appears to be clearly superior. McDonnell and Hall (1969) also used the model form of equation (6) and achieved a very good fit (see Fig. 10).

Early researchers; Mortimer (1941), Fair *et al.* (1941) and Baity (1938) recognized the importance of oxygen tension to the oxygen dependent reactions in sediments. Each of these papers reports a sudden decrease in oxygen uptake rate as oxygen decreases to below 2 mg/ℓ.

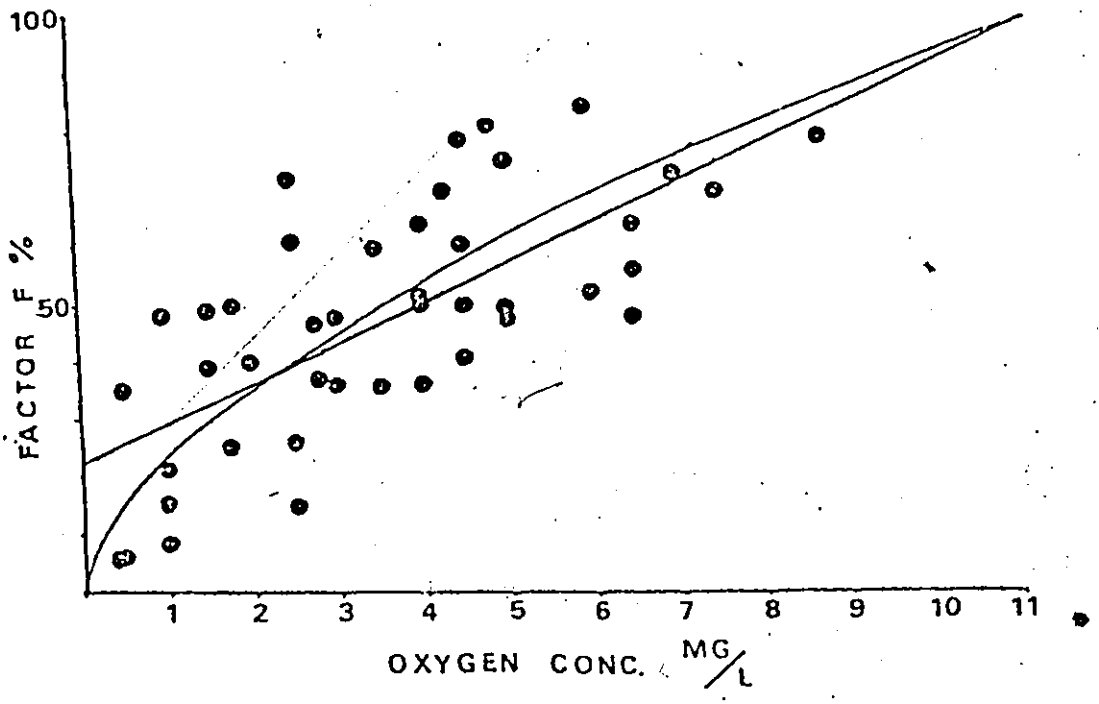


Figure 9. Oxygen concentration, C versus F where F = 0.0707 · C + 0.22 and is equal to a percentage of the TSOD at 11 mg/ℓ. Two lines are shown to describe the data.

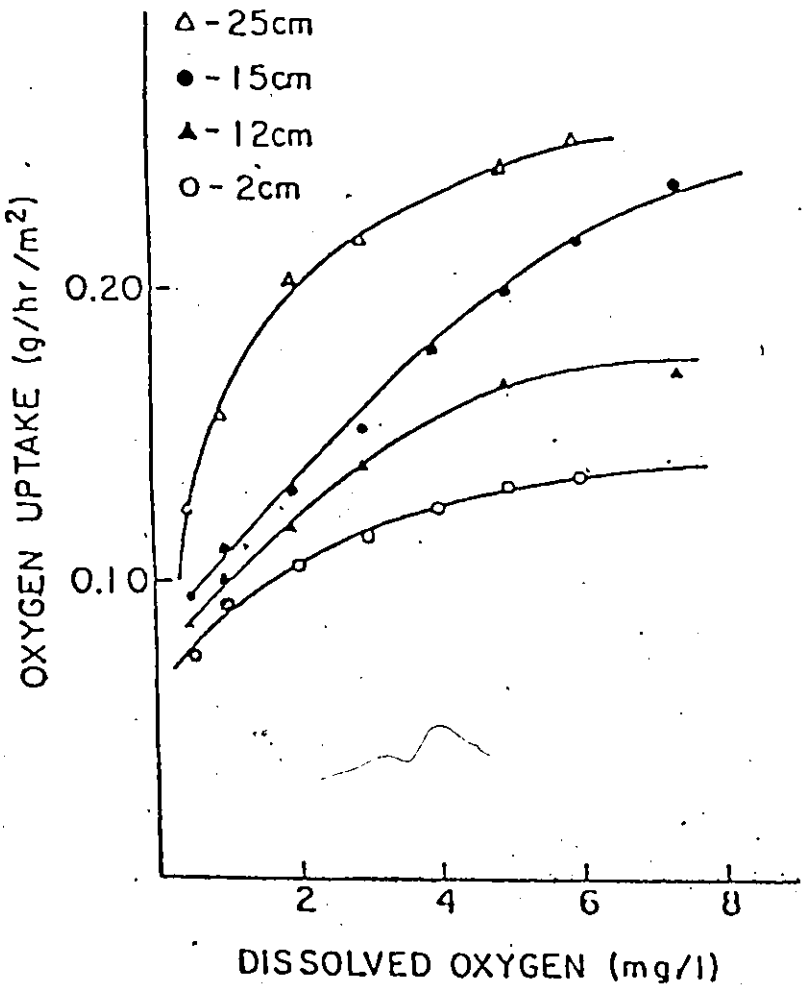


Figure 10. Oxygen consumption versus oxygen concentration from various depths in sediment (from McDonnel and Hall, 1969).

Wurhmann (1960) showed that 1 mg/ℓ of oxygen supports an oxygen uptake of 10^{-4} mg O_2/sec/cm^3 in particle flocs up to 350 μ in diameter. Smaller plate shaped flocs, 100 μ in diameter and 40 μ thick, can maintain this uptake rate in an oxygen concentration of only 0.2 mg/ℓ. Particle size and shape distribution are, therefore, important. These conclusions are based on diffusion limited systems. Baity (1938) and Fair *et al.* (1941) concluded that above this critical oxygen concentration, the diffusion rate of oxidizable material to the sediment surface is the limiting factor in SOD.

Crook and Bella (1970) used computer-aided sensitivity analysis to assess the important mechanisms of oxygen uptake. The analysis showed that the passage of oxygen into the deposits was at least one order of magnitude more important than the release of reduced species to the overlying water and subsequent reaction with oxygen.

While oxygen limitations in sediment oxidation seem to be generally accepted, there is no concensus regarding the degree of limitation at either high or low oxygen concentrations. In addition, the mechanism is not clear. Some evidence suggests that oxygen

diffusion into the sediment is the limiting step as oxygen concentrations decrease below 2 mg/ℓ. As yet, only empirical models have been proposed to characterize uptake rates as a function of oxygen concentration. Very little work has been done to delineate the effects of oxygen concentration on the chemical and biological portions of SOD.

Macroinvertebrates respond to low oxygen concentrations in a similar manner to bacterial communities. Knowles *et al.* (1962) used polarographic techniques to study the oxygen uptake rates of river sediments which contained large populations of macroinvertebrates. The measurements yielded the curves in Figure 11. A definite limitation to oxygen uptake by oxygen concentration occurs at oxygen concentrations below 3 mg/ℓ. The water overlying the cores was stirred continuously. Berg *et al.* (1962) measured oxygen uptake rates (by communities) of known species and numbers of macroinvertebrates in bottles. Representative curves of uptake versus oxygen content are reproduced from this work in Figures 12 to 15. This is an excellent illustration of oxygen limitations to respiration rates of worms. All curves, although different in magnitude, are similar in shape. This is also a

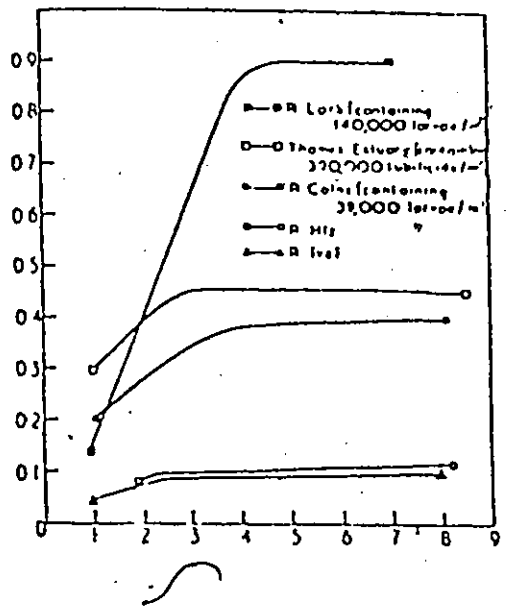


Figure 11. Oxygen consumption of mud cores containing macroinvertebrates versus oxygen concentration (from Knowles *et al.*, 1962).

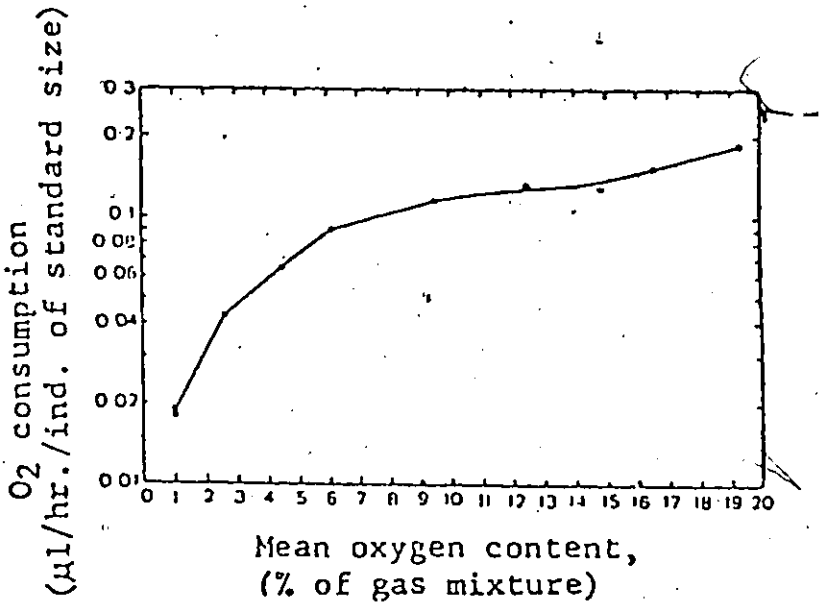


Figure 12. Oxygen consumption rates of *Pisidium casertanum* in relation to the oxygen content (from Berg *et al.*, 1962).

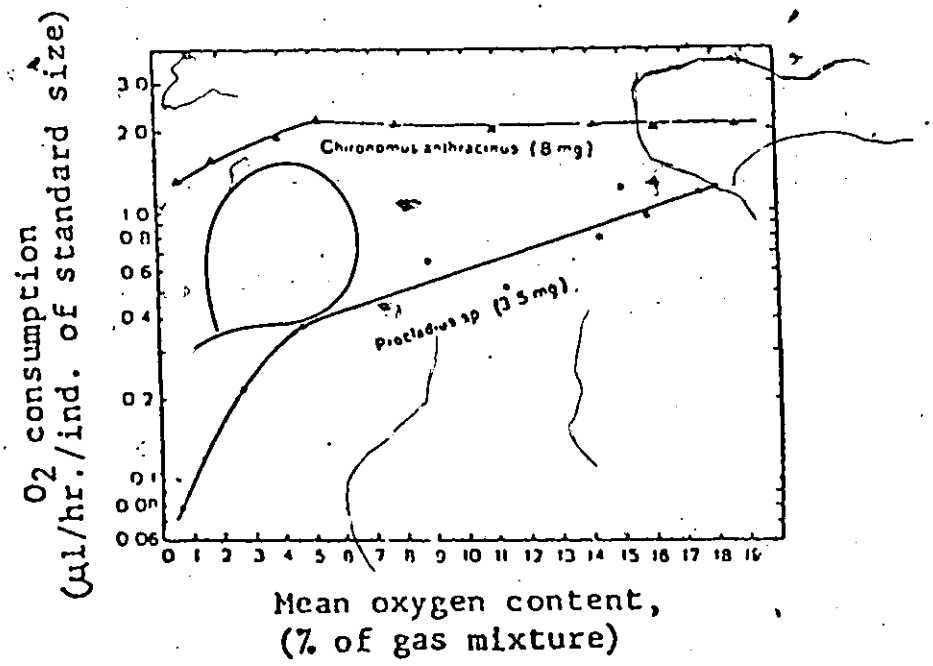


Figure 13. Oxygen consumption rates of *Chironomus anthracinus* and *Procladius sp.* in relation to the oxygen content (from Berg *et al.*, 1962).

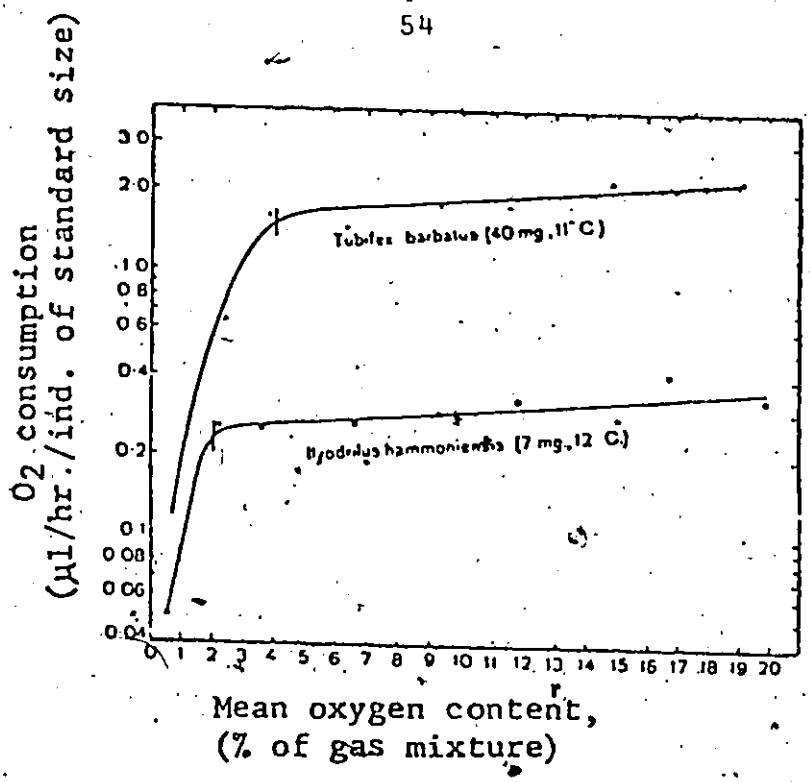


Figure 14. Oxygen consumption of *Tubifex barbatus* and *Ilyodrilus hammoniensis* in relation to oxygen content (from Berg *et al.*, 1962).

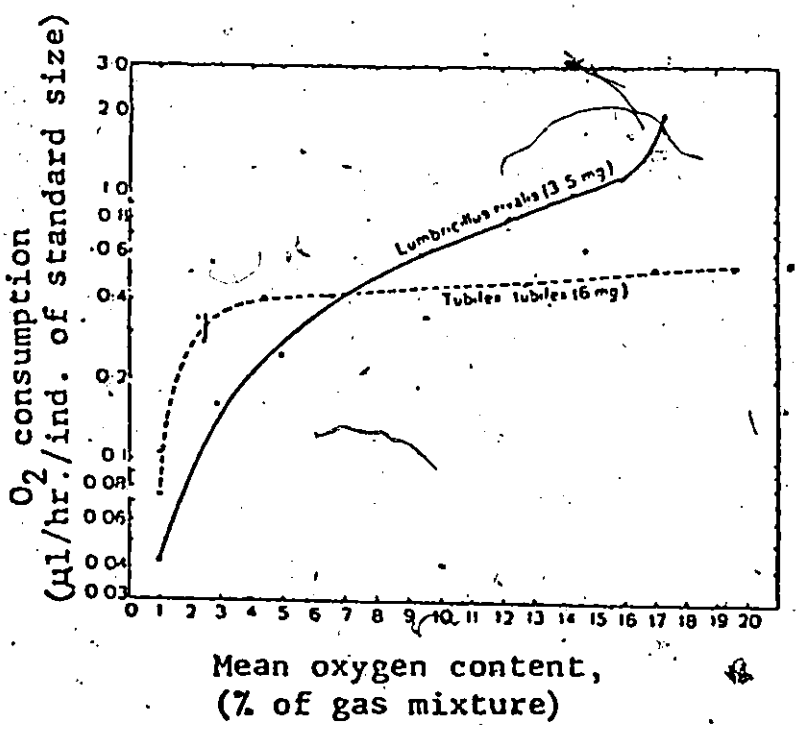


Figure 15. Oxygen consumption of *Lumbricillus rivalis* and *Tubifex tubifex* in relation to oxygen content (from Berg *et al.*, 1962).

useful summary of individual species unit respiration rates.

The information summarized above suggests that bacterial and macroinvertebrate respiration respond similarly to low oxygen concentration. Both communities experience reduced respiration at very low oxygen tension.

2.8. Macroinvertebrates and SOD

Organic sediments support heterotrophic bacterial populations which are generally the primary mechanism in the oxidation process. However, in polluted waters, small animals flourish in the profundal zone and contribute significantly to decomposition. In these situations, their predators are virtually non-existent due to low oxygen concentrations. Several authors have recognized the importance of burrowing animals in sediments and have made quantitative assessments of their direct contribution to SOD and their influence on the total sediment system.

Crook and Bella (1970) measured SOD in an estuary which was inhabited by high densities of animals. They measured total uptake rates which were 4 to 6 times higher than those rates measured in a nearby location which showed no visible signs of worms. They

concluded that the major effect of the animals was to increase the mud-water interfacial area and the rate of transfer of soluble material across the interface by their burrowing action. Similarly, Edwards (1958) observed that *Chironamid riparius* in sewage sludges substantially increased the depth of the aerobic zone. In so doing, they had increased the available surface for colonization by aerobic bacteria and subsequently the density of bacteria in the lower depths of the sediment profile.

Smith *et al.* (1972) partitioned the total community respiration of the Bermuda seabed into its component parts by injecting selective poisons into an *in situ* respirometer. It was found that the macrofauna contributed about 1.9 to 2.6% to the total SOD. Animal densities were low at 66 to 84 individuals/m^2. In the sediment near Wood's Hole sewage outfall, Smith *et al.* (1973) found that the macrofaunal community contributed about 20% of the total respiration. Nearby, in the less contaminated Buzzard's Bay, macrofauna accounted for 50% of the total uptake of oxygen. In this location, the animal biomass was larger and the individual animals were also larger. Granéli (1978) found *Chironamus plumosus* in some south Swedish lakes

which exerted 6 to 13% of the total aerobic respiration. Edwards and Rolley (1965) credited 40% of the respiration in some river muds to the tubificid species, *Ascellus aquaticus* and *Expobdella otoculata*.

Individual respiration rates of several species of macrofauna and the authors who reported them are summarized in Table 4. Locations and temperatures are included when available. Due to the large differences in animal size, these respiration rates are highly variable. Hargrave (1969a) lists the individual rates for 10 groups of organisms with a difference of eight orders of magnitude. Brinkhurst *et al.* (1972) reports respiration rates for 3 species of oligochaetes at 4 temperatures. In these measurements, healthy animals were placed in sterile sand overlain with distilled water. These are then rates of endogenous respiration. Alternately, Hargrave and Smith *et al.* (1973) reported oligochaete respiration rates estimated from *in situ* measurements. Their values are higher as they include respiration resulting from an actively producing community.

Some authors have observed the indirect effects of macroinvertebrates in sediments. Edwards and Rolley (1965) injected lithium chloride (LiCl) into the water above sediments with different densities of larvae

Table 4

Macroinvertebrate Respiration Rates on an Individual Basis Reported in Literature

Author	Location	Species or taxon grouping	Temperature °C	Respiration gm O_2/individual/day · 10^4
Smith *et al.* (1972)	Bermuda sea bed	*Glycera* sp.	25-27	2.75
		Divaricella quadriculata	25-27	1.53
		Mellita quinquiesperforata	25-27	30.8
Smith *et al.* (1973)	Wood's Hole (o); Buzzard's Bay (B)	*Coelenterata*	Summer	0.206 (o)
		Rhynchocoela	Summer	0.516 (o); 0.508 (B)
		Nematoda	Summer	0.179 (o)
		Ectoprocta	Summer	0.043 (o)
		Oligochaeta	Summer	0.156 (o)
		Polychaeta	Summer	0.831 (o); 1.813 (B)
		Gastropoda	Summer	0.319 (B)
		Pelecypoda	Summer	1.645 (o); 1.152 (B)
		Cephalocarida	Summer	0.116 (B)
		Amphipoda	Summer	0.106 (o); 0.0991 (B)
		Decapoda	Summer	4.219 (B)
		Ostracoda	Summer	0.0585 (o); 0.0309 (B)
Brinkhurst *et al.* (1972)	From Toronto Harbour placed in sterile, non-organic substrate	*Tubifex tubifex*	5	0.0329
		Tubifex tubifex	10	0.0288
		Tubifex tubifex	15	0.0548
		Tubifex tubifex	20	0.0699

		Limnodrilus hoffmeisteri	5	0.0247
		Limnodrilus hoffmeisteri	10	0.0288
		Limnodrilus hoffmeisteri	15	0.0475
		Limnodrilus hoffmeisteri	20	0.0658
		Peloscolex multisetosus	5	0.0134
		Peloscolex multisetosus	10	0.0120
		Peloscolex multisetosus	15	0.0144
		Peloscolex multisetosus	20	0.0192
Hargrave (1969a)	Marion Lake, B.C.	Bacteria	Summer	$1.34 \cdot 10^{-4}$
		Protozoa	Summer	$3.43 \cdot 10^{-5}$
		Amphipoda	Summer	0.240
		Chironomidae	Summer	0.127
		Copepoda	Summer	0.034
		Mollusca	Summer	0.600
		Oligochaeta	Summer	0.257
		Hirudinea	Summer	1.029
		Trichoptera	Summer	3.430
		Odonata	Summer	6.000

(0, 25,000 and 50,000 individuals/m^2). Six hours after the injection, the sediments were frozen, sliced into depth layers and the layers were analyzed for lithium (Li) concentration. A positive relationship was demonstrated between animal density and rate of penetration of Li into the sediment. The researchers felt that this was due to an increased exchange rate of soluble material between sediment and water, caused by the larvae.

Teal and Kanwisher (1961) found that worm tunnels constituted 22% of the total mud-air interfacial area in one sediment sample. Nichols (1974) recorded worm tunnel depths to 7 cm in sediment with the average being 4 to 5 cm. Nichols calculated that it is theoretically possible for a typical community of macroinvertebrates to completely overturn the oxidized zone in 4 years.

Rhoads (1973) observed an increase in the productivity of oyster beds and a higher turbidity in the water due to the polychaete, *Pectinaria californiensis*. It was felt that the polychaetes significantly increased the nutrient concentration of the overlying water by recycling buried sediment material. Nichols (1974) calculated that a typical macroinvertebrate community could recycle 50% of the phosphorus in buried surface

sediments to the overlying water. Brinkhurst *et al.* (1972) observed that the feces of macroinvertebrates is higher in organic content and calorific value than the sediment. Since worms are selective in their feeding and expel feces onto the top of the sediment surface they enrich surface deposits, stimulating sediment oxidation.

Sediment macroinvertebrates are generally tolerant of low oxygen concentrations. This allows them to survive, and even thrive in an environment which is unsuitable for their predators. At low oxygen concentrations, their behaviour is noticeably altered. Berg *et al.* (1962) observed that at low oxygen concentrations (10 to 25% saturation) worms and larvae become physically active, moving their posterior ends rapidly above the sediment. When oxygen concentration is high and food is not available, they curl up and restrict their movement. Several species have been shown to display oxygen consumption rates which are pseudo first-order with respect to oxygen concentration when concentrations are low (< 25% saturation) (see Figs. 12-15). Ewer (1942) and Walshe (1948) observed that the respiration of *Chironomus* larvae is dependent on oxygen concentration to a larger extent at low concentrations. Edwards and Rolley (1965) concurred in

their study, concluding that when oxygen concentration is above 1.5 mg/ℓ macroinvertebrates display zero-order uptake.

Respiration rates for macroinvertebrates, measured by Berg *et al.* (1962), responded positively to temperature change with Q_{10}'s of about 2. The Q_{10} of the measured values decreased at higher temperatures. Endogenous respiration rates of oligochaetes was shown to increase with temperature, yielding Q_{10}'s of 1.5 to 2.5 (Brinkhurst *et al.*, 1972).

Sanders (1958) characterized the habitat of some groups of macroinvertebrates in general terms. The filter feeders (amphipods) dominate sandy sediments while deposit feeders (polychaetes) are most predominant in silty sediments. Smith *et al.* (1973) observed that smaller animals, with low species diversity, dominated rich organic sediments, such as those at the Wood's Hole outfall, while larger animals with larger diversities dominated sandier regions.

In summary, the work of these researchers has clearly shown that macroinvertebrates contribute significantly to sediment oxidation. Firstly, the direct respiration by these animals can be a large part of the total oxygen demand of sediments. This is particularly important in the rich organic sediments of

polluted waters. Secondly, their activity tends to accelerate bacterial community activity by increasing the depth of the aerobic zone and increasing soluble material transfer across the sediment-water interface. Thirdly, macroinvertebrates cause the enrichment of surface deposits by selective feeding and deposition of rich organic material and lead to more complete sediment oxidation by recycling buried material.

Macroinvertebrate response to temperature change follows trends, similar to bacterial communities, in terms of activity. They usually only reproduce once annually. In all temperature related studies the populations were constant.

Many species of macroinvertebrates are very tolerant of low oxygen concentration, in fact, respiration appears to be independent of oxygen concentrations above 1.5 mg/ℓ.

More quantitative research is required, however, to characterize the indirect effects of macroinvertebrates on total community respiration. This work should explore the interspecific relationships between the macroinvertebrate and bacterial communities.

2.9. Sediment Oxidation

In the study of sediment oxygen uptake, several authors attempted to obtain a more fundamental understanding of the mechanisms of sediment material oxidation rather than to merely measure O_2 flux across the sediment-water interface in relation to various water parameters. Pamatmat *et al.* (1973) writes:

> "The biggest gaps in our knowledge concern the rates of the various processes and the quantitative effect of conditions in nature that effect these rates. It is now widely recognized that these gaps are critical in considering many aspects of man's use and management of the earth's natural resources."

To understand these rates and mechanisms one must fraction SOD into at least two parts: the biological respiratory uptake, including bacteria and macroinvertebrates, and the chemical uptake which accounts for the oxygen uptake due to inorganic reactions. The latter results, at least in part, from the anaerobic decomposition of organic material, found deep within the sediments where reducing conditions exist. Pamatmat (1968) stated that all reduced substances are the result of microorganism activity and, therefore, no purely inorganic oxidation occurs in sediments.

Hargrave (1972a) studied lakes high in sulphides and found that when eH was low, chemical oxidation was the major oxygen uptake process. Edberg (1976) stated that even when anaerobic conditions prevail in sediments the evolved reduced species cause a significant oxygen demand in the overlying water. Graetz *et al.* (1973) observed that even as sediments stabilize and become anoxic, ammonia is released to the overlying water and builds up in the interstitial water. On aeration, ammonia is oxidized to nitrite and nitrate, constituting an oxygen demand. The premise is that anaerobic decomposition occurs at all times so there will eventually be oxygen uptake when molecular oxygen becomes available.

Vanderborght and Billen (1975) found nitrate concentrations to be higher in the interstitial water of sandy sediments than in muddy sediment. It was felt that the availability of oxygen and diffusion of oxygen are important in oxidation. Pamatmat (1971) found high rates of denitrification and nitrate uptake by anaerobes utilizing nitrate as an electron acceptor.

Otsuki and Hanya (1972) observed the anaerobic decomposition of algae. It was found that rates were first-order with respect to available organic carbon and nitrogen. Also observed was a high concentration of dissolved organic carbon in equilibrium in their

reactors. Dissolved organic carbon tied up in organic acids would then ferment and release methane.

The consensus among researchers is that CSOD is a result of anaerobic decomposition of organic material. This decomposition takes place under reducing conditions, thus yielding many soluble reduced ions which migrate upward to an oxidized zone. The reduced ions react with oxygen. It is not clear whether the rate of oxygen uptake is dependent on diffusion of oxygen into the sediment or diffusion of reduced ions upward to the oxidized zone. It is felt that high concentrations of reduced ions accumulate in the deeper zones of the sediment. This would indicate that the production of reduced ions is not an oxygen uptake limiting step. This then argues that either diffusion of oxygen into the sediments or the reaction of oxygen with these reduced species is the rate limiting step.

Hargrave (1972b) studied the direct oxidation of organic sediments by the aerobic heterotrophs. Oxygen uptake rates and the weight of organic material in various samples was compared. This then gave a measure of biodegradability and a basis of comparison between sediment samples. Rates were lower in more humic sediments. He notes that,

> "the amount of total organic matter in sediment does not indicate its availability to either microorganisms or invertebrates."

Lower rates of biodegradation occur in sediment with more bioresistant material such as humics and lignins. The rate of supply of easily oxidizable material is also important and greatly effects the oxygen uptake rates. The observations of oxygen uptake by invertebrate feces confirmed these ideas. Initially, the rates of uptake were high whereas on Phragmite leaves rates decreased soon after the start and remained low. Organic content was similar in both cases. Hargrave also shows a correlation between biological activity and particle size and between biological activity and organic content. He uses the regression:

$$y = -2.15 + 0.90x \qquad (9)$$

where y is the logarithm (base 10) of oxygen uptake and x is the logarithm (base 10) of the % organic content.

Otsuki and Hanya (1972a) also studied aerobic decomposition of algae. In their study it was noted that cell contents were oxidized quickly while the cell wall material was degraded much more slowly. In general, rates were high for 20 days at which time labile material becomes exhausted and rates of oxygen uptake slow down.

Foree and McCarty (1970) and Jewell and McCarty (1971) studied anaerobic and aerobic decomposition of algae, respectively. In both studies, the algae decomposed quickly at first as the elemental storage products reacted, then a longer, more stable period followed during which 30 to 70% of the biomass degraded. After this period, decomposition was very slow as the refractory portion was gradually decomposed. One surprising observation of these studies was that both anaerobic and aerobic decomposition occurred at a similar rate.

In the studies of Waksmann and Hotchkiss (1937), Allen *et al.* (1953) and Volkmann and Oppenheimer (1962), varying proportions of organic matter was found to be bioresistant. Waksmann and Hotchkiss suggested that the rate of oxidation of organic matter should be used as a measure of the availability of the organic fraction. Pamatmat and Banse (1969) state that the rate of supply of organic matter is the major source of SOD variation. This phenomenon was observed by Smith and Teal (1973) and Smith *et al.* (1973) in the ocean at 1850 metres and around the sewage outfall at Wood's Hole. Smith felt that the very low rates of oxygen uptake at 1850 metres was due to a substrate limitation; while in the sewage outfall, both supply of organics and organic content of sediments led to high oxygen uptake.

Granéli (1978) examined SOD variability on a seasonal basis and tested the hypothesis that fresh organic supplies enhance SOD. Part of the water column in a lake was isolated by placing 2 three-metre diameter plastic columns reaching from the sediment to the water surface. Placed in one were fish which would feed on zooplankton and continuously supply sediment as feces to the bottom. The other column was left without fish. In the column with fish, productivity was high in the water with frequent algal blooms but the newly deposited sediment had the same SOD rates as the sediment in the column without fish. Granéli felt that temperature variations could explain all the seasonal variability in SOD. This supports the conclusion of Hargrave (1972a) that SOD rates reflect long term prevailing conditions rather than the more recent input characteristics.

Pamatmat *et al.* (1973) measured elevated SOD rates below fish pens in the ocean. Two months after the pens were removed SOD rates dropped from 4.3 to 0.8 gm O_2/m^2-day. It was deduced that the pens reduced circulation thus allowing sediment to accumulate. Also noted, was the fact that the steady supply of fish feces probably enhanced the SOD rate. Pamatmat stated that one must differentiate between labile and humic sediments

as he had himself observed lower rates of uptake in more humic material.

Pamatmat and Bhagwat (1973) used dehydrogenase activity as a means of comparing activity in sediments. A decrease of dehydrogenase activity with depth in sediment was observed.

Ulen (1969) attempted to relate adenosinetriphosphate (ATP) to biomass or activity in sediments. When the biomass is small, the ATP content relates positively to biomass but that when biomass is high ATP relates best to activity.

Pamatmat (1971) concluded that variability in SOD can be explained by:

1. Unevenness of surface and non-homogeneity of sediments;
2. Organic supply rate;
3. Amount of reduced matter; and
4. Rates of diffusion and compactness of sediment.

Most authors agree with the above summary of Pamatmat, yet some disagreement exists. More work is necessary. We do know that sediment characteristics and organic structure are important to the SOD. More quantitative work must be done to classify lake sediments with respect to organic nature and biodegradability.

3. *IN SITU* MEASUREMENTS

3.1. Introduction

Sediment Oxygen Demand (SOD) boxes, a type of respirometer, have been used by many researchers in the past. The versatility of the instruments allows them to be used in lakes, deep rivers, and in the sea. The substrate upon which they operate may be soft or hard. In addition, they may be left in place for long periods of time. As explained in Chapter 2, these devices have been used to estimate SOD as well as the component parts of the total rate due to bacterial, chemical and animal oxygen consumption. Generally, results have been reliable and display reasonably good repeatability.

In this study, an SOD box was constructed, tested in the laboratory and operated under a variety of conditions in several water bodies. The purpose of this portion of the study was to make some actual measurements. These estimates could then be used as an independent data set to compare with the measurements made on the disturbed sediment samples in the laboratory.

It was also hoped that the techniques involved could be assessed and improved and some insight could be gained into the temporal and spatial variability of SOD.

The SOD box is a relatively simple device primarily consisting of an inverted, open box which is set gently onto the sediment surface. A proper seal is essential in order that the effects of the oxygen uptake activity of the enclosed sediment are limited to the water isolated within the box. Dissolved oxygen monitoring equipment is attached to the box to keep a record of the rate of oxygen decrease within. The rate at which oxygen leaves the water and diffuses into the sediment matrix, as well as that rate which is due to consumption at the sediment surface, is then reported as areal uptake rate.

The measurement system works best when disturbances around the box's contacting edge are minimized and when the mixing rate of water inside the box is minimal in order to avoid resuspension of sediment particles.

3.2. Design

The SOD box was constructed of common, inexpensive building materials: plywood, water resistant glue, paint and stainless steel screws. A hexagonal surface

shape was used in order to reduce the volume of possible stagnant areas within (see Fig. 16). A 3-inch wide cutting edge of galvanized metal was fastened to the bottom edge of the box to limit the disturbances to the sediment and to gain a good seal. Above the cutting edge and around the circumference of the box was a 2 inch flange which was designed to limit penetration of the box into the substrate. At each of three alternate top corners, a brass one-way valve was fastened. These valves allowed water to pass upward , through the box while it was lowered through the water column. It was felt that the measurements should be made with actual bottom water trapped over the sediment rather than oxygen-rich surface water. This procedure would minimize shocks to the sediment community which might accompany a sudden change in overlying water dissolved oxygen concentration. The valves remained closed when the unit was in place.

The chamber contained a removable top section which held a dissolved oxygen probe and a 6-volt submersible stirrer with batteries.

A 1/8 inch nipple on the chamber top could be connected to small diameter tygon tubing leading to the surface. Metabolic poison solutions could be injected by syringe from the surface into the trapped

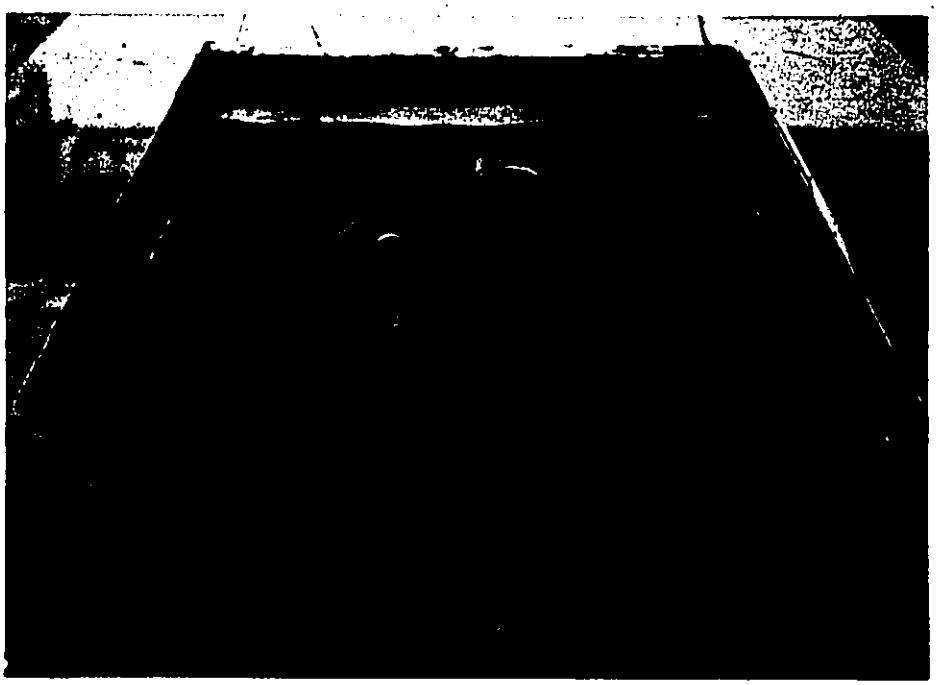


Figure 16. Sediment oxygen demand chamber showing mixer.

water whenever desired without disturbing the instruments.

The unit was lowered by rope and could be tied at the surface to a spar or float (see Fig. 17).

A water and pressure resistant canister was connected by rope and an underwater electrical cable to the SOD box and lowered at the same time. The canister housed the electronic monitoring and recording equipment. This group of components consisted of a YSI (Yellow Springs Instrument Co.) dissolved oxygen meter (model 54A), a Rustrak recorder, an interfacing amplifier coupling the meter and recorder plus a group of 12-volt batteries to power the recorder and amplifier (see Fig. 18). The electronic system was designed to provide continuous *in situ* operation for up to 48 hours. This is the time required in some low temperature situations to register a significant decrease in dissolved oxygen concentration.

In general, the unit was designed to operate in a wide variety of situations and conditions of temperature and pressure. The shape was such that relatively clean sediments would cause a noticeable decrease in trapped dissolved oxygen in a short time.

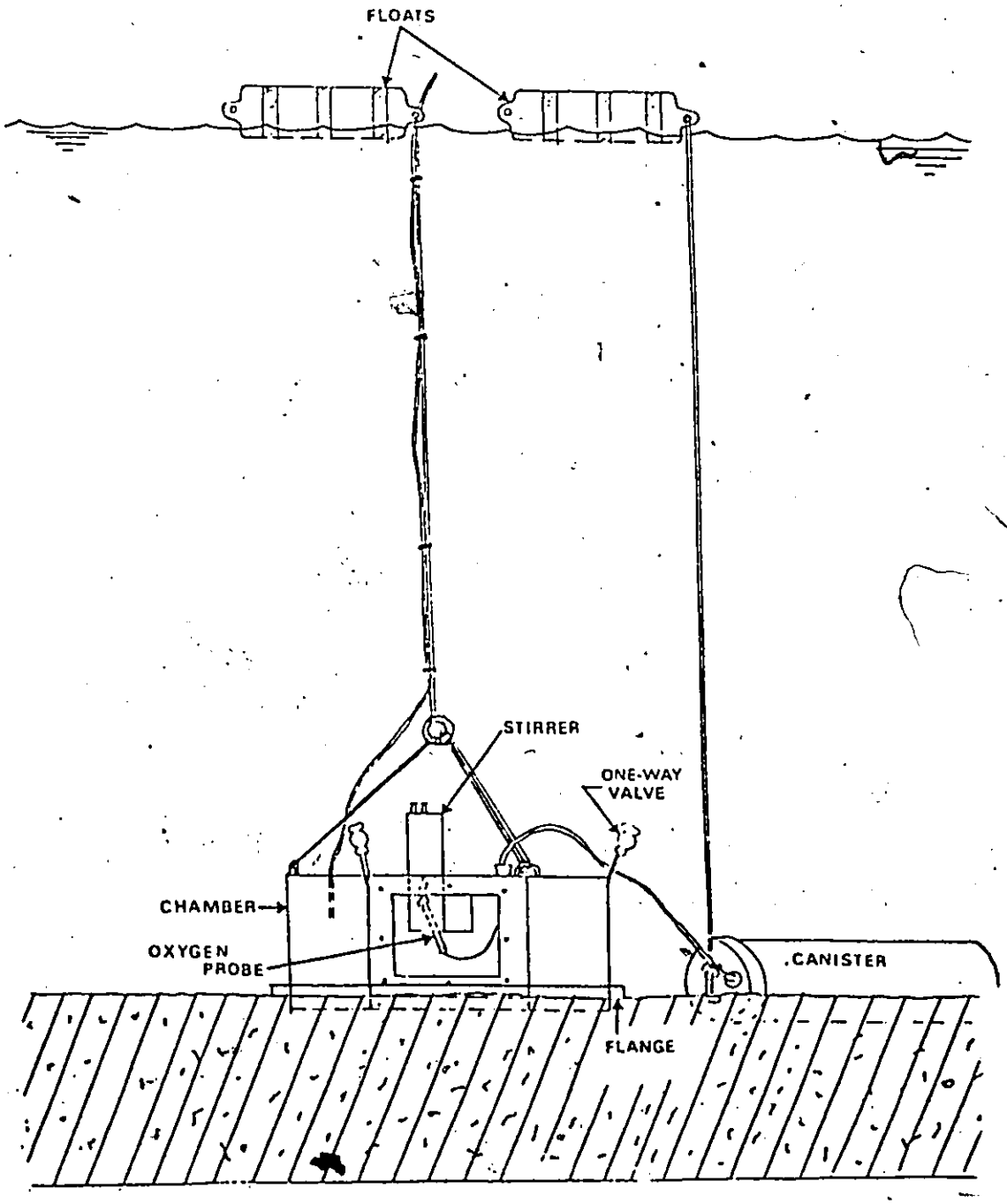


Figure 17. Sediment oxygen demand *in situ* equipment in place.

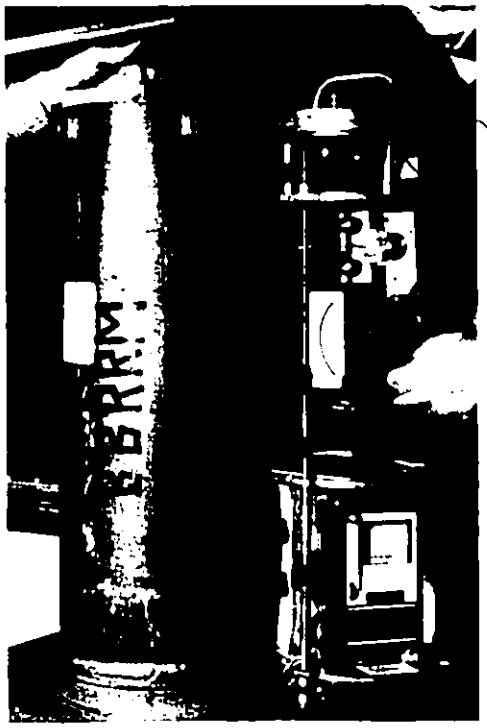


Figure 18. *In situ* equipment electronics canister showing meter, amplifier, recorder and batteries.

3.3. Equipment Testing

Before attempting to operate this device in the field, it was tested in a laboratory tank for water tightness, degree of mixing and the time period over which calibration would remain true.

Mixing is an important operating parameter and should closely simulate natural water movement. If mixing is too slow, then unnatural oxygen gradients will develop at the sediment-water interface and will result in depressed rates of oxygen diffusion into the sediment matrix. The oxygen probe manufacturer also recommends that a minimum water velocity of 10 cm/sec be maintained past the probe membrane for proper operation. Alternately, if mixing is too rapid sediment particles will be re-suspended and SOD rates will elevate as surface area is increased.

To evaluate the internal mixing pattern, rhodamine WT dye was injected into the chamber while it rested submerged in the laboratory tank. In each test, the dye was gently dispersed within the box in 5 to 7 minutes. Although the cutting edge contacted the hard tank floor very little dye leaked from around the bottom.

A similar test was carried out with the chamber suspended upside down and filled with water. Dye

injected at the probe was visually estimated to be carried past the probe membrane at a velocity in excess of 10 cm/sec. The chamber also proved to be watertight under these conditions.

A 48-hour test was conducted to determine the degree to which the probe would diverge from calibration. The unit was operated in a tank of tap water and recorded dissolved oxygen values were periodically compared to measurements made by the Azide Modification of the Winkler method for dissolved oxygen analysis (Water Pollution Control Federation (WPCF), 1975). Good agreement was achieved for 48 hours at which time the 6-volt stirrer batteries began to wear down and adequate mixing was no longer achieved.

3.4. Methods

The following procedure was used in operating the SOD box for the measurement of total sediment oxygen demand (TSOD) and chemical sediment oxygen demand (CSOD):

(i) The oxygen probe and meter are calibrated and visually checked in the laboratory. Fresh batteries are placed in the mixer shroud.

(ii) The chamber with the probe and mixer in place is lowered from a boat and held just under the water surface.

(iii) Trapped air bubbles are expelled through a stoppered hole on one top corner of the box and the stopper is tightly replaced.

(iv) The meter, amplifier and recorder are checked for proper operation while still in the boat and then the canister is sealed.

(v) The canister and chamber are lowered to the lake bottom slowly (to allow for the upward passage of water through the one-way valves), and gently set on the lake bottom.

(vi) The ropes and tubing are fastened to a spar or float and left in place for up to 24 hours (depending on the expected rate of oxygen decrease within the box).

(vii) Metabolic poison is added to the chamber water by syringe through the tubing and the chamber is left for another period of several hours.

3.5. Results and Discussion

From August to October in 1976, seventeen *in situ* SOD measurements were made in Hamilton Harbour with the equipment described earlier in this chapter. Station locations are shown in Figure 19. In addition, three measurements were made in Gisborne Lake (Cape Breton Island) in late August, 1976. Five measurements

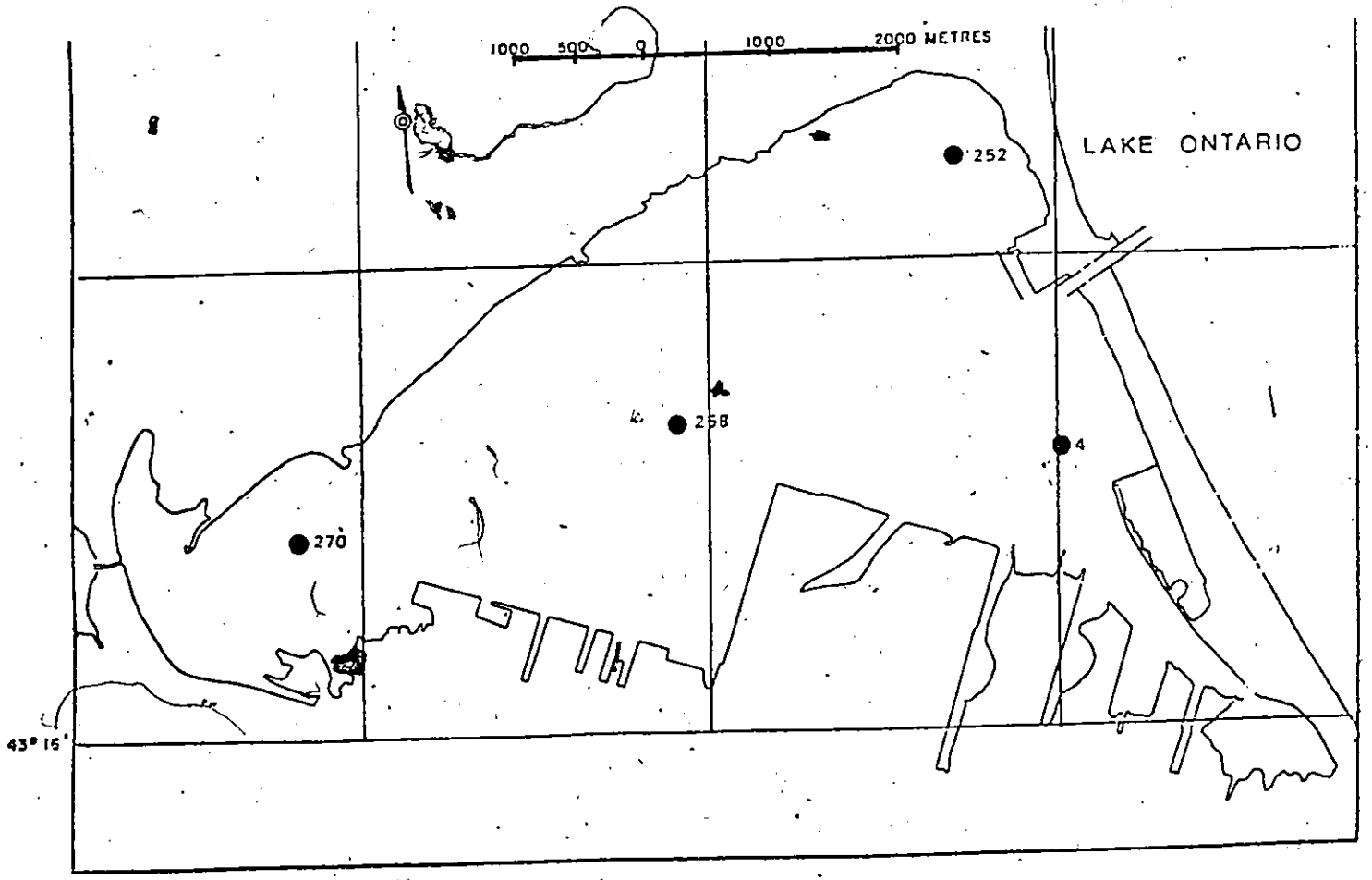


Figure 19. Hamilton Harbour sediment sampling locations.

were made in which KCN was added as a metabolic inhibitor. The results, conditions and KCN concentrations in the water are listed in Table 5.

Initial dissolved oxygen concentrations varied widely (1.1 to 10.7 mg/ℓ) over the period of measurements. In fact, thermal stratification of the Harbour existed during some of the early tests and the deeper stations displayed depressed oxygen levels. Later tests were conducted under well-mixed conditions.

In each of the five tests in which KCN was added, the resultant rate was the lowest observed at that location. In determining and interpreting these results, one must take care. On each occasion that poison was added, a time lag was observed from the time of addition until a smooth line was achieved on the recorder tape. During this time period (usually lasting 4 to 5 hours), the rate of SOD gradually decreased until it reached the lowest steady value, listed in Table 5. It is apparent from this phenomenon that the poison is not an instant inhibitor of direct bacterial oxygen consumption. There are two possible explanations for this delay. Firstly, it is probable that cells retain some oxidase enzyme with which to acquire oxygen for some short time period after the KCN restricts their ability to produce more enzyme. Secondly, there

Table 5

In situ Measurements of TSOD and CSOD

Location	Date (1976)	Duration (hrs)	Dissolved oxygen range (mg/ℓ)	SOD gm/m^2/day	Temperature °C
Station 252	6/ 8	21	8.5-7.0	0.46	13
(H.H.)	12/ 8	27	7.0-6.0	0.24	13
Station 270	10/ 8	4.5	6.0-5.8	0.29	13
(H.H.)	21/ 9	28	4.3-1.1	0.74	13
	22/ 9	26	2.2-1.4	0.20(C), 200 mg/ℓ KCN	13
	16/10	30	7.8-4.0	0.82	13
	16/10	4.3	3.0-1.8	1.81	13
Station 258	7/ 9	5.25	2.7-1.6	1.30	13
(H.H.)	7/ 9	2	2.6-2.3	1.14	13
	16/ 9	30	6.5-5.8	0.15(C), 700 mg/ℓ KCN	13
	13/10	7	6.0-4.2	1.67	13
Station 4	12/ 9	6.5	6.5-4.6	1.9	13
(H.H.)	13/ 9	6	4.3-3.2	1.19	13
	13/ 9	7	8.4-6.6	1.67	13
	14/ 9	16	8.0-6.0	0.81(C), 320 mg/ℓ KCN	13
	15/ 9	6	7.7-7.0	0.76	13
	15/ 9	21	8.5-7.0	0.46(C), 700 mg/ℓ KCN	13
Gisborne Lake	25/ 8	8	6.8-6.1	0.57	17
	26/ 8	13	8.4-7.5	0.45	17
	26/ 8	11	10.7-10.6	0.06(C), 360 mg/ℓ KCN	17

will be a time associated with transferring KCN to the site of the bacterial community. While the surface cells will contact KCN almost immediately, those cells just under the surface will be insulated for a short time. In fact, if one assumes that these sediments have a diffusion coefficient of 3×10^{-5} cm^2/sec (a liberal assumption) then approximately 10 hours would be required for 2% of the CN^- to reach a depth of 2 cm into the sediment, a depth still within the aerobic zone. It is this author's contention that at least 5 hours should be allowed for chamber water and sediment bacteria to adjust to the addition of poisons.

In interpreting these results, one should remember that since KCN is an inhibitor of bacterial oxygen transfer, the resultant rate is equal to TSOD minus direct oxygen consumption by aerobic organisms near the surface of the sediment. The inhibitor does not affect the process of oxygen diffusion into the sediments to the site of oxidizing agents such as Fe^{2+}.

TSOD measurements were conducted on 15 occasions in Hamilton Harbour and Gisborne Lake (see Table 5). It was observed on all recordings that an initial unstable period exists during which time rates of TSOD are unreliable. This condition is characterized by curved line recordings of dissolved oxygen as illustrated

by an example in Figure 20. During this period, TSOD rates are gradually decreasing until a condition of stability is reached. Undoubtedly, this phenomenon is at least in part due to the initial disturbance to the system caused by the placing of the box. As the box is placed, sediment is resuspended by displaced water and the action of the cutting edge. The TSOD rate returns to a more natural rate as the particles settle. It was, therefore, the policy in this study to disregard the first 3 hours of a recording and to visually confirm that a straight line recording had been achieved at higher oxygen concentrations.

Results for TSOD at the various sites show good agreement with the exception of those tests which had a duration of less than 6 hours and are possibly exhibiting unstable rates. It is also interesting to note that stations 252 and 270 have consistently lower rates of TSOD than do stations 258 and 4, the deeper stations. This confirms that sediment composition is not spatially consistent in Hamilton Harbour.

A conclusion from this work is that SOD boxes are a useful tool in sediment oxidation studies. Also, these devices allow for the fractioning of the TSOD into the component parts caused by aerobic and anaerobic processes (BSOD and CSOD, respectively).

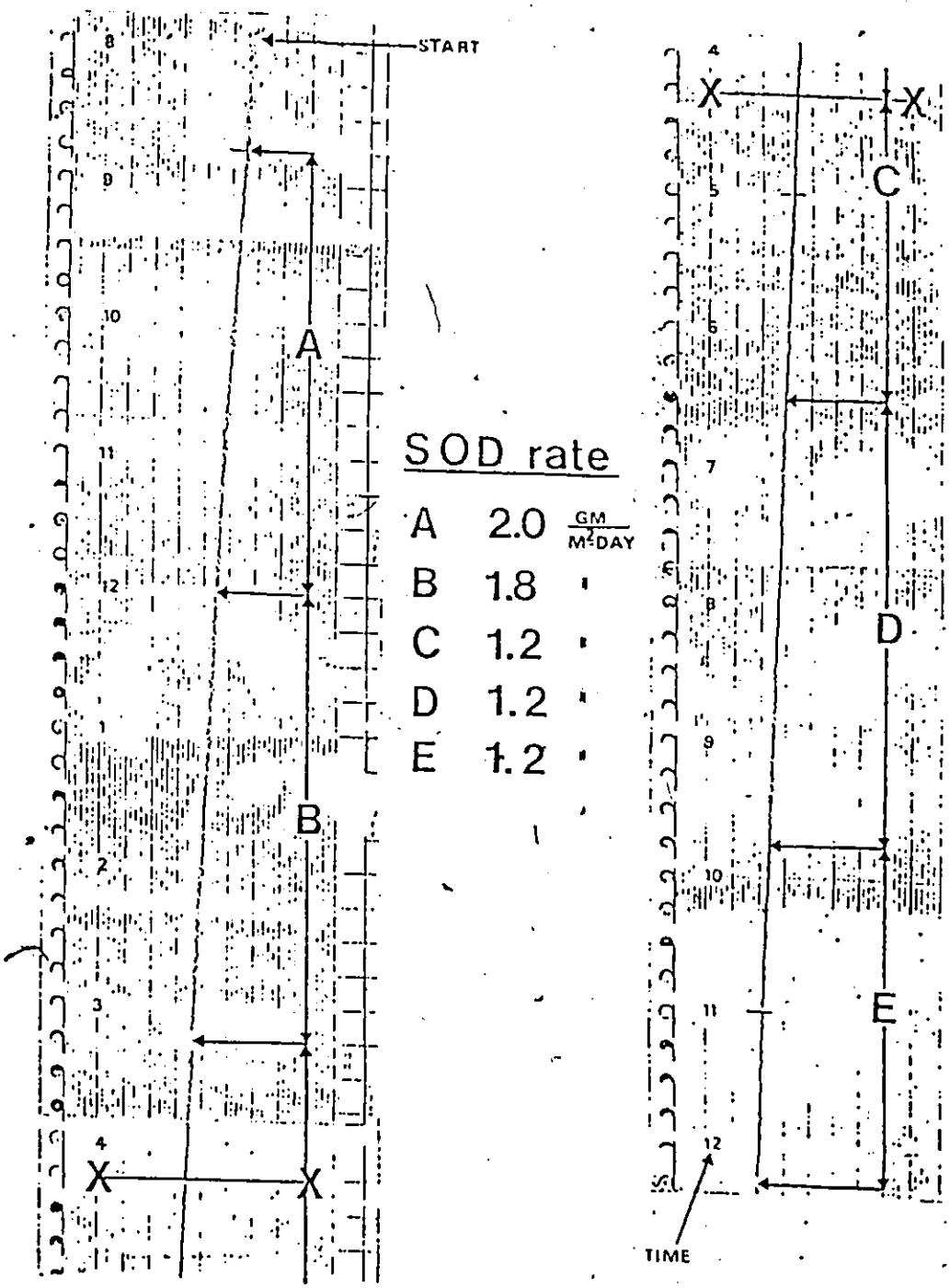


Figure 20. Recording tape from SOD *in situ* measurement. Recorded at station # 4, Hamilton Harbour on September 13, 1976. Full tape scale equals 10 mg/ℓ of dissolved oxygen. Rates are shown for time periods A-E.

The repeatability was not as good as was hoped in this work and further studies should be done to determine the cause. Possibly non-homogeneity in sediment composition in Hamilton Harbour was a factor contributing to the variations in rate observed.

Initial disturbances of the sediment by the box causes unstable rates which last up to 4 hours. This necessitates long measurement times (up to 24 hours) in order that the initial unstable periods can be ignored. Likewise, time must be allowed after the addition of poisons for the system to reflect the inhibited condition.

4. SEDIMENT ORGANIC PROPERTIES

4.1. Introduction

Sediment organic content was determined in order to examine possible relationships between sediment oxidation rates and sediment properties. The objective in this portion of the study, was to attempt to isolate a chemical parameter which would be a good indicator of sediment oxidative potential. This procedure involved investigating some common organic parameters of the sediments taken for measurement and of other lake sediments. The sampling program was designed to gain some insight into spatial and temporal variability of sediment chemistry. The latter point is important in characterizing lake sediments, sampling programs and extrapolating *in situ* measurement results to larger areas.

Three analytical methods and parameters were investigated: loss on ignition (LOI), organic carbon (OC) and carbohydrate (CARB). A discussion of the methods and results follows.

4.2. Methods

Sediment samples were collected with an Eckman dredge at the site of all *in situ* SOD measurements (see Fig. 19). Also, samples were collected from lakes in the Ontario Ministry of the Environment Lakeshore Capacity Study area. These lakes included Dickie, Harp, Jerry, Chub, Blue Chalk and Red Chalk Lakes. Gisborne Lake on Cape Breton Island is also included. Each sample was actually composed of 3 to 4 samples taken over the side of an anchored boat. Sub-samples for analysis were kept frozen until analysed (within 60 days).

Sample preparation was identical for all three parameters. A small sub-sample of 100 to 200 grams (wet weight) was taken from each sample. These were thawed, dried for 24 hours at 100°C and pulverized using a mortar and pestle. The pulverized samples were then passed through a #50 mesh (0.297 mm) and stored in a dessicator.

4.2.1. Loss on Ignition (LOI)

This parameter, common in wastewater and sediment chemistry, was chosen as a measure of the volatile fraction of the sample. The method is simple and accurate. The procedure used is outlined in Standard Methods

(WPCF, 1975). Material lost in the digestion by heat is termed volatile and includes organic matter and some inorganic salts. Each sample was analysed in triplicate and the results from this method are reported as percent by dry weight which is volatile.

4.2.2. Organic Carbon (OC)

Organic carbon was determined on each sample by the Walkley Black Method (Black *et al.*, 1967). In this procedure, the oxidizable fraction of the sample is digested by the strong oxidizing agent potassium chromate ($K_2Cr_2O_7$). Sulphuric acid is also added in order to supply the heat of reaction and accelerate the digestion. After digestion, the residual $Cr_2O_7^=$ is determined by titration and from this the amount of sample oxidized is calculated. Some errors are inherent in this method. The forms of organic carbon which are relatively more inert will not be oxidized in the course of this procedure. In fact, 15 to 40% may remain undigested. To account for this a correction factor must be applied to all results. Secondly, inorganic compounds such as the reduced forms of iron, chlorides and higher oxides of manganese will interfere with the results. These errors can be minimized, and in this study were, by allowing for a sufficiently

long drying period. The more readily oxidizable inorganic compounds will be oxidized in a well-vented drying oven. Chlorides do not exist in large quantities in the fresh water systems sampled.

This method is an easy, reliable determination of soil and sediment organic carbon. Samples were analysed in duplicate and results reported as percent of dry weight which is organic carbon.

4.2.3. Carbohydrates (CARB)

The modified Phenol-Sulphuric Acid method of Liu *et al.* (1973) was used to determine carbohydrate content. Carbohydrate analysis was chosen because it was felt that this would be a measure of the readily oxidizable organic material. The method involves digestion of organic material and, with the aid of phenol, a colour development. The sample is centrifuged and the supernatant colour is compared to standards of agar. At lower carbohydrate concentrations, there is a positive linear relationship between colour and concentration. The method is easy and reliable. Duplicate analyses were performed on all sediments and results are reported as percent of dry weight which is carbohydrate.

4.3. Results

The data obtained from the analytical procedures previously described are contained in Table 6. A large number of lakes were sampled in the hope that a large range of properties would be observed. In fact, this was to be the case.

Temporal variability of sediment organic properties can be assessed by examining the analysis results from Hamilton Harbour stations 270, 258 and 4 plus Blue Chalk, Red Chalk and Chub Lakes since the time period between samples spans at least four weeks. Station 270 displays considerable variability during the 3-month sampling period. This variability is evident in the variance about the mean for all 3 parameters measured. This could be due to actual temporal or spatial variability in the vicinity of the sampling station. The other lakes mentioned in this comparison display very low temporal variability; although in the case of station 4 and Chub Lake, samples were taken only 4 weeks apart.

Spatial variability in any one lake can be assessed by examining the four stations in Hamilton Harbour. All other lakes were sampled at approximately the same location. In Hamilton Harbour, the sample

Table 6

Sediment Sample Organic Content (% by Dry Weight)

Sample location	Date sampled	Organic Parameters Measured*								
		Loss on Ignition (LOI)			Organic Carbon (OC)			Carbohydrates (CARB)		
			$\bar{X}$	$\bar{\sigma}^2$		$\bar{X}$	$\bar{\sigma}^2$		$\bar{X}$	$\bar{\sigma}^2$
252	17/ 7/76	4.9	5.6	1.0	4.5	5.3	1.3	2.3	2.3	0.002
252	19/ 7/76	6.3			6.1			2.4		
270	19/ 7/76	5.4			4.8			1.8		
270	3/ 8/76	9.5			8.5			3.0		
270	4/ 8/76	5.6	8.0	5.1	5.3	7.3	4.5	2.0	2.6	0.4
270	10/ 8/76	10.0			9.3			2.9		
270	12/10/76	9.3			8.7			3.3		
258	20/ 7/76	15.3			13.2			4.7		
258	4/ 9/76	15.2	14.9	0.2	15.1	13.7	1.0	5.2	5.0	0.05
258	7/ 9/76	15.0			12.9			5.1		
258	12/10/76	14.2			13.4			5.0		
4	10/ 8/76	14.8	14.4	0.3	15.9	14.5	3.9	5.2	5.3	0.02
4	12/ 9/76	14.0			13.1			5.4		
Blue Chalk	22/ 7/76	33.3			33.5			10.9		
Blue Chalk	9/ 7/76	29.5			31.9			12.0		
Blue Chalk	5/10/76	28.7	31.0	4.4	29.5	31.6	2.25	9.9	11.0	0.6
Blue Chalk	5/10/76	32.9			32.2			11.5		
Blue Chalk	5/10/76	30.5			30.9			10.7		
Red Chalk	6/ 8/76	43.9	42.9	1.7	50.7	48.6	9.2	16.8	16.4	0.2
Red Chalk	7/10/76	42.0			46.4			16.1		

Chub	9/ 9/76	44.6			44.0			18.3		
Chub	6/10/76	42.0			42.6			18.1		
Chub	6/10/76	46.1	44.8	3.9	44.7	44.0	0.7	18.4	18.4	0.1
Chub	6/10/76	47.2			44.6			19.0		
Chub	6/10/76	44.2			44.1			18.3		
Gisborne	25/ 8/76	29.6	30.5	1.7	30.3	31.1	1.1	10.4	10.4	0.0
	26/ 8/76	31.5			31.8			10.4		
Dickie	20/ 7/76	36.6			39.2			13.1		
Harp	7/ 7/76	26.7			24.5			10.3		
Jerry	21/ 7/76	29.5			31.5			10.0		
Composite	6/10/76	11.9			12.1			4.0		

* Duplicate and triplicate analyses were in close agreement and are reported as averages.

stations display a significant spatial variation. Stations 258 and 4 have consistently higher values and are similar to each other in all three parameters. Stations 252 and 270 are also similar to each other but contain about half of the organic carbon and carbohydrates found at stations 258 and 4. One possible explanation for this difference lies in the location of the stations (see Fig. 19). Stations 258 and 4 are deep stations (> 20 m). They are located well below the thermocline in summer and are not situated near effluent outfalls or channels which may experience strong currents. Station 258 is close to the geographical centre of the bay and, like station 4, is likely a recipient of deposition material eroded from the near shore areas because of its depth and location. Stations 270 and 252 are subject to transient conditions, sediment loads and erosion. Station 270 is influenced by the inflow from the channel at the western extremity of the Harbour. This station, situated at a depth of 15 metres, is subject to considerable deposition of sediment from streamflow entering from the west. Station 252 is located near a sewage outfall at a depth of about 6 to 8 metres. This station, therefore, receives highly organic and most likely highly degradable material from the outfall. The depth of this

station is near the thermocline in summer and may at times be in or out of the hypolimnion depending on wind direction. Stations 270 and 252 do not reflect the Harbour's prevailing conditions.

There is a strong relationship between the three organic parameters measured (LOI, CARB, and OC). Figure 21 illustrates the degree of fit of a linear model, intercepting the origin, found to describe the relationship between organic carbon and the other parameters (LOI and CARB). Considering the large variation in the sediment properties of the lakes sampled in this study, this is a discouraging result. The results indicate that none of the three parameters is an independent measure of biodegradability. Each parameter is simply proportional to the total organic fraction. Because of its ease and good repeatability, loss on ignition is recommended for measuring the relative organic content of lake sediments.

Hamilton Harbour sediments had the lowest concentration of organic properties of all lakes sampled despite the high effluent loading in the Harbour. All of the other lakes, except Gisborne, are located in Ontario's Precambrian Shield. They receive low nutrient loadings and low inorganic loads. Hamilton Harbour's high inorganic loading and high sediment oxidative rates

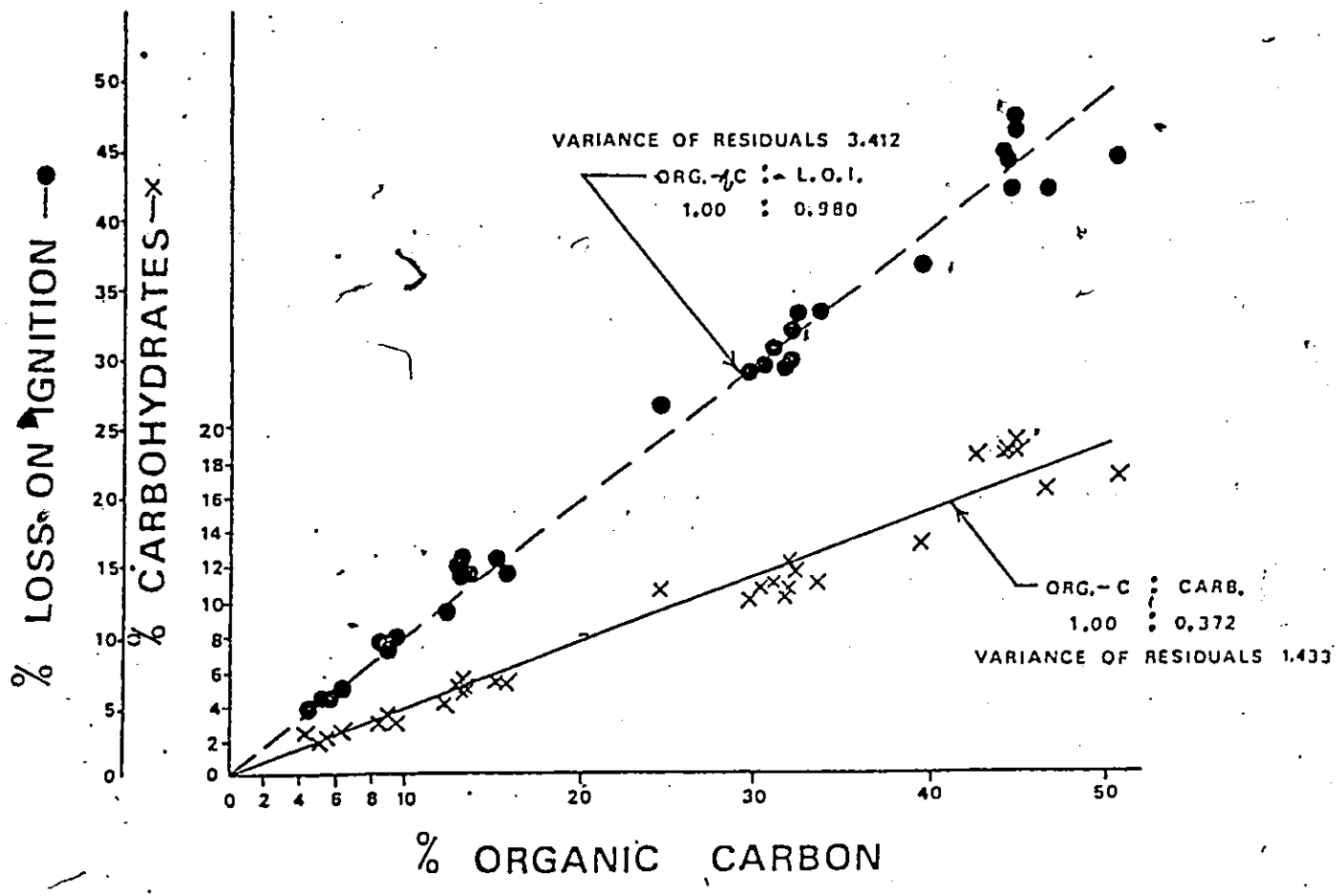


Figure 21. Correlations of organic carbon content to carbohydrate content and loss on ignition for sediment samples.

result in high sediment density. Inorganic loads of high density tend to bias the measurement of organic concentration by weight. As indicated in Appendix A the organic concentration by volume in Hamilton Harbour is high and similar to those in the Muskoka lakes. Organic content of sediment should be reported in volumetric units.

5. LABORATORY METHODS

5.1. Introduction

The methodologies used in this study follow a fundamental plan commonly used in biochemical experimentation. George W. Salt (1969) writes,

> "Hypotheses are generated from observations in the field. These are then tested and quantified by laboratory experimentation. Experimental results are next used to construct a computer model from which predictions of events in nature are generated."

The laboratory phase of this study involved preparing artificial sediment-water systems in batch reactors and conducting experiments under controlled conditions. The reactors contained six sediment subsamples (see Chapter 4). During the period from November, 1976 to March, 1977, kinetic information was derived and later related to sediment characteristics and environmental conditions. Various visual observations were also made possible.

Two methodologies exist for the study of sediment oxidation and in particular, sediment oxygen uptake. In one, SOD is measured *in situ* or on undisturbed cores

at *in situ* temperatures within minutes of collection. This method ensures the least disturbance and should, therefore, be the most reliable method of estimating oxidation rates under the prevailing conditions. The other method, involving artificial sediment-water systems, justifies disturbance in order to study the response of these systems to various environmental conditions. This study employs both methods. In this chapter, the methods used to measure SOD rate in the laboratory are discussed.

Justification for conducting measurements on disturbed sediment samples has been supplied by investigators in recent past. Their work shows that sediments do return to near-natural conditions if allowed sufficient time after a disturbance. The response of the system is then typical of natural systems.

A short review of information, taken from Chapter 2, is included here to clarify the methods and assumptions used in this study. Hayes and MacAuley (1959) demonstrated that sediment samples, whether gathered intact or by dredge, would eventually respond in a similar manner with respect to oxidation rate in the laboratory. Edberg and Hofsten (1973) found that after 20 days of acclimatization a sediment system would attain a steady maximum SOD rate. This was the

time period that they discovered to be necessary for bacterial and macroinvertebrate communities to re-establish their numbers and tunnel structure. Pamatmat *et al.* (1973) and Vanderpost (1972) through experimentation and chemical analysis, respectively, demonstrated a high degree of homogeneity in surface sediments which in turn justifies sediment disturbance. James (1974) and Edwards and Rolley (1965) conducted experiments on altering the degree of mixing in the overlying water of sediment-water systems. Their common conclusion was that mixing velocity was unimportant at velocities which did not exceed that required to resuspend the sediment. The findings discussed above, assisted in the experimental design of this study and justify the following list of assumptions used throughout.

1. After an acclimatization period, disturbed sediment returns to a near-natural condition when placed in columns under lake water. This assumption refers to the sediment physical structure and its biological community. It is important that the physical structure be similar to the original sediment structure since this structure effects the rate of diffusion of soluble material within the matrix. The biological community is the prime force causing oxidation of sediment organics

and, therefore, the number of individuals in the community is of prime importance.

2. The artificial sediment core system continues to respond in a natural way for the duration of the experiments (4 months) despite the elimination of fresh organic inputs as in the *in situ* case. This assumption is valid if the system is not limited by the availability of biodegradable organic material. In these experiments, the quantity of organic material contained in each reactor is much greater than that which would be oxidized. In fact, if the overlying water is allowed to be consumed ten times over from saturation in each reactor, then the organic material in no more than 3 grams of dry sediment would be consumed (assuming that 1.5 grams of oxygen are required to oxidize one gram of organic material). Each reactor contained in excess of 100 grams of dry sediment.
3. The bacteria and macroinvertebrates in these systems are able to adjust to changes in temperature and oxygen concentration within a short acclimatization period (2 to 5 days). Bacterial populations should be sufficiently diverse in these systems that if the acclimatization period exceeds several of their doubling times, they will be able to adjust. The

duration of these experiments is much shorter than the doubling time for macroinvertebrates and therefore their numbers are not expected to change significantly. Provided that the worm tunnels remain intact; the worms' adjustment to temperature and oxygen should be rapid (< 1 day).

5.2. Sampling Procedure

Six different sediments were prepared for the laboratory phase of this study. Two sediments were taken from Hamilton Harbour at stations 258 and 270 (see Fig. 19) on October 12, 1976 after fall overturn of the hypolimnion. Three other samples were taken from Blue Chalk Lake, Red Chalk Lake and Chub Lake (Muskoka lakes included in the Ontario Ministry of the Environment's Lakeshore Capacity Study). These samples were gathered on October 5 and 7, 1976. Organic parameters measured on these samples are listed in Table 6. The sixth sample was prepared as a composite sample from approximately equal portions of the other five samples. All samples were gathered with an Eckman dredge.

Hamilton Harbour sediments were used in this study since their origin is highly varied. The Harbour is characteristic of a warm, eutrophic lake. Bottom temperatures rise to about 13^{o}C during summer

stratification. Oxygen depletion of hypolimnetic waters is complete shortly after summer stratification. High autochthonous sediment rates are encouraged by the input of treated domestic sewage from three sewage treatment plants. In addition, the Harbour receives urban runoff from 2 cities and 2 steel mills as well as runoff from a heavily cultivated area to the west.

The Muskoka lakes are all small, deep lakes displaying low productivity. Hypolimnetic waters are generally not depleted of oxygen during the summer and generally bottom temperatures remain near 4°C during the summer. Allochthonous inputs to these lakes are generated from areas of heavy forest cover in the Precambrian Shield. A small number of cottages are contained within the drainage basin of each lake.

Each sample was composed of 4 to 5 separate 'grabs' with the Eckman dredge. This device takes material from 5 to 15 cm below the sediment surface, depending on the density. Samples were sealed in plastic bags and kept at 4°C for about 2 weeks prior to reactor preparation. Water for use in the reactors was taken from Hamilton Harbour and filtered through Whatman #40 filters to remove zooplankton. The water was also stored at 4°C. The relatively dilute overlying water was not expected to significantly effect the sediment chemistry of the Muskoka sediments.

5.3. Reactor Columns

The reactor columns were constructed of plexiglass cylinders (inside diameter = 7 cm, length = 54 cm, wall thickness = 0.48 cm). The bottom was sealed with a large rubber stopper. The top was fitted with a movable airtight and watertight plunger. The plunger could be moved up or down to expel collected gas through a small stoppered hole and to readjust the reactor volume after withdrawal of water samples.

Three columns were prepared from each of the six sediment types. First, sediment was placed in the columns to a depth of about 15 cm. Hamilton Harbour water was then used to cover the sediment to a depth of about 30 cm (see Fig. 22).

The sediment-water columns were allowed to settle for one day and then the overlying water was gently aerated for one month in a dark room at a controlled temperature of 12°C. It was hoped that this time period would be sufficient for the sediment system to become acclimatized to the new conditions. The hardness of the sediment columns' overlying water was measured after three weeks. The columns containing Muskoka lake sediments had alkalinity less than 15 mg/ℓ as $CaCO_3$. Columns containing only Hamilton Harbour

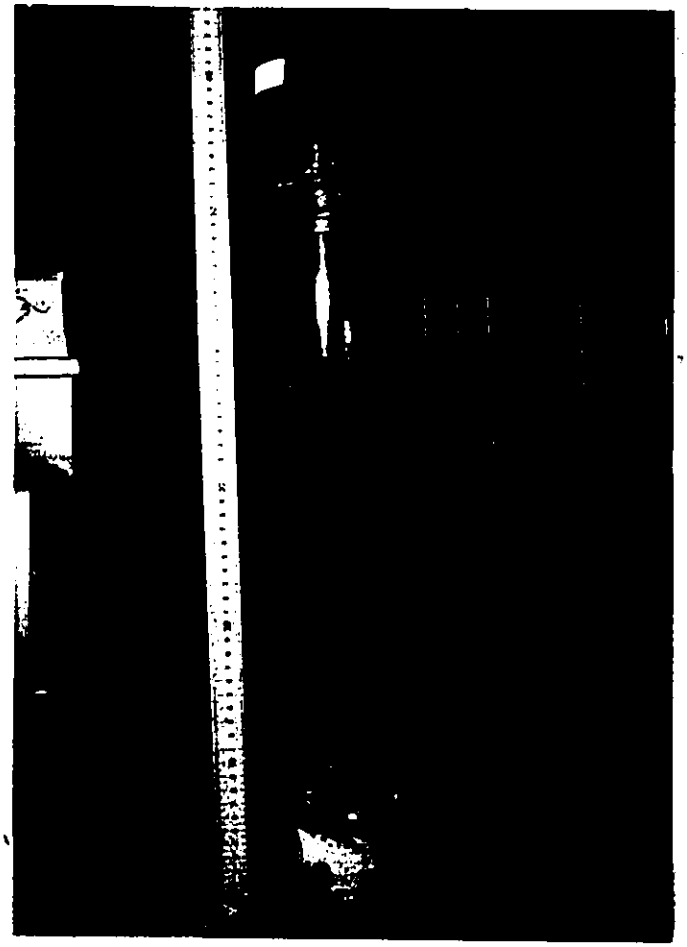


Figure 22. Laboratory sediment-water column with plunger style top.

sediments contained water with alkalinity of at least 100 mg/ℓ as $CaCO_3$. In order to prevent pH depression in the columns with low water hardness, a phosphate buffer was added to raise the hardness to 100 mg/ℓ as $CaCO_3$. In the natural environment, the buffering capacity of the entire hypolimnion would be in effect to resist pH changes at the sediment surface. In the columns with Muskoka sediment, however, only the low natural buffering of the sediment and the small volume of overlying water was available for that purpose. It was felt that the addition of a buffer would be justified as it would prevent an unnatural pH depression from occurring.

After acclimatization, one column from each of the six sets of three was poisoned with enough potassium cyanide (KCN) to raise the concentration of cyanide ion (CN^-) in the overlying water to 500 mg/ℓ. These columns were aerated for one more week to allow the inhibitor to penetrate the aerobic zone of the sediment.

5.4. Experimental Design

For convenience, the experimental procedures used in this study are divided into three parts. In the first part, poisoned columns were monitored and observed as the chemical sediment oxygen demand (CSOD) reactors.

Each column was aerated for the acclimatization period and then sealed. All visible gases were expelled and the columns were kept in darkness at controlled temperatures. At regular time intervals, depending on the rate of oxygen depletion in the overlying water, each column was opened and the oxygen concentration measured in the overlying water. Oxygen concentration was measured with a Yellow Springs Instruments (YSI) oxygen meter and probe with an electric stirrer, calibrated daily. To prevent disturbance at the sediment surface, a tin plate was lowered by wire about 20 cm into the water below the stirring action during measurements. When the dissolved oxygen was reduced to less than 0.5 mg/ℓ, the column was aerated again and the temperature was changed by 4 or 6 C^{o}. Poisoned columns were monitored in this fashion at 4, 8, 12, 16 and 22^{o}C.

In another part of the study, measurements were carried out on duplicate unpoisoned columns. The procedure was identical to that used on the poisoned columns. The frequency of dissolved oxygen measurement was usually higher and in fact, at 22^{o}C, some measurements were made at hourly intervals to ensure that the oxygen depletion curve could be smoothly reconstructed. These columns displayed total sediment oxygen demand (TSOD) rates and experiments were conducted at 4, 8, 12, 16 and 22^{o}C.

The third phase of the study procedure commenced when the TSOD phase was complete. All of the columns which had visual signs of macroinvertebrate activity were separated from the remaining columns. This sample group included the six columns with sediments from Hamilton Harbour stations 258 and 270 and the composite sediment. There were no visual signs of worms in the Muskoka lakes' sediments and were, therefore, not included in this portion of the study. One of each of the three pairs of columns was sent to the biology laboratory at the Stoney Creek office of the Ministry of the Environment (MOE) for macroinvertebrate species indentification and counting. The remaining three columns were treated with sufficient solution of equal parts streptomycin and penicillin to raise the concentration in the overlying water to 50 mg/ℓ. Experiments were then conducted, as in the previous two parts of the laboratory phase, with these three columns at 4, 12, 16 and 22°C.

Along with oxygen monitoring, other pertinent observations and measurements were made on the sediment-water systems. An attempt was made to verify that oxygen diffusion through the plexiglass walls of the columns was insignificant during the course of this study. This was done by placing deoxygenated distilled water in a column, sealing it in the normal manner and

allowing it to remain untouched for 47 days. After this time period, there was no significant increase in the oxygen concentration of the water within, therefore this possible source of error was concluded to be negligible.

Visual observations were made on the extent and colour of the aerobic zone in all columns, of macroinvertebrate activity and tunnel development and of the production of gases from the sediment. The colour of the overlying water was observed to deepen, especially in the six KCN poisoned columns. At the end of the CSOD phase of the laboratory study, the colour of the water in these columns was measured in cobalt-platinum (Co-Pt) units using a HACH colour kit.

Hardness and pH were periodically measured on water samples taken from each column to ensure that pH depression did not occur. Hardness was measured according to Standard Methods (WPCF, 1975).

The oxygen demand of the overlying water was determined at 4, 8, 12, 16 and 22°C. Water samples were taken from each column and placed in a standard BOD_5 bottle. Distilled water was used to replace the sample volume. These bottles were incubated at the various temperatures for several days to estimate a volumetric oxygen demand potential.

6. MODEL SELECTION AND PARAMETER ESTIMATION

6.1. Introduction

Procedures used to select models and estimate model parameters from the laboratory data are discussed in this chapter. Models were chosen which provide a suitable representation of the oxygen concentration-dependent trends of oxygen uptake rates observed in the laboratory columns. Selected models were fit to the study data yielding a set of model parameters which were used for comparative purposes and as independent data sets with which to select appropriate models to describe temperature-dependent trends. These methods were used to establish oxygen concentration- and temperature-dependent models for chemical, biological and macroinvertebrate oxygen uptake at the sediment-water interface.

6.2. CSOD Oxygen Model Selection

The literature, as outlined in sections 2.5 and 2.6, describes SOD as a function of temperature and oxygen concentration. In preliminary graphical

analysis, it was discovered that a smooth curve could be drawn through the oxygen concentration versus time data from the six poisoned columns. When transformed into the rate versus oxygen concentration form, this data can be closely modelled with a straight line, intercepting the origin. Typical curves of this form are illustrated in Figures 23 and 24. On the basis of this analysis, a first-order model was selected to describe CSOD. This model appears as:

$$CSOD = k_c \cdot [O_2] \cdot f \qquad (10)$$

where CSOD = the rate of oxygen uptake due to anaerobic processes in areal units ($M\ L^{-2}T^{-1}$),

k_c = the first-order rate constant (T^{-1}),

f = a conversion factor from volumetric to areal units (L),

and $[O_2]$ = oxygen concentration ($M\ L^{-3}$).

The above model was fit to 30 experiments (6 sediment types at 5 temperatures) involving CSOD. The computer program, UWHAUS (McMaster University, Chemical Engineering Department, Appendix B) was used to estimate the 'best' values of k_c. This program employs optimization techniques to select values for model parameters which result in a minimum sum of squares of residuals. Results of this analysis are discussed in Chapter 7.

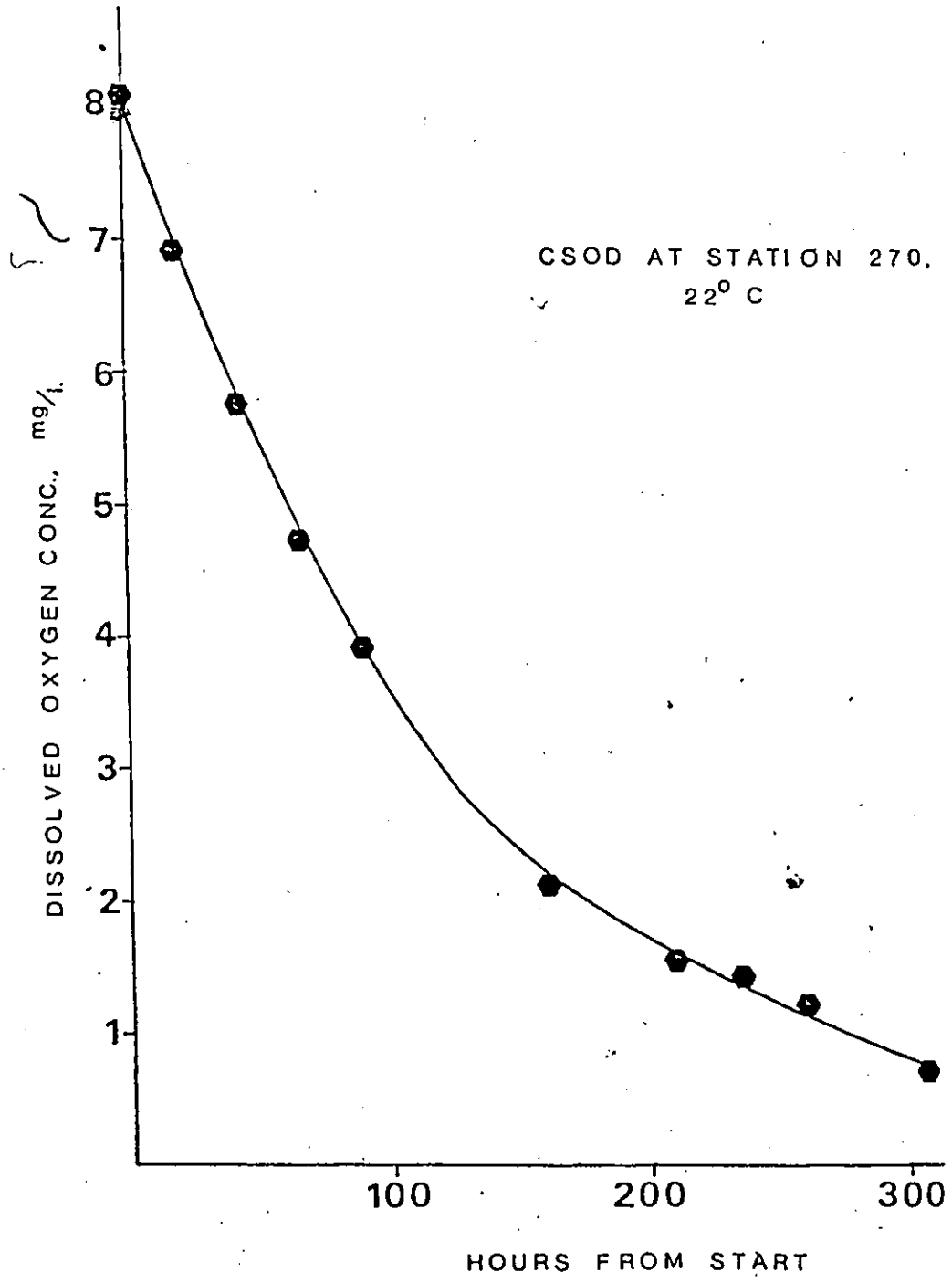


Figure 23. Typical laboratory column D.O. versus time data from laboratory column with chemical oxidation only.

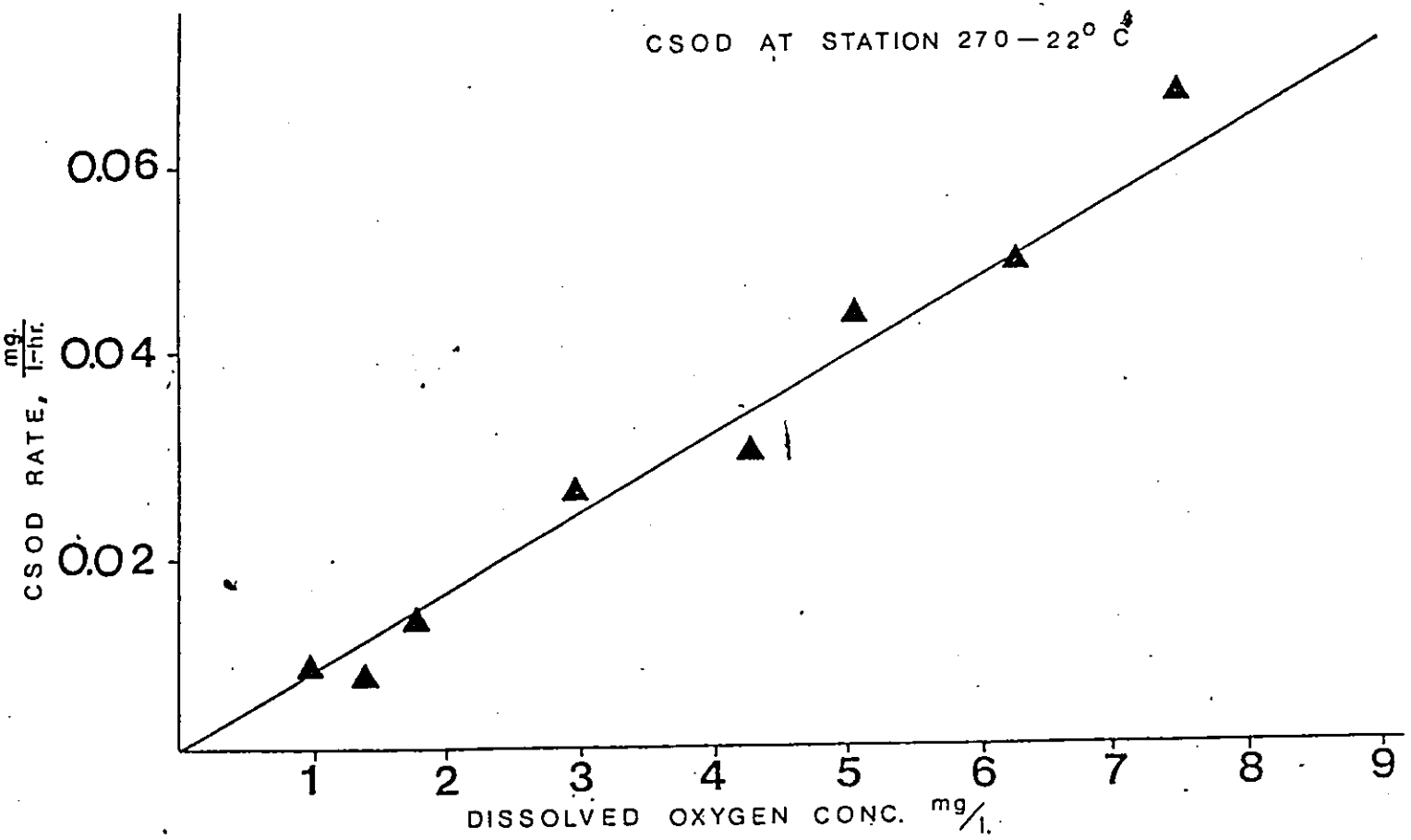


Figure 24. Chemical sediment oxygen demand rate versus oxygen concentration from laboratory column.

6.3. BSOD Oxygen Model Selection

The model selection procedure for the BSOD portion of the study was similar to the CSOD portion. A graphical approach was used to examine the shape of the curves and to illustrate the trends that occurred. Figure 25a is a reproduction of the oxygen concentration versus time data collected from an unpoisoned column in the laboratory. When this data is converted to rates and plotted against oxygen concentration, the curve in Figure 25b is derived. The upper curve (T) in this figure represents the total demand. The lower curve (T-C) results after the subtraction of the portion of the uptake attributed to chemical uptake as it appears in Figure 24. This curve (T-C) represents the BSOD and is therefore independent of purely chemical or anaerobic processes which are part of the top curve (T).

No simple kinetic expression could be used to adequately describe the shape of curve T-C as the curve appears to migrate from first-order at low oxygen concentrations to zero-order at higher oxygen concentrations. For this reason, the kinetics first proposed by Michaelis and Menton in 1913 was selected (Levenspeil, 1972). This model form also called Monod kinetics is presented graphically in Figure 26. This model was first proposed

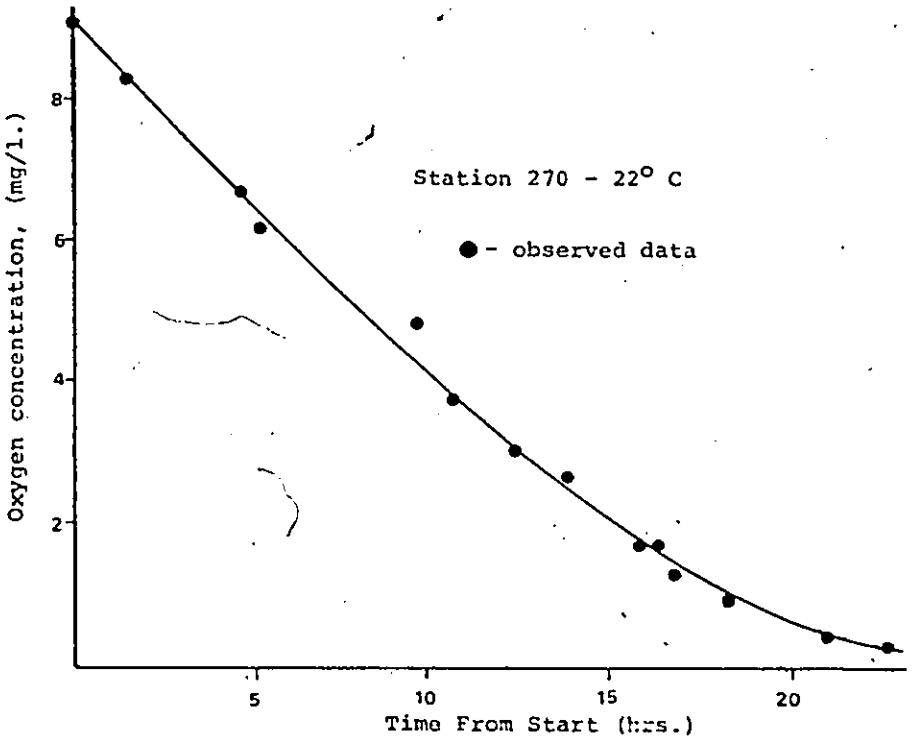


Figure 25a. Typical total sediment oxygen demand (TSOD) oxygen concentration versus time trace.

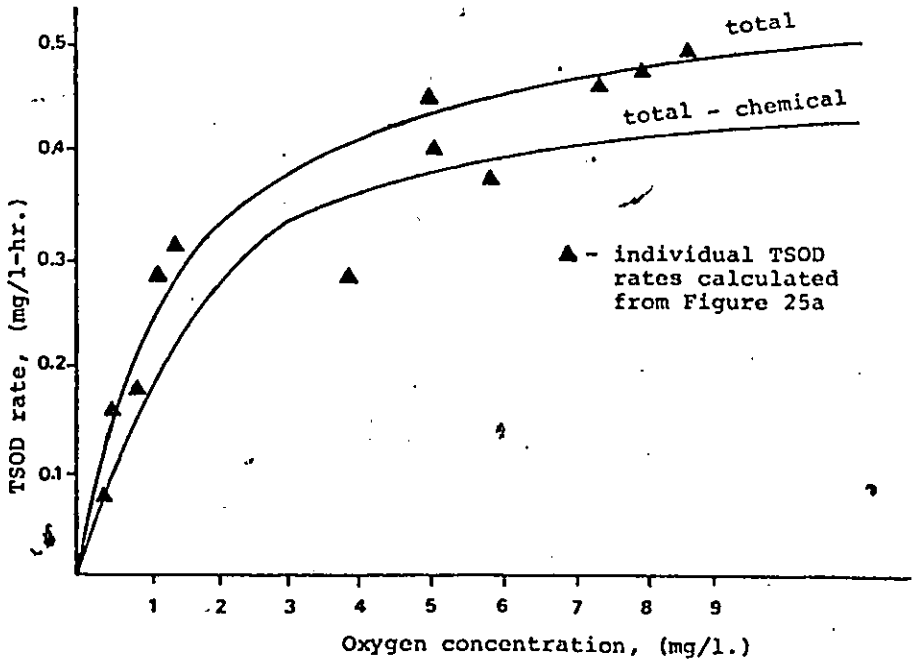


Figure 25b. Rate versus oxygen concentration form of Figure 25a showing total and total-chemical sediment oxygen demand.

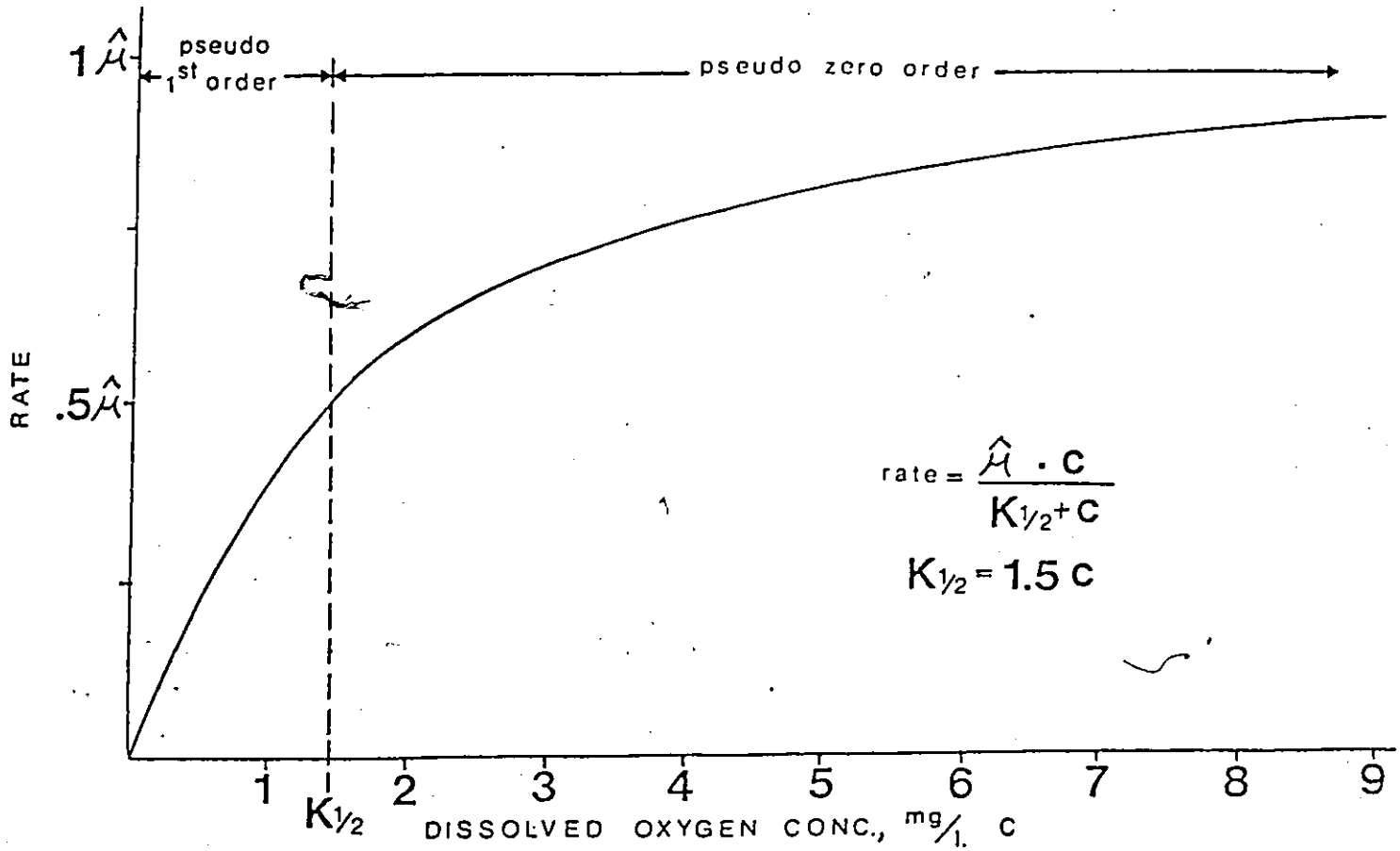


Figure 26. Michaelis-Menton model in the rate versus concentration form. $\hat{\mu}$ is the specific rate constant.

to describe enzyme catalysed reactions or surface catalysed reactions. It is used in situations wherein a reactant (oxygen) is associated with a limited but fixed entity (bacterial enzyme surface) and mechanistic studies have confirmed this shift in reaction order. The model involves two constants represented here as $\hat{\mu}_{max}$ and $K_{\frac{1}{2}}$. At the extremes of concentration C, the model reduces to the forms:

$$\text{Rate} = \hat{\mu}_{max} \text{ when } C_o \to \infty \text{ (zero-order)} \tag{11}$$

$$\text{and Rate} = \frac{\hat{\mu}_{max}}{K_{\frac{1}{2}}} \cdot C_o \text{ when } C_o \to 0 \text{ (first-order)} \tag{12}$$

The term $\hat{\mu}_{max}$ acts as a zero-order rate constant in equation (11) and $\hat{\mu}_{max}/K_{\frac{1}{2}}$ acts as a first-order rate constant in equation (12). The $K_{\frac{1}{2}}$ term, called the half saturation constant, is numerically equal to the oxygen concentration when the rate is equal to $\hat{\mu}_{max}/2.0$.

With the aid of the program UWHAUS, the 60 experiments involving TSOD were fit to the two models mentioned. The model took the form:

$$\text{TSOD} = \left(\frac{\hat{\mu}_{bmax} \cdot [O_2]}{K_{\frac{1}{2}} \cdot [O_2]} + k_c \cdot [O_2] \right) \cdot f \tag{13}$$

where TSOD is the total SOD rate in areal units ($M\ L^{-2}T^{-1}$) and $\hat{\mu}_{bmax}$ is the zero-order rate constant

for the aerobic bacterial portion of the SOD ($M\ L^{-3}T^{-1}$). The values for k_c were input directly in this stage of the analysis. The k_c value used was predicted by the temperature model (see section 6.4) for the same sediment type.

To simplify the comparisons among the various sediments it was decided to standardize the $K_{\frac{1}{2}}$ term and rerun the program so that all variations were included in the $\hat{\mu}_{bmax}$ term. The standard value of $K_{\frac{1}{2}}$ was chosen as the numerical mean of the 60 estimated values. This procedure is based upon the assumption that temperature has a negligible effect on $K_{\frac{1}{2}}$ and that the model is not highly sensitive to changes in $K_{\frac{1}{2}}$. If this is the case, then the $\hat{\mu}_{bmax}$ values should change only slightly in the second series of runs. This was, in fact, what occurred. In some cases, $K_{\frac{1}{2}}$ changed significantly with a relatively small resultant affect on $\hat{\mu}_{bmax}$ (see Table 10, Chapter 7).

The rates of oxygen uptake by macroinvertebrates were analysed in the same way as the BSOD. Maximum uptake is termed $\hat{\mu}_{mmax}$. The standard value for $K_{\frac{1}{2}}$ was used and the k_c values used in the regression were the values determined for the appropriate sediment type and temperature determined in the CSOD data analysis. The kinetics of oxygen uptake by benthic animals,

observed by Edwards and Rolley (1965), Ewer (1942) and Walshe (1948), was similar to that observed in the BSOD portion of this study. The benthic animals exert a lower oxygen demand at lower oxygen concentrations; however, the uptake rate is independent of oxygen concentrations at high concentrations.

6.4. Temperature Models

The analysis described in sections 6.2 and 6.3 resulted in the estimation of 72 $\hat{\mu}_{max}$ values and 30 k_c values for the six sediment types. It is obvious from the values calculated (see Table 10, Chapter 7) that temperature has a strong effect on oxygen uptake. Figures 27 and 28 illustrate this trend for CSOD and BSOD as the values of k_c and $\hat{\mu}_{bmax}$ increase substantially between 4 and 22°C. Models were chosen to describe the effects of temperature on the CSOD, BSOD and the macroinvertebrate SOD. In the final analysis, these models each yielded a constant which was independent of oxygen concentration and dependent solely on sediment type used. Comparisons can be made among the sediments with this constant.

The model selected for describing temperature effects on SOD is of the general form:

$$K(T) = K(T_o) \cdot B^{(T_o - T)} \qquad (14)$$

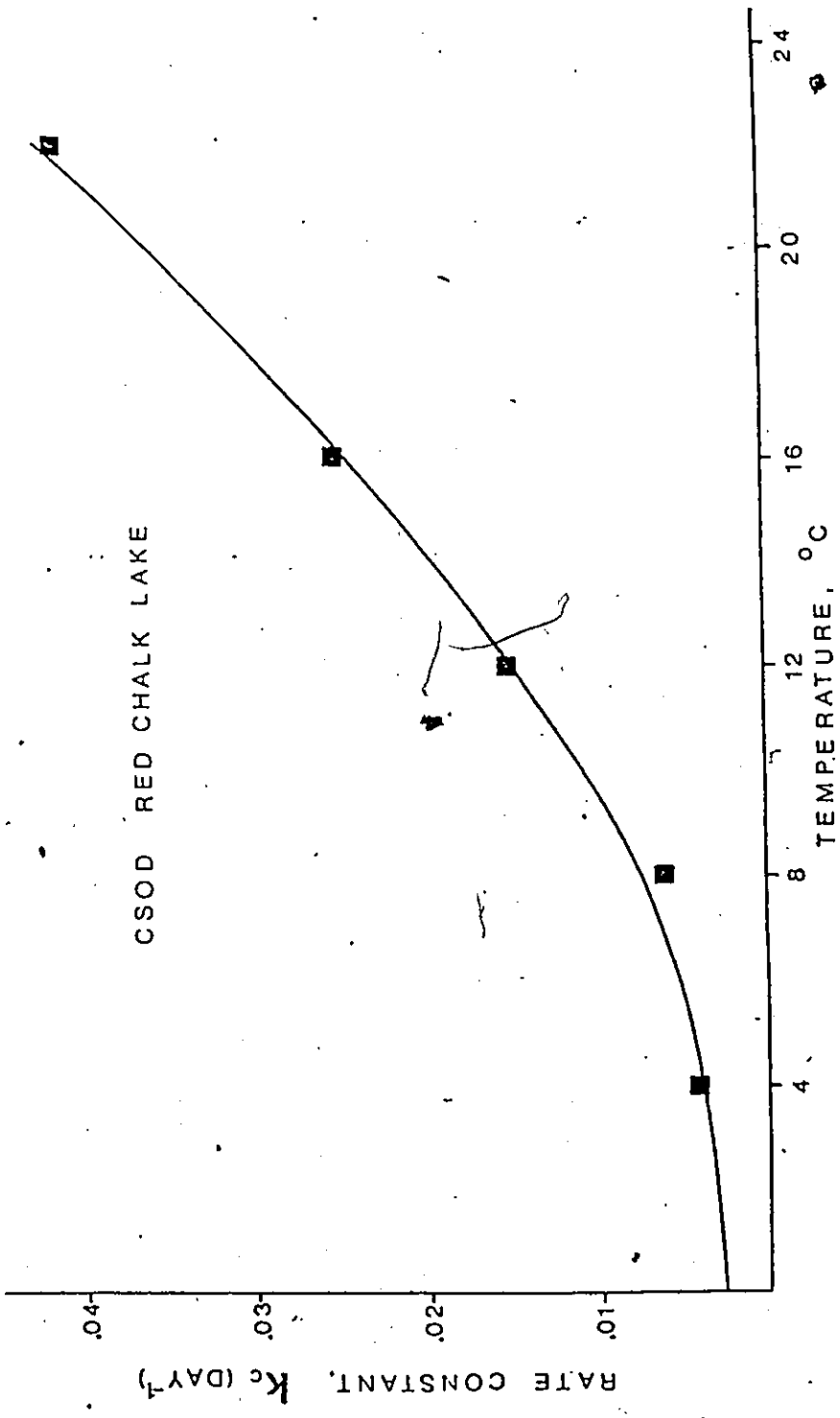


Figure 27. CSOD rate constant, k_c versus temperature.

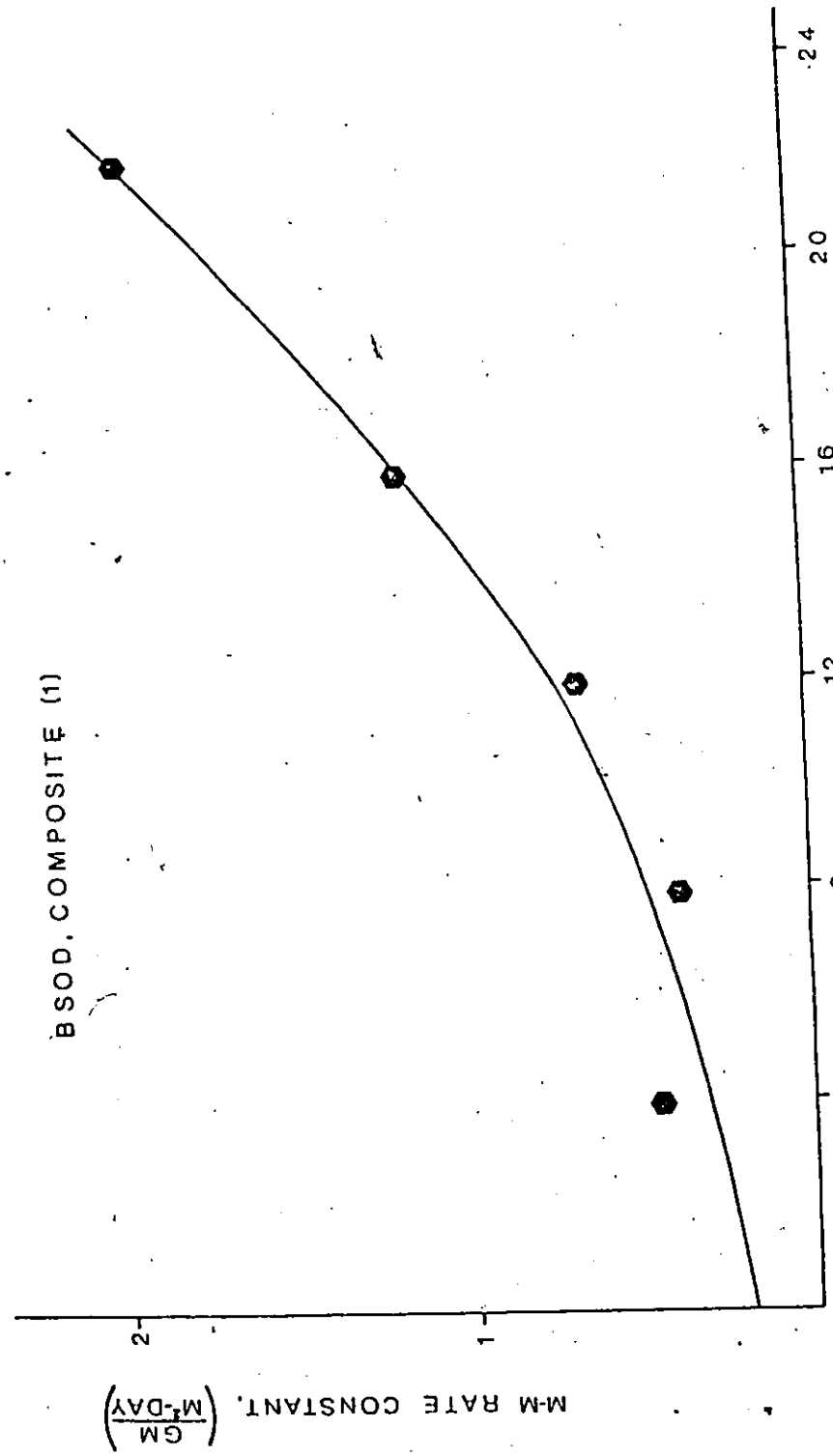


Figure 28. Michaelis-Menton (M-M) rate constant, $\hat{\mu}$ versus temperature.

where $K(T)$ = the rate constant at temperature T (^{o}C),

$K(T_o)$ = the rate at some standard temperature T_o (^{o}C),

and B = a model constant.

This model was chosen because it reflects the significant effect of temperature on the rates observed and has been successfully used in models of diverse biological systems such as those encountered in natural water systems and biological waste treatment reactors. The program UWHAUS, was again used to select values of $K(T_o)$, B and T_o for each of the six poisoned sediments. It was intended that this model would be universal, that is the shape of the model would be the same in all similar systems. For this reason, the values of B and T_o must be the same for all the sediments. The mean of the six T_o values was very close to $20^{o}C$; therefore, T_o was set equal to $20^{o}C$. The six program runs were repeated with T_o fixed. This set of runs yielded six slightly different values for B. These six values were averaged and B set equal to 0.907. The program was run a final time with B fixed to estimate the K(20) values for each of the sediments. The final model was:

$$k_c = k(20) \cdot 0.907^{(20 - T)} \qquad (15)$$

The value, k(20) is therefore a parameter of comparison among the sediments used. In each of the runs, it was

found that the 'floating' parameter (k(20)) is not highly sensitive to the adjustment of the fixed parameters (B and T_o). This is apparent because during the second and third series of computer runs, relatively small changes in k(20) resulted when B and T_o were fixed. This is discussed further in Chapter 7 with the results obtained.

Temperature models for the BSOD and the MSOD were derived in a similar manner. The BSOD runs resulted in the model:

$$\hat{\mu}_{bmax}(T) = \hat{\mu}_{bmax}(25) \cdot 1.085^{(T - 25)} \qquad (16)$$

As in the CSOD experiments, the values of $\hat{\mu}_{bmax}(25)$ were found to be relatively insensitive to substantial changes in B and T_o which were closely distributed about the final fixed values. These results are expanded upon in Chapter 7.

Due to the small amount of data available from the macroinvertebrate columns, the values of B and T_o obtained from the BSOD experiments were used in the macroinvertebrate temperature model. The model therefore appears as:

$$\hat{\mu}_{mmax}(T) = \hat{\mu}_{mmax}(25) \cdot 1.085^{(T - 25)} \qquad (17)$$

The computer analysis yielded 3 values for $\hat{\mu}_{mmax}(25)$ and these are presented in Table 13 and discussed in Chapter 7. These values are only first approximations of the relative contribution of worms to the total aerobic community effect on TSOD. These values can also be related to the worm densities measured on the same sediments and to animal respiration rates reported in the literature.

7. RESULTS AND DISCUSSION

7.1. Chemical Sediment Oxygen Demand

The chemical oxidation of sediment was observed in 30 separate experiments at five controlled temperatures. As described in Chapter 4, KCN was added to six columns containing sediments from five locations and one composite sample. Individual experiments continued until dissolved oxygen concentrations were low (< 1.5 mg/ℓ) or until approximately four weeks elapsed. Experiments conducted at 4 and 8°C often displayed extremely low uptake rates. Graphical analysis of several experiments indicated that the reactions could be represented by a first-order model wherein oxygen concentration is the dependent variable. The first-order rate constant k_c was estimated by computer for each of the experiments (see Chapter 6). Table 7 lists the k_c values derived. These constants appear in volumetric units for each column and in areal units after being converted by the factor, f (see Appendix E). This factor is specific to each column and is dependent on the depth of overlying water in the column. Note that the k_c values generally

Table 7

Computed CSOD First-Order Rate Constants, k_c

Sediment sample	Temp. °C	k_c, hr^{-1}	$k_c \cdot f$ m/day	P_1, m/day
270	4	0.00151	0.0103	
	8	0.00264	0.0181	
	12	0.00408	0.0280	0.0482
	16	0.00570	0.0390	
	22	0.00786	0.0519	
258	4	0.00151	0.0125	
	8	0.00052	0.0043	
	12	0.00145	0.0120	0.0313
	16	0.00315	0.0261	
	22	0.00440	0.0365	
Composite	4	0.00110	0.0078	
	8	0.00155	0.0110	
	12	0.00302	0.0214	0.0372
	16	0.00367	0.0261	
	22	0.00608	0.0432	
Blue Chalk	4	0.00097	0.0075	
	8	0.00091	0.0070	
	12	0.00124	0.0090	0.0210
	16	0.00198	0.0150	
	22	0.00320	0.0246	
Chub	4	0.00077	0.0061	
	8	0.00377	0.0301	
	12	0.00377	0.0302	0.0601
	16	0.00660	0.0528	
	22	0.00796	0.0636	

Table 7
(Cont'd)

Computed CSOD First-Order Rate Constants, k_c

Sediment sample	Temp. °C	k_c, hr^{-1}	$k_c \cdot f$ m/day	P_1, m/day
Red Chalk	4	0.00057	0.0043	
	8	0.00079	0.0060	
	12	0.00201	0.0151	0.0345
	16	0.00338	0.0253	
	22	0.00553	0.0415	

increase with temperature for each column and are highly variable from one sediment to another.

A sample ANOVA (Analysis of Variance) table along with the F statistics for all 30 CSOD experiments are contained in Appendix D, Tables D-1 and D-2. The F statistic and the degrees of freedom were used to evaluate the level of significance (LOS) which is achieved by the model and estimated model parameters. Table 8 is a summary of the least LOS achieved with the 1% level being the lowest tested. The 1% level was achieved in 27 of the 30 experiments. These results indicate that the model selected is appropriate and that the k_c values associated with each experiment are good estimates of the constant. The model fit achieved along with the 95% confidence interval for a typical experiment are illustrated in Figure 29.

The first-order model is directly dependent on the concentration of oxygen throughout the range of concentrations. This is strong evidence that the reaction is limited by the supply of oxygen to the site of the reaction (usually 1 to 5 cm below the sediment-water interface), at a given temperature, in a specific column. A reddish zone, about 1 to 2 cm below the sediment surface, delineated the extent of the upper oxidized zone in the Hamilton Harbour sediments.

Table 8

Levels of Significance Achieved by Models

Model	Temp. °C	Level of significance (%) by sediment type					
		270	258	Comp.	B. Chalk	Chub	R. Chalk
CSOD (oxygen)	4	1	1	1	1	1	1
	8	1	5	5	1	1	5
	12	1	1	1	1	1	1
	16	1	1	1	1	1	1
	22	1	1	1	1	1	1
BSOD (oxygen)	4	1	1	1	1	1	1
	4	1	1	1	1	1	1
	8	1	1	1	1	1	1
	8	1	1	1	1	1	1
	12	5	5	1	1	1	1
	12	1	1	1	1	1	1
	16	1	5	1	1	1	1
	16	1	1	1	1	1	1
	22	1	1	1	1	1	1
	22	1	1	1	1	1	1
MSOD (oxygen)	4	1	1	1	-	-	-
	12	5	1	1	-	-	-
	16	1	1	1	-	-	-
	22	1	1	1	-	-	-
CSOD (temperature)	-	1	5	1	1	1	1
BSOD (temperature)	-	10 10	10 10	1 5	50 50	50 >50	>50 50
MSOD (temperature)	-	10	25	20	-	-	-

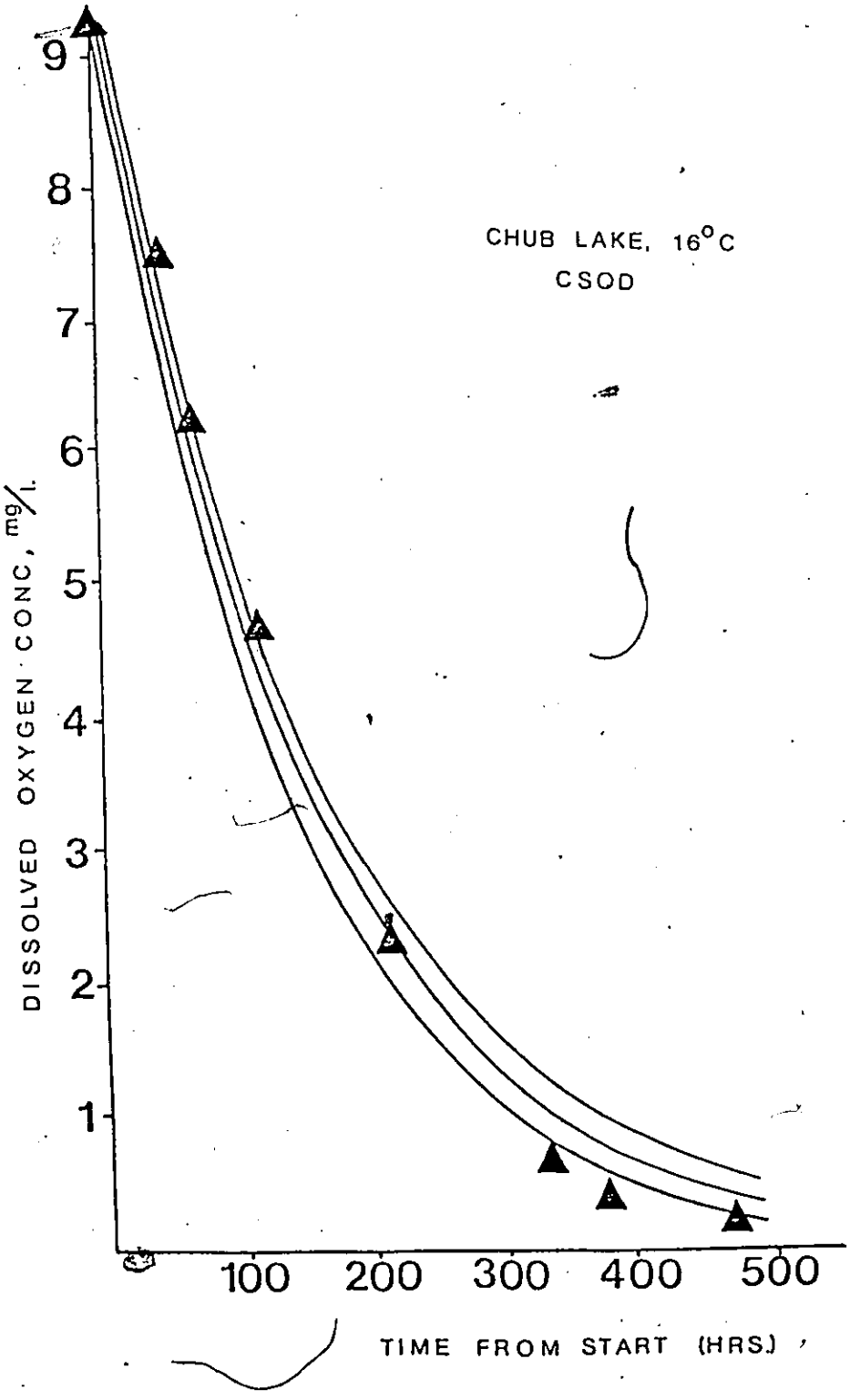


Figure 29. Regression for dissolved oxygen versus time with 95% confidence limits.

In the Muskoka sediments, the zone was distinguished by a light grey zone atop black sediments. This zone extended some 2 to 3 cm below the sediment surface.

The oxygen demand of the overlying water was measured on several occasions. Resultant uptake was negligible in all cases in relation to the sediment oxygen demand. This observation is to be expected in a solely chemically oxidizing system since it is generally accepted that the reaction takes place near the lower limit of the sediment's oxidized zone, well below the sediment-water interface. Each of the six sediments studied was subjected to five different temperatures in order to assess the effect of temperature change. A graphical approach was again used to obtain a preliminary evaluation of the system response to various temperatures. Figure 30 illustrates the trend found to be typical in these sediment-water systems when the computer-selected k_c values are plotted against temperature. The temperature model chosen is outlined in Chapter 6. It is capable of describing rapid, non-linear increases in k_c due to temperature change. The procedure followed in estimating the model parameters P_1, P_2 and P_3 is also described in Chapter 6. Estimated parameter values are listed in Table 9.

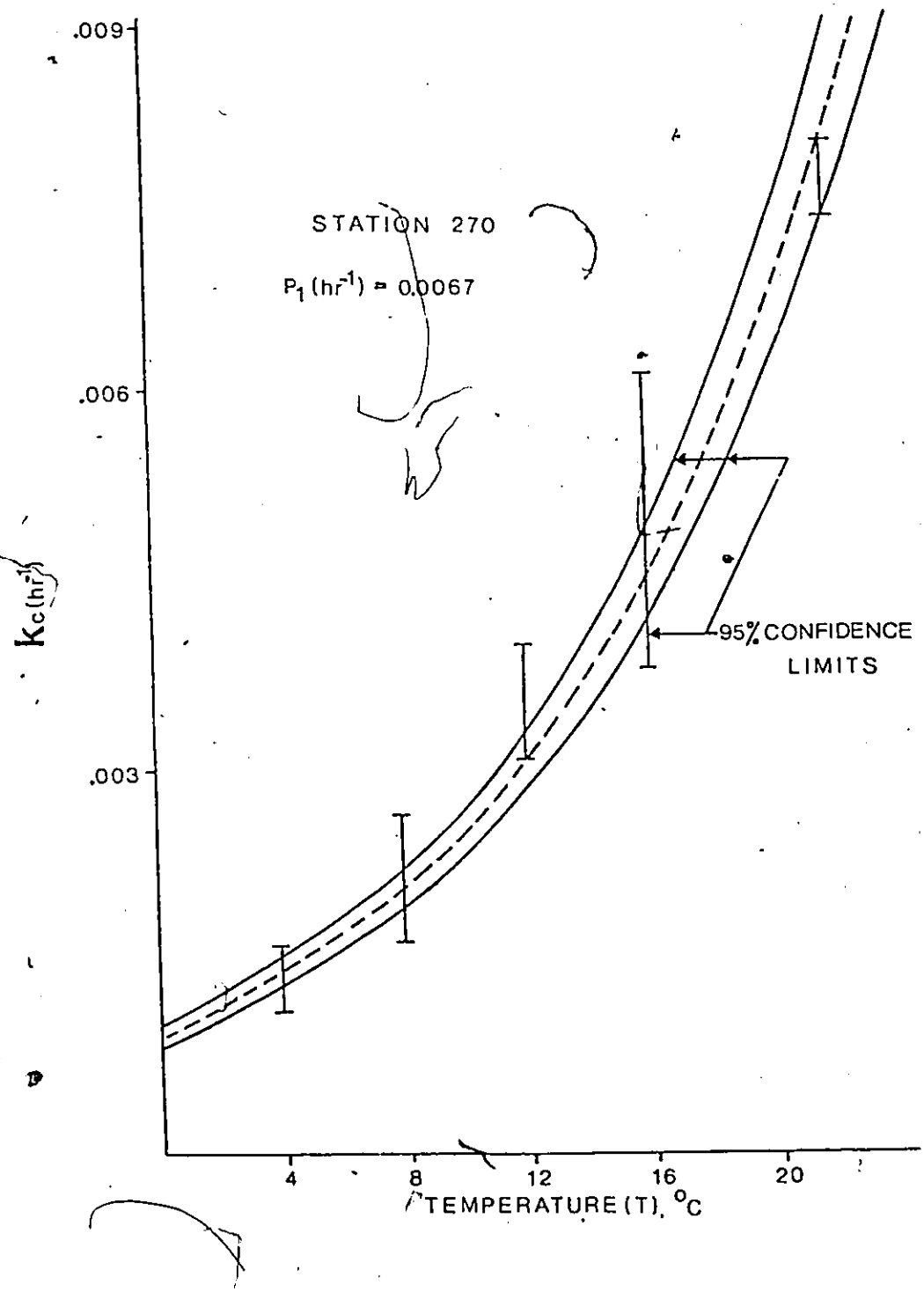


Figure 30. Computed k_c values with individual confidence limits and regression with confidence limits for k_c versus temperature.

Table 9

Estimated CSOD Temperature Model Parameter Values

Model used: $C_t = P_1 \cdot P_2^{(P_3 - Temp.)}$

Sediment sample	P_1	P_2	P_3	$\Sigma(residuals)^2 \cdot 10^5$	$P_3 = 20$			$P_2 = 0.907$	
					P_1	P_2	$\Sigma(residuals)^2 \cdot 10^5$	P_1	$\Sigma(residuals)^2 \cdot 10^5$
270	0.042	0.918	19.2	1.36					
258	0.027	0.905	19.3	6.61					
Composite	0.035	0.913	19.8	0.93					
Blue Chalk	0.027	0.910	22.4	0.93					
Chub	0.029	0.907	13.6	0.06					
Red Chalk	0.035	0.890	19.5	0.77					
Mean		0.907	19.0	1.78					
Variance		0.005	7.0						
270					0.045	0.918	1.36		
258					0.030	0.905	6.61		
Composite					0.036	0.913	0.93		
Blue Chalk					0.022	0.910	0.93		
Chub					0.057	0.907	0.06		
Red Chalk					0.037	0.890	0.77		
Mean						0.907	1.78		
Variance						0.005			
270								0.048	2.91
258								0.031	6.68
Composite								0.037	1.42
Blue Chalk								0.021	0.93
Chub								0.060	3.08
Red Chalk								0.035	3.02
Mean									3.01

Three separate sets of computer 'runs' were required to systematically standardize parameters P_2 and P_3. After the first run, P_3 values were averaged and a value of 20.0 was assigned to it. The mean and variance of P_3 values are given in Table 9. The program was rerun with P_3 fixed, yielding new values for P_1 and P_2. Note that these new values are only slightly different than those in the first run. In fact, the sum of squares of residuals does not change significantly. This is evidence that the model is not sensitive to adjustments of P_3, therefore, fixing its value for simplicity is justifiable. The parameter P_2, displayed very low variance after the second 'run' and its value was also standardized at the mean of the six estimated values. In the third series of 'runs', P_2 was fixed at 0.907 leaving only P_1 to float. Table 9 shows that in the final series of 'runs' the values of P_1 changed slightly and the sums of squares of residuals increased by about a 70% average. Table 8 shows the levels of significance achieved by this final regression with all but one experiment achieving the 1% level.

The success of this model in describing the system response to temperature assists in explaining the important mechanisms involved. The chemical sediment

oxygen demand measured in these experiments was highly temperature-dependent, yielding a Q_{10} of 2.65 (the quotient of rates corresponding to a 10°C change in temperature). The dissolved oxygen model described earlier, indicated that CSOD was limited by oxygen supply throughout the normal range of concentrations at a specific temperature. The strong temperature-dependence suggests that biological metabolism is important in limiting the reaction and not purely chemical or physical reactions. Diffusion and chemical reaction would display lower Q_{10} values (in the range of 1 to 1.5). CSOD is an indirect result of anaerobiosis and it follows that as temperatures increase so does the supply of reduced chemical species from the site of anaerobic reactions. Higher reaction rates result in higher reactant gradients and following this, higher reactant transport rates as the system temperature increases. The term CSOD can be misleading and perhaps a more appropriate term might be indirect biological or anaerobic oxygen demand since bacteria mediate the process.

A comparison of the parameter P_1, in Table 9, among the six sediments shows that large differences exist in chemical uptake rates after temperature and dissolved oxygen are eliminated as dependent variables.

Figure 31 illustrates these differences in the form of a histogram of P_1 values. Neither the Hamilton Harbour sediments nor the Muskoka sediments, as a group, display significantly higher P_1 values. The composite sample, however, has a P_1 value which is very near the mean of the other five sediments. The overall rate limiting factor appears to be integrated in this sediment sample.

Various observations were made of the sediment systems, of a descriptive nature, which help to explain the different P_1 values. Water colour was measured in the overlying water of each column at the termination of experiments. The results of this measurement appear in Appendix A as colour in cobalt-platinum (Co-Pt) units. Chub, Red and Blue Chalk Lake sediments imparted a dark brown colour to the water, typical of humic lakes. Humic acids are relatively bioresistant and low rates of oxidation can be expected in sediments dominated by this type of material. This, of course, does not explain the high P_1 value estimated for the sediment of Chub Lake.

The Hamilton Harbour sediments appeared to have a larger particle size than the Muskoka sediments. This most likely results in higher permeability within the matrix and a higher transport rate of soluble

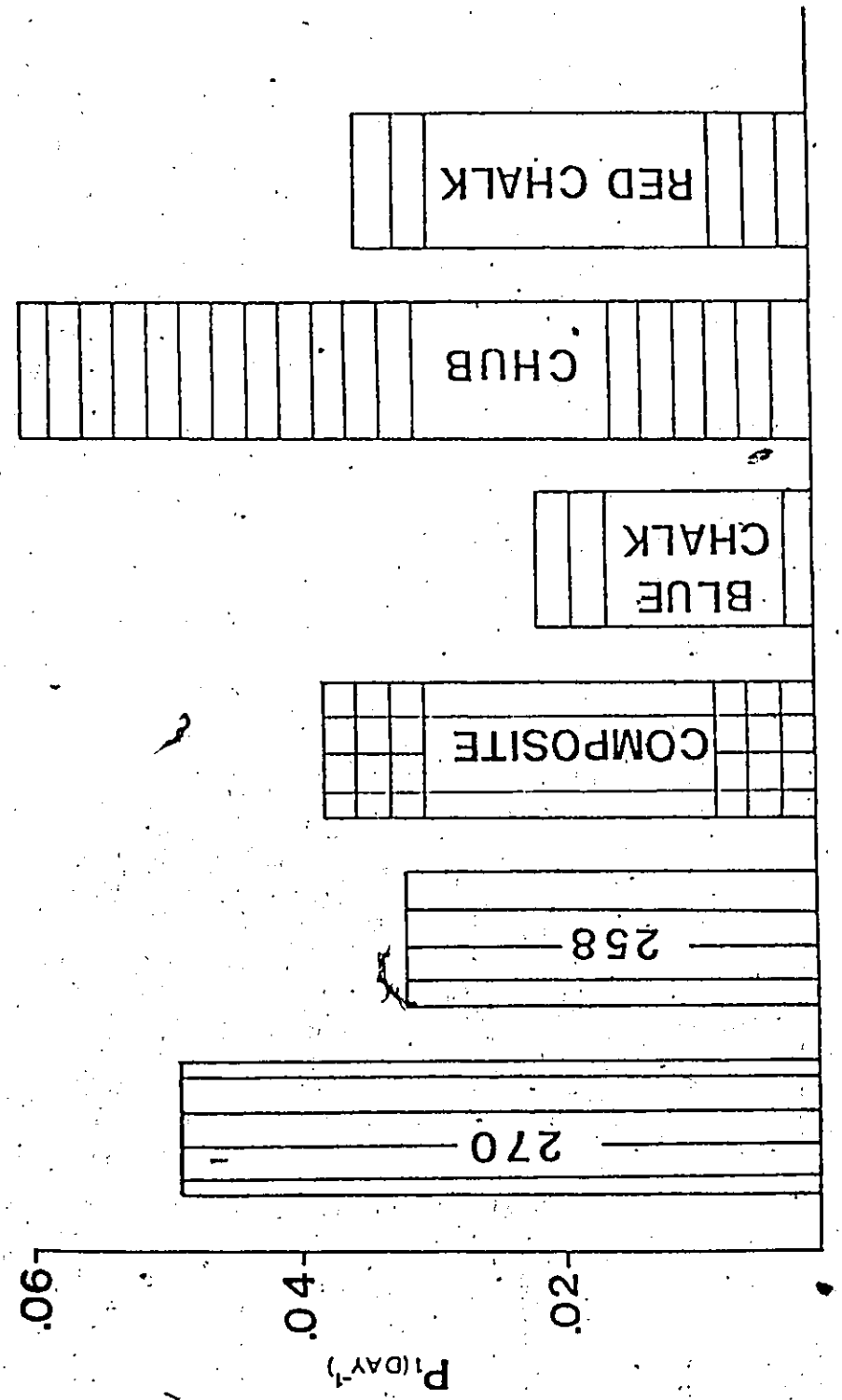


Figure 31. Histogram of computed P_1 values, the independent variable, for each of the laboratory sediments.

material. In fact, Hamilton Harbour sediment columns had an oxidized zone thickness of only about 1 to 2 cm while the Muskoka sediments had an oxidized zone thickness of about 2 to 3 cm. It follows that a thinner oxidized zone results in a larger oxygen gradient. This could be a result of more rapid upward mobility of reduced ions and less resistance to interstitial movement. This explains higher relative rates in the Harbour sediments than in Red and Blue Chalk Lake sediments.

Bubble formation was clearly visible in the Hamilton Harbour sediments and was not apparent in the Muskoka sediments. These bubbles, most probably methane, tend to grow beneath the sediment surface, then rise up through the water column disturbing and mixing the sediment. Soluble material transport is drastically affected when a large bubble rises.

These observations do not explain the high rates measured in the Chub Lake sediment but do emphasize that there are significant physical, chemical and biological differences among samples. Future research in this area should explore the characteristics of diffusion, the chemical and physical structure and the biological community in the sediments in an attempt to explain this phenomenon.

7.2. Biological Sediment Oxygen Demand

The total uninhibited (unpoisoned) sediment oxygen demand (TSOD) of six sediment types was observed in 60 separate experiments conducted at five temperatures. All experiments were conducted in duplicate on identical pairs of sediment samples. These experiments were allowed to continue until dissolved oxygen was near the lower limits of detection or until four weeks elapsed. Graphs of dissolved oxygen versus time aided in the selection of an appropriate model to describe the biological portion of the sediment oxygen demand (BSOD). The first-order CSOD model, discussed in the previous section, was included in the TSOD model and the computer-estimated rates were used to account for this fraction. The Michaelis-Menton (M-M) model, described in Chapter 6, was selected to represent the BSOD fraction.

The M-M model contains two parameters termed $\hat{\mu}_{max}$, the specific rate constant, and $K_{\frac{1}{2}}$, the half-saturation constant. For simplicity, and to aid in further comparisons, $K_{\frac{1}{2}}$ was standardized. This necessitates an additional set of computer 'runs' to estimate the best value of $K_{\frac{1}{2}}$. Table 10 lists the computer-selected values for $\hat{\mu}_{bmax}$ and $K_{\frac{1}{2}}$ derived in the first series of 'runs'. For the second series of 'runs',

Table 10

BSOD Oxygen Model Estimated Parameter Values

Sediment sample	Temp. °C	First run		$K_{\frac{1}{2}} = 1.4$
		$\hat{\mu}_{bmax}$	$K_{\frac{1}{2}}$	$\hat{\mu}_{bmax}$
270	4	0.301	0.705	0.336
	4	0.741	2.606	0.638
	8	0.801	5.099	0.478
	8	1.061	1.957	0.969
	12	0.642	0.004	0.812
	12	0.470	0.261	0.581
	16	1.333	1.526	1.306
	16	1.181	1.715	1.523
	22	3.747	0.766	4.250
	22	4.706	2.276	4.023
258	4	0.573	1.649	0.589
	4	0.657	1.141	0.723
	8	1.096	1.876	0.983
	8	1.350	4.662	0.865
	12	0.756	1.575	0.715
	12	0.535	0.007	0.661
	16	1.224	0.797	1.361
	16	1.628	0.396	1.965
	22	5.595	1.553	5.431
	22	8.407	3.418	5.940

Table 10
(Cont'd)

BSOD Oxygen Model Estimated Parameter Values

Sediment	Temp. °C	First run		$K_{\frac{1}{2}} = 1.4$
		$\hat{\mu}_{bmax}$	$K_{\frac{1}{2}}$	$\hat{\mu}_{bmax}$
Composite	4	0.404	0.916	0.436
	4	0.410	1.161	0.426
	8	0.396	1.586	0.384
	8	0.366	1.118	0.385
	12	0.622	0.981	0.662
	12	0.271	0.00002	0.354
	16	1.163	1.389	1.165
	16	0.486	0.099	0.632
	22	1.916	1.306	1.949
	22	2.280	7.096	1.152
Blue Chalk	4	0.345	0.276	0.415
	4	0.238	0.086	0.306
	8	0.436	1.570	0.424
	8	0.455	2.210	0.403
	12	0.124	0.282	0.127
	12	0.254	1.390	0.254
	16	0.220	0.715	0.252
	16	0.259	0.931	0.285
	22	0.592	1.919	0.540
	22	0.583	1.200	0.607
Chub	4	0.225	0.008	0.269
	4	0.350	0,569	0.401
	8	0.601	4.465	0.405
	8	0.501	2.544	0.422
	12	0.276	2.147	0.246
	12	0.252	0.571	0.294
	16	0.203	0.167	0.271
	16	0.246	0.727	0.284
	22	0.474	0.686	0.553
	22	0.454	0.554	0.549

Table 10
(Cont'd)

BSOD Oxygen Model Estimated Parameter Values

Sediment sample	Temp. °C	First run		$K_{\frac{1}{2}} = 1.4$
		$\hat{\mu}_{bmax}$	$K_{\frac{1}{2}}$	$\hat{\mu}_{bmax}$
Red Chalk	4	0.616	1.682	0.591
	4	0.335	0.223	0.401
	8	0.178	0.261	0.218
	8	0.183	0.316	0.224
	12	0.202	2.492	0.171
	12	0.221	2.135	0.198
	16	0.137	0.213	0.182
	16	0.107	0.418	0.132
	22	0.318	0.911	0.351
	22	0.480	1.393	0.481

the value of $K_{\frac{1}{2}}$ was fixed at 1.4, the numerical average of the 60 estimated values. Sixty new values of $\hat{\mu}_{bmax}$ were estimated with $K_{\frac{1}{2}}$ fixed. The sums of squares of residuals from these final regressions appear in Table 11. Note that in most cases the second set of sums of squares is only slightly higher than those in the first 'run' despite some significant changes in $K_{\frac{1}{2}}$. These values indicate that the $\hat{\mu}_{bmax}$ value of the M-M model is not highly sensitive to changes in $K_{\frac{1}{2}}$ and, therefore, it is justifiable to fix this term. Table 10 contains the final values of $\hat{\mu}_{bmax}$ for each experiment. Note that the $\hat{\mu}_{bmax}$ values from duplicate sediments are generally in good agreement and increase as temperatures increase. Considerable variation exists among sediment types.

A series of F statistics calculated from the regressions involving the BSOD oxygen model appears in Appendix D, Table D-2. The levels of significance achieved by the regressions are summarized in Table 8. The 1% level was the lowest level tested in this analysis. Note that only three of the 60 regressions did not satisfy the 1% level of significance and these three satisfied the 5% level. These results indicate that the model selected to describe the biological fraction of the TSOD is appropriate and that the $\hat{\mu}_{bmax}$ values

Table 11

BSOD Oxygen Model Regression Sums of Squares

Sediment sample	Temp. °C	Sums of squares of regression	
		$K_{1\frac{1}{2}}$ floating	$K_{1\frac{1}{2}} = 1.4$
270(1)	4	0.07	0.14
	8	1.52	1.90
	12	2.77	3.96
	16	3.40	3.40
	22	0.43	0.52
270(2)	4	0.21	0.28
	8	0.39	0.42
	12	1.22	1.59
	16	0.90	1.06
	22	1.22	1.30
258(1)	4	0.10	0.13
	8	2.03	2.08
	12	6.57	6.38
	16	0.43	0.48
	22	0.84	0.84
258(2)	4	0.46	0.42
	8	0.45	0.72
	12	2.52	3.48
	16	0.42	0.62
	22	0.60	0.75

Table 11
(Cont'd)

BSOD Oxygen Model Regression Sums of Squares

Sediment sample	Temp. °C	Sums of squares of regression	
		$K_{1/2}$ floating	$K_{1/2}$ = 1.4
Composite(1)	4	0.42	0.49
	8	0.23	0.24
	12	0.21	0.23
	16	0.62	0.62
	22	1.73	1.73
Composite(2)	4	0.82	0.83
	8	0.05	0.07
	12	0.32	1.00
	16	1.56	1.74
	22	9.00	9.83
Blue Chalk(1)	4	0.98	1.53
	8	0.19	0.19
	12	2.30	2.30
	16	0.18	0.24
	22	0.34	0.35
Blue Chalk(2)	4	2.38	3.52
	8	0.46	0.54
	12	0.42	0.42
	16	0.13	0.15
	22	0.46	0.46
Chub(1)	4	5.68	7.05
	8	0.19	0.71
	12	0.36	0.38
	16	0.04	0.37
	22	0.13	0.18

Table 11
(Cont'd)

BSOD Oxygen Model Regression Sums of Squares

Sediment sample	Temp. °C	Sums of squares of regression	
		$K_{1/2}$ floating	$K_{1/2}$ = 1.4
Chub(2)	4	1.09	1.34
	8	0.55	0.69
	12	0.04	0.14
	16	0.01	0.07
	22	0.31	0.39
Red Chalk(1)	4	0.18	0.20
	8	1.01	1.94
	12	0.46	0.70
	16	0.30	0.58
	22	0.32	0.42
Red Chalk(2)	4	1.35	2.54
	8	0.86	1.32
	12	0.18	0.22
	16	0.60	0.86
	22	0.50	0.52

estimated are accurate for a specific column at a controlled temperature. Figure 32 illustrates a typical set of dissolved oxygen versus rate data as well as the model regression with the 95% confidence interval for the BSOD and TSOD curves.

The M-M model reflects a transition in terms of oxygen dependency. At low concentrations, the reaction becomes limited in a first-order manner by the low supply of oxygen to the sediment surface and into the thin oxidized layer. At high oxygen concentrations, BSOD is independent of oxygen concentration and some other reactant limits the reaction.

The oxygen demand of the overlying water was measured on several occasions as it was in the poisoned columns. The overlying water exerted a negligible oxygen demand in the columns which contained Muskoka sediments. In the columns which contained Hamilton Harbour sediment, the oxygen demand exerted in the water was significant and highly variable. These columns also contained substantial populations of macroinvertebrates and undoubtedly a strong causal relationship exists between macroinvertebrate activity and oxygen demand in the water. The water above the Muskoka sediments which contained no macroinvertebrates was relatively clear, while the water in the Harbour columns

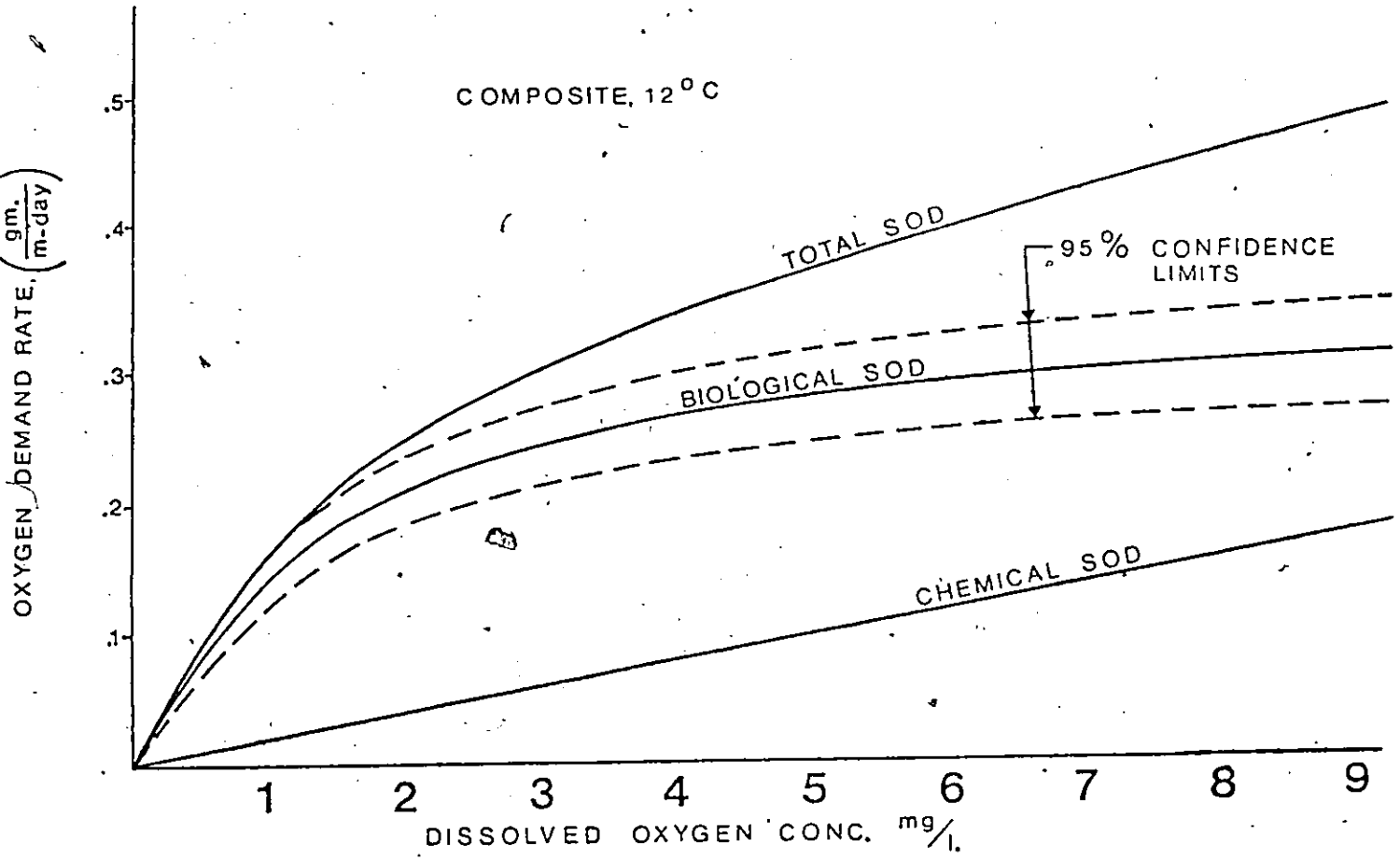


Figure 32. Total sediment oxygen demand (TSOD), biological sediment oxygen demand (BSOD), with 95% confidence limits and chemical sediment oxygen demand (CSOD) versus oxygen concentration at 12°C.

was turbid. Macroinvertebrates are known to excrete organic material into the water resulting in accelerated oxidation rates and a transport of sediment organic material (see section 2.8). It was decided that this component of the total oxygen demand of the system should be included in the BSOD term since this phenomenon is sediment related. This zone of accelerated activity in the water column is likely limited to a shallow layer directly above the sediment surface within the zone of influence of the macroinvertebrates. The water in the columns, in question, was clearer near the top.

Each of the six sediment types (12 columns) was subjected to five controlled temperatures. To assess the response of these systems to temperature, the $\hat{\mu}_{bmax}$ values were plotted against temperature, as shown in Figure 33. The model form discussed in Chapter 6 was selected because of its applicability in situations involving bacterial communities. This model is very similar to that used to describe the response of the poisoned columns to temperature. The modelling procedure involved estimating three parameters: R_1, R_2 and R_3. The routine used to systematically standardize R_2 and R_3 was identical to that described in section 7.1.

The R_1, R_2 and R_3 values estimated for each sediment in the preliminary analysis along with the

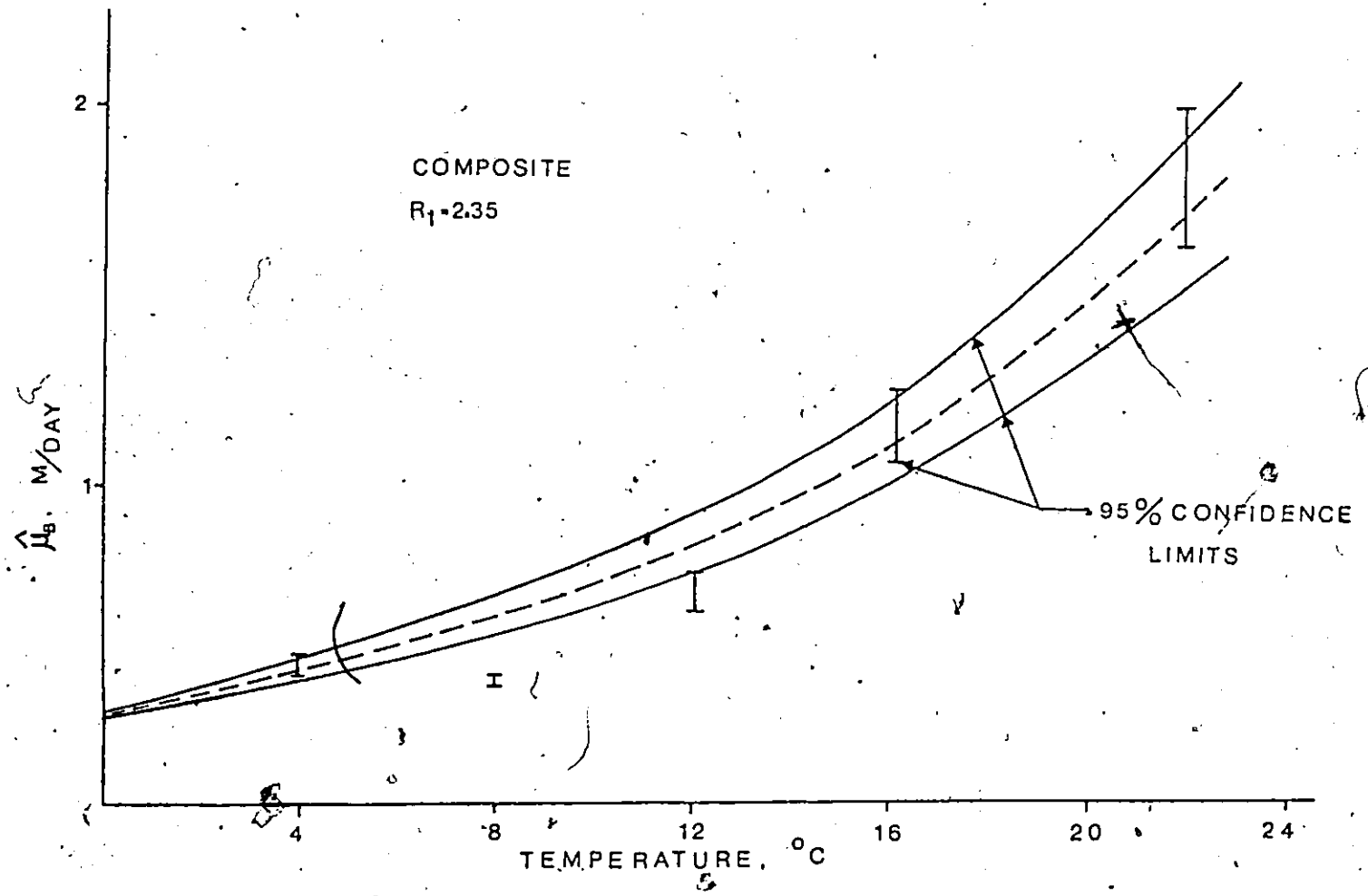


Figure 33. $\hat{\mu}_{bmax}$ versus temperature with regression and confidence limits.

sums of squares of residuals and the mean and variance of R_2 and R_3 are listed in Table 12. The second section in this table lists new values of R_1 and R_2 resulting from regressions with R_3 fixed at 25. Note that in most cases the sum of squares of residuals did not change despite some significant changes in R_3 (see station 258(2) and Chub (2), Table 12). The 12 R_2 values were then averaged and an estimated value of 1.085 was obtained. This parameter had a very low variance in the first two series of regressions. The final set of regressions with R_2 and R_3 fixed yielded new R_1 values and slightly higher sums of squares of residuals. In most cases, duplicate sediments had similar R_1 values.

Appendix D, Table D-2 contains the F statistics for the 12 temperature model regressions. Levels of significance achieved are summarized in Table 8. The Hamilton Harbour sediments and the composite sample displayed levels of significance below 10% while the regressions for the Muskoka sediments were not acceptable. The poor results of regression with the Muskoka sediments were due, in part, to the low number of degrees of freedom involved. However, a mechanistic explanation is also possible. The $\hat{\mu}_{bmax}$ values for the Muskoka sediments, as recorded in Table 10, generally decrease from 4° to 8° and 12° and then increase at 16°

Table 12

BSOD Temperature Model Parameter Estimates

Model used: $\hat{\mu}_{bmax} = R_1 \cdot R_2^{(Temp. - R_3)}$

Sediment sample	R_1	R_2	R_3	$\Sigma(residuals)^2$	$R_3 = 25$			$R_2 = 1.085$	
					R_1	R_2	$\Sigma(residuals)^2$	R_1	$\Sigma(residuals)^2$
270(1)	1.87	1.19	17.3	0.07	7.12	1.19	0.07	4.17	2.34
270(2)	1.95	1.15	17.1	0.46	6.08	1.15	0.46	4.20	1.57
258(1)	1.88	1.21	16.5	0.68	9.48	1.21	0.68	5.20	4.54
258(2)	1.96	1.19	15.7	0.49	10.03	1.19	0.49	5.83	4.89
Composite(1)	1.55	1.11	19.6	0.03	2.65	1.11	0.03	2.35	0.08
Composite(2)	1.16	1.08	27.6	0.05	1.41	1.08	0.05	1.42	0.05
Blue Chalk(1)	0.52	1.02	37.0	0.10	0.43	1.02	0.10	0.73	0.17
Blue Chalk(2)	0.70	1.04	28.8	0.05	0.60	1.04	0.05	0.81	0.08
Chub(1)	0.65	1.04	29.9	0.04	0.54	1.04	0.04	0.75	0.07
Chub(2)	0.57	1.02	36.5	0.04	0.47	1.02	0.04	0.80	0.13
Red Chalk(1)	0.35	1.00	46.7	0.14	0.14	0.94	0.09	0.55	0.26
Red Chalk(2)	0.47	1.02	35.9	0.08	0.37	1.02	0.08	0.60	0.12
Mean		1.08	26.96	0.187		1.085	0.183		1.27
Variance		0.006	106.7			0.007			

and 22°. It is possible that during the course of the experiments a transition in bacterial community occurred which resulted in a psychrophilic (low temperature) population dying out to be replaced by a mesophilic (warm temperature) dominant population. In reality, the Muskoka lake sediments seldom rise above 6°C; consequently, they are likely to support a significant psychrophilic bacterial community unacclimatized to large temperature change. In the laboratory this community would be partially inhibited at the 8 and 12°C temperatures. The mesophilic population would begin to establish itself at 12 and 16°C and the response to temperature change in this range would be more typical of a warm water community.

The regressions on the Hamilton Harbour data were reasonably good and no community transition is apparent. Hamilton Harbour sediments exceed 12°C annually. A Q_{10} of 2.26 corresponds to the resultant model and is typical of aerobic bacterial communities.

Significant differences exist between the sediment reaction rates when $\hat{\mu}_{bmax}$ values are compared. Table 10 shows $\hat{\mu}_{bmax}$ values at 22° for station 258 which are more than 10 times greater than those at 22° in Red Chalk sediments. Undoubtedly, the presence of macroinvertebrates in the Harbour sediments has a

significant direct and indirect effect on these rates. This question is examined in more detail in the following section. Other observations made on the poisoned columns (see section 7.1) are also applicable here. The humic content and the physical structure of the sediment matrix also strongly influence oxidation rates. It was stated in section 7.1 that the Harbour sediments are most likely more permeable and contained less humic material than the fine grained material from the Muskoka lakes. Undoubtedly, these characteristics influence ultimate reaction rates of the sediments.

7.3. Macroinvertebrate Oxygen Uptake (MSOD)

An attempt was made in this study to estimate the relative contribution of the macroinvertebrates to the BSOD. Three sediment-water columns were treated with streptomycin and penicillin to block bacterial oxygen uptake. This treatment reportedly leaves the macroinvertebrate population unaffected. Chemical sediment oxygen uptake continues as long as reduced ions exist below the oxidized layer. Three duplicate columns were dismantled and the macroinvertebrate species in each column were identified and counted. Twelve experiments at 4 different temperatures were conducted on the intact columns. These experiments proceeded in the

same manner as the previously discussed CSOD and BSOD experiments. The purpose of this portion of the study was to estimate the relative contribution of macroinvertebrate respiration to the total BSOD. No quantitative evaluation was made of the indirect effects of these animals on the TSOD, nor was there an attempt made to examine other possible kinetic expressions to describe the oxygen dependency or temperature relationships of the macroinvertebrate community. For simplicity, the same models were used to estimate the MSOD parameters, $\hat{\mu}_{mmax}$ and M_1 as discussed in section 7.2 for BSOD. The literature regarding macroinvertebrates (see sections 2.7 and 2.8) indicates that similarities exist in the oxygen and temperature kinetics of macroinvertebrates and aerobic bacteria. The models for MSOD, therfore, appear as:

$$MSOD = \frac{\hat{\mu}_{mmax} \cdot [O_2]}{1.4 \cdot [O_2]} \qquad (18)$$

$$\hat{\mu}_{mmax} = M_1 \cdot 1.085^{(T - 25)} \qquad (19)$$

The same k_c values were used in estimating $\hat{\mu}_{mmax}$ as were used to estimate $\hat{\mu}_{bmax}$.

Table 13 lists $\hat{\mu}_{mmax}$ and M_1 values estimated for the 12 experiments involving sediments from Hamilton Harbour and the composite sample. The $\hat{\mu}_{mmax}$ values

Table 13

MSOD Oxygen and Temperature Model Parameter Estimates

Models used: (Oxygen) $MSOD = \frac{\hat{\mu}_{mmax}}{1.4 + [O_2]}$

(Temperature) $\hat{\mu}_{mmax} = M_1 \cdot 1.085^{(Temp - 25^{o})}$

Sediment sample	Temp. ^{o}C	$\hat{\mu}_{mmax}$	M_1	$\Sigma(Residuals)^2$
270	4	0.054		
	12	0.312	0.844	0.021
	16	0.323		
	22	0.774		
258	4	0.270		
	12	0.423	2.191	0.613
	16	0.551		
	22	2.199		
Composite	4	0.061		
	12	0.311	1.067	0.046
	16	0.408		
	22	0.955		

increase with temperature and are highly variable from one column to another. Appendix D, Table D-2 contains the F statistics for the 12 regressions used to calculate the $\hat{\mu}_{mmax}$ values. Table 8 summarizes the levels of significance achieved by these regressions. Only one experiment had a level of significance greater than 1% in this set of 'runs'. The temperature model was less successful as M_1 values were estimated with levels of significance ranging from a low of less than 10% to almost 25%. This disappointing statistic is undoubtedly due, in part, to the low number of data points used in these regressions and the subsequent low number of degrees of freedom. It is clear from these results, however, that the macroinvertebrate community respiration is limited by low oxygen concentrations and responds to temperature in a manner similar to mixed bacterial communities.

The values of M_1 and the sum of squares of residuals from these regressions are listed in Table 13. The M_1 value, by definition, is a constituent part of the R_1 values. When the M_1 values are compared to R_1 values for the corresponding sediment, it can be seen that the contribution of macroinvertebrate respiration to BSOD is significant. M_1 accounts for 20% of R_1 for sediment 270, 40% of R_1 for sediment 258 and 57%

of the composite R_1. Table 14 lists macroinvertebrate species identified and counted in the three columns (A.W. McLarty, West-Central Region, Ontario Ministry of the Environment, personal communication). Three species were identified with the majority of animals being of the species *Limnodrilus hoffmeisteri* and *Tubifex tubifex*. The numbers found in each column are listed along with the projected density. No clear relationship exists between densities and respiration rates as represented by M_1.

The observed respiration rates can be compared to those reported in the literature (see section 2.7, Table 4). Table 15 contains the respiration rates reported by various authors (at 20°C or summer conditions) as well as the rates of respiration projected for a community of the same density estimated in this study. Brinkhurst *et al.* (1972) reported respiration rates by species and so it was possible to estimate the total community respiration by combining the respiration of each species of macroinvertebrate. However, Brinkhurst's values represent endogenous respiration as his experiments were carried out in inorganic environments. The values reported by Smith *et al.* (1973) and Hargrave (1969) were derived in natural environments. The range of reported values is broad

Table 14

Macroinvertebrate Species and Densities in Laboratory Columns

Species	Sediment sample		
	270	258	Composite
Limnodrilus hoffmeisteri	30	77	13
Tubifex tubifex	47	41	3
Peloscolex multisetosus	3	6	2
Total density individuals/m^2	20800	32240	4700

Table 15

Macroinvertebrate Respiration Rates Predicted From This Study and Reported in the Literature

Sediment column and (animal density)	Smith *et al.* (1973) (summer)	Hargrave (1969) (summer)	Brinkhurst (1972) (20°C)	Predicted MSOD (8 mg/ℓ D.O.) (20°C)
270 (20800)	0.33	0.54	0.14	0.48
258 (32240)	0.50	0.83	0.21	1.24
Composite (4700)	0.07	0.12	0.03	0.60

but the values predicted from this study are well within the same order of magnitude.

The indirect effects of macroinvertebrates are also likely significant in contributing to TSOD. Figure 34 is a photograph of a laboratory column showing worm tunnels. The oxidized zone depth in the KCN-poisoned columns was about 1 to 2 cm while in these columns it appears to have been extended to a 3 or 4 cm depth. This deepening of the oxidized zone by the worms has the effect of increasing the active surface area available for colonization by bacteria. These tunnels also act as channels along which oxygen can diffuse and thereby increase the supply of oxygen to the site of reaction. The macroinvertebrates tunnel with their posterior pointing upward into the water. They excrete material into the water or onto the sediment surface. As a result, the water becomes more turbid; more oxygen consumption occurs in the water column and the surface sediments are enriched with organic material. Worms tend to overturn the surface layer of sediments, homogenizing this layer and making previously unavailable material available for aerobic oxidation. The net result of these activities is to increase TSOD and to lead to more complete oxidation of sediment organics. The macroinvertebrate-bacteria relationship is a true symbiosis.

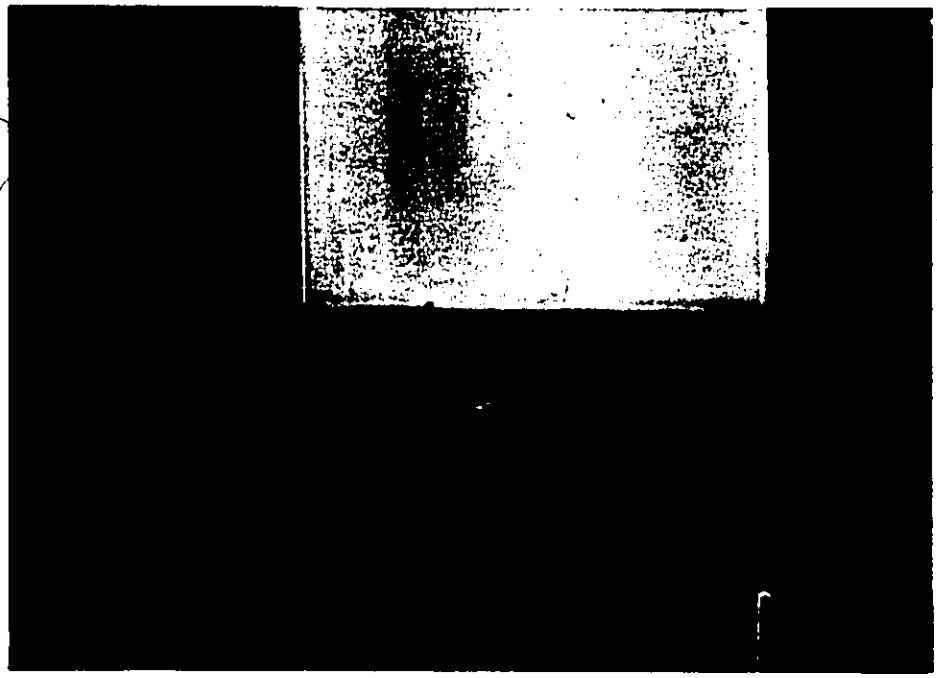


Figure 34. Laboratory column with visible macroinvertebrate tunnel network.

7.4. Model Predictions Compared to *In situ* Measurements

SOD predictions are made for Hamilton Harbour and compared to *in situ* measurements in this section. Table 16 contains the *in situ* SOD measurement values collected in 1976 in Hamilton Harbour at the sites of sediment sample stations 270 and 258. Predicted values are calculated by the four models discussed in this chapter as follows:

CSOD

A. Temperature model,

$$C_3 = P_1 \cdot 0.907^{(20 - 12)}$$
$$= P_1 \cdot 0.458 \qquad (20)$$

P_1 for station 258 = 0.031 m/day from Table 9 and 0.048 m/day for station 270, therefore

$$C_3(258) = 0.031 \cdot 0.458 = 0.014 \text{ m/day} \qquad (21)$$

$$C_3(270) = 0.048 \cdot 0.458 = 0.022 \text{ m/day} \qquad (22)$$

B. Oxygen model,

$$CSOD(258) = [O_2] \cdot 0.014 \text{ gm/m}^2\text{-day} \qquad (23)$$

$$CSOD(270) = [O_2] \cdot 0.022 \text{ gm/m}^2\text{-day} \qquad (24)$$

Predicted CSOD portions of the rate are listed in Table 16.

Table 16

Predicted and Measured SOD Rates from Hamilton Harbour

Station	Temp. °C	$[O_2]$, mg/ℓ	*In situ* gm/m²-day	Predicted, gm/m²-day		
				chemical	biological	total
270	12	6.0-7.8	2.21	0.13	1.15	1.28
270	12	1.1-4.3	1.30	0.06	0.87	0.93
270	12	1.8-3.0	1.82	0.05	0.91	0.96
270 (CSOD)	12	1.4-2.2	0.30	0.04	-	-
258	12	5.2-6.0	2.03	0.07	1.49	1.56
258	12	1.6-2.7	1.27	0.03	1.14	1.17
258	12	2.3-2.6	1.14	0.03	1.22	1.25
258 (CSOD)	12	5.8-6.5	0.30	0.09	-	-

BSOD

A. Temperature model,

$$\hat{\mu}_{bmax} = R_1 \cdot 1.085^{(12 - 25^{o}C)}$$
$$= R_1 \cdot 0.346 \qquad (25)$$

R_1 for station 258 is 5.516 from Table 12 and R_1 for station 270 is 4.184, therefore,

$$\hat{\mu}_{bmax}(258) = 5.516 \cdot 0.346 = 1.91 \text{ m/day} \qquad (26)$$

$$\hat{\mu}_{bmax}(270) = 4.184 \cdot 0.346 = 1.45 \text{ m/day} \qquad (27)$$

B. Oxygen model,

$$BSOD(258) = \frac{[O_2] \cdot 1.91}{[O_2] + 1.4} \text{ gm/m -day} \qquad (28)$$

$$BSOD(270) = \frac{[O_2] \cdot 1.45}{[O_2] + 1.4} \text{ gm/m -day} \qquad (29)$$

Predicted versus actual measurements of TSOD are presented in Figure 35. Also in this figure are the *in situ* measurements made by Polak and Haffner (1978) at station 270. The values of Polak and Haffner were standardized to 12° C with the model in equation (25). Note that predicted values are generally slightly lower than the measured values. In addition, predicted CSOD values listed in Table 16 are consistently lower than actual values. One possible explanation for this lies in the fact that macroinvertebrates were not viable in

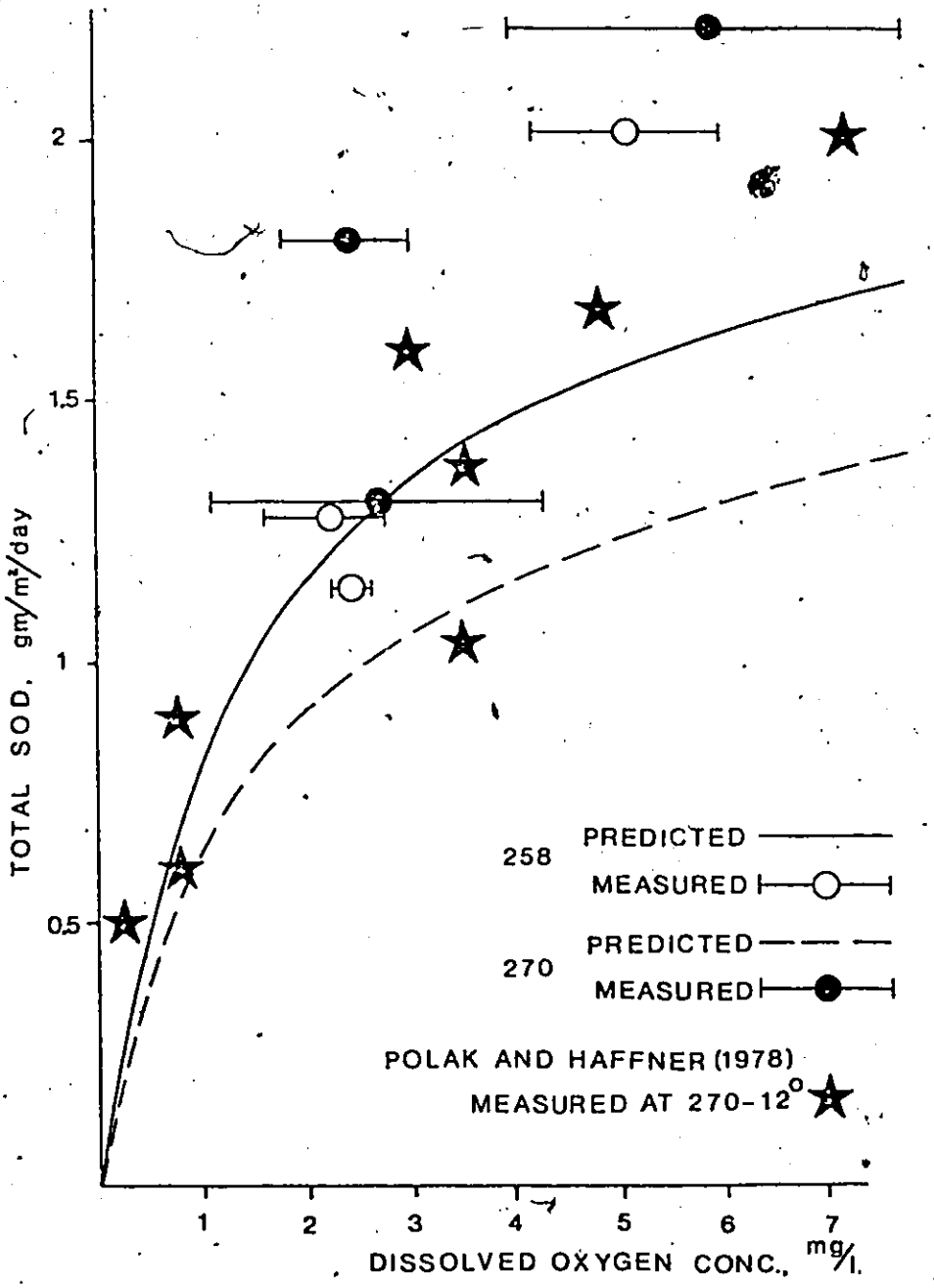
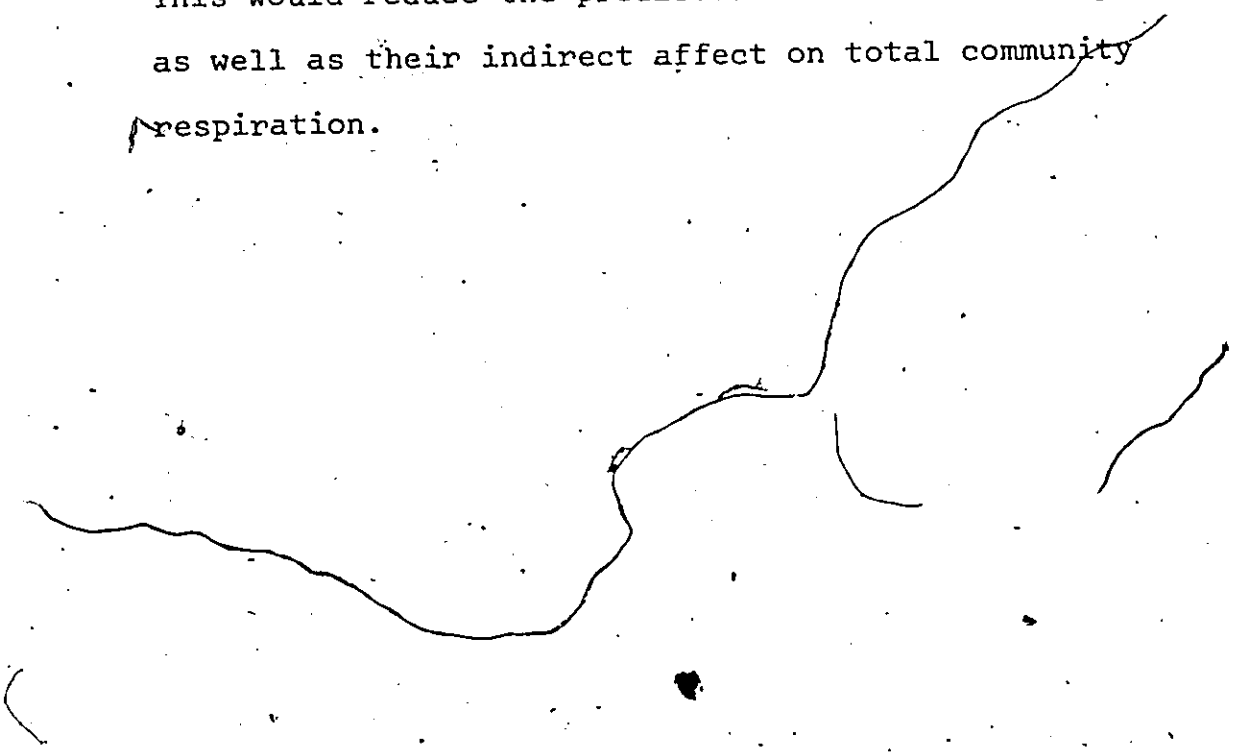


Figure 35. Predicted versus *in situ* values of TSOD at 12°C in Hamilton Harbour. The range of oxygen concentrations over which measurements were made is given.

the laboratory columns used to measure CSOD. Therefore, the indirect effects of macroinvertebrates on CSOD (tunneling and more rapid mixing) were not incorporated into the CSOD models in this study. These factors are important in Hamilton Harbour, however, and undoubtedly accelerated chemical oxidation in the *in situ* measurements. The purpose of this study was to explore the important mechanisms of sediment oxygen uptake through modelling. For simplicity, macroinvertebrates had to be eliminated from the KCN poisoned columns. Also, the density of animals found in the laboratory columns may not have been as high as the densities present in the Harbour when the *in situ* measurements were made. This would reduce the predicted direct animal respiration as well as their indirect affect on total community respiration.



8. SUMMARY

In this work, sediment oxygen demand was measured in the field. Techniques involved were evaluated. To complement this work and the laboratory experimentation, sediment samples were collected and analysed for organic parameters. As well, samples were placed in columns in the laboratory and the oxygen uptake rates were monitored under various conditions of temperature and oxygen concentration. An attempt was made to partition the total uptake into the parts due to chemical oxidation, bacterial respiration and macroinvertebrate respiration. These reactions were modelled to describe the effects of oxygen concentration and temperature on each component part of the TSOD and to gain insight into the important physical, chemical and biological mechanisms involved.

In situ measurement was found to be a valuable tool for estimating SOD for a specific location under the prevailing conditions. It is, perhaps, the most accurate in that it perturbs the system the least. The method is, however, subject to error, inasmuch as the equipment tends to cause local disturbances. These disturbances can be minimized with careful handling

techniques and proper equipment design. The subsequent errors can be reduced by allowing measurements to proceed for long periods of time (24 hours) and allowing the system to return to near natural conditions. The chemical portion (CSOD) of the total uptake can be partitioned with *in situ* measurements if, once again, measurements are allowed to proceed for long periods of time to allow the inhibitors to be effective. Repeatability in these measurements was only fair. This study is not able to conclude whether observed variability is due to measurement error or actual spatial and temporal variability in sediment properties. The former, to some extent, is likely.

Three organic parameters were used as measures of sediment organic characteristics in an attempt to measure biodegradability. It was found that loss on ignition, organic carbon and carbohydrate analysis were not independent of each other despite the large sample set analysed. Each method is indicative of the total organic fraction rather than the more readily available fraction of the organics. Considerable spatial variability in the organic content was found to exist in Hamilton Harbour. As well, large variations existed at two of the stations indicating that spatial variability, at least in some regions, is significant in

the small scale. These stations were subject to local pollutant loads and fluctuations in the lake's thermal regime. Despite an apparent low organic fraction by weight, the Harbour sediments were found to contain an equivalent amount of organic material in volumetric units to Muskoka sediments which have very high organic contents by weight. It is recommended that organic fractions of sediments be reported in volumetric units.

The effect of the oxygen concentration in the overlying water on CSOD was found to be of a first-order type. This dependency was successfully modelled in this study indicating that the reaction is most likely limited by diffusion of oxygen through the oxidized zone of sediments to the site of the reaction, at a fixed temperature. As temperature increases, the rate of CSOD increases. This effect was successfully modelled with an expression which is typical of biological reactions. It is most likely that the metabolic activity of anaerobic bacteria limit the CSOD at a fixed oxygen concentration. Variations in CSOD among sediments at the same temperature and oxygen concentration is partially explainable in terms of sediment physical and chemical structure. More research is needed in this area.

The respiration of the aerobic bacterial community (BSOD) was successfully modelled with a Michaelis-Menton

model. The model indicates that at high oxygen concentrations BSOD is independent of oxygen concentration and as oxygen is depleted, oxygen uptake becomes limited in a first-order fashion with respect to oxygen concentration. A temperature model, typical of biological systems, was found to be reasonably accurate in describing the response of the Hamilton Harbour sediment system to temperature change. The same model was not successful when applied to the Muskoka sediments. This result is possibly explainable, in that, a change in bacterial community, from psychrophilic to mesophilic, may have taken place during the course of the experiments. Substantial rate increases occurred in the higher temperature range for these sediments. Oxygen consumption in the overlying water was observed to be significant in columns which supported macroinvertebrates. It was concluded that since this phenomenon was due to sediment-related activity it should be included in the BSOD term. Considerable differences existed in the SOD of the various sediments involved in this study after the effects of temperature, oxygen concentration and the direct respiration of macroinvertebrates had been eliminated. It was felt that these differences were due to the physical and chemical differences of the sediments particularly as they are affected by macroinvertebrates.

Macroinvertebrate oxygen uptake was successfully modelled with the same kinetic expressions for oxygen concentration and temperature as were used to describe BSOD. Higher levels of significance were due, in part, to a low number of degrees of freedom in these experiments. The worms respond in a similar manner to oxygen concentration and temperature as do bacteria. Macroinvertebrates were found to contribute as much as half of the BSOD in some sediments in this study. As well, the indirect effects of macroinvertebrates was observed and appeared significant in terms of increasing the depth and permeability of the oxidized zone, enriching surface sediments, recycling buried organic matter and pumping material into the overlying water. Reported literature respiration rates for similar densities of animals at similar temperatures agreed favourably with rates measured in this study. More research is needed in this area, particularly into the indirect effects of macroinvertebrates on SOD.

Model predictions of SOD in Hamilton Harbour, based on the laboratory study, were compared to *in situ* measurements. Correspondence was fair with predicted values generally slightly lower. This result was probably due to the fact that the CSOD predictions were underestimates in that the indirect effects of

macroinvertebrates on CSOD was not included in the laboratory study or the CSOD models. Animal densities in the laboratory may have been lower than those encountered in the field.

The models developed in this study were, in general, found to be successful in simulating the response of sediment communities to various conditions of temperature and oxygen concentration and in assisting in the explanation of the important mechanisms involved. These models are, however, site specific in that no quantitative account is made of the absolute values of potential sediment oxidizability in universal terms. This is the area which deserves the most intensive research in the future.

LIST OF ABBREVIATIONS

ANOVA	analysis of variance
BSOD	biological sediment oxygen demand
B	temperature model constant in general terms
CARB	carbohydrate
C_o	concentration of a reactant in general terms
C_3	CSOD temperature model parameter
cm	centimetres
CSOD	chemical sediment oxygen demand
f	conversion factor from volumetric to areal units, $M \cdot hr \cdot day^{-1}$
F	F statistic
gm	grams
H.H.	Hamilton Harbour
hrs	hours
K(T)	temperature model rate at temperature T
k_c	first-order rate constant for CSOD oxygen model
$K_{\frac{1}{2}}$	half saturation constant for BSOD and MSOD
L	length
ℓ	litres
LOI	loss on ignition
M	mass
M_1	MSOD temperature model parameter
m	metres

mm	millimetres
mg/ℓ	concentration - milligrams per litre
MSOD	macroinvertebrate sediment oxygen demand
OC	organic carbon
pH	negative log of the hydrogen ion concentration
P_1, P_2, P_3	CSOD temperature model parameters
Q_{10}	increase in rate over a 10°C change of temperature
R_1, R_2, R_3	BSOD temperature model constants
SOD	sediment oxygen demand, also TSOD
STN #	station number
TSOD	total sediment oxygen demand, also SOD
T	temperature, °C, or time
$\overline{\sigma}$	standard deviation
$\overline{\sigma}^2$	variance
$\overline{X}$	mean
[X]	concentration of X
∞	infinity
μ	microns
$\hat{\mu}$	Michaelis-Menton specific rate constant
$\hat{\mu}_{bmax}$	Michaelis-Menton specific rate constant for BSOD
$\hat{\mu}_{mmax}$	Michaelis-Menton specific rate constant for MSOD

APPENDIX A

LABORATORY SEDIMENT AND WATER SAMPLE ANALYSIS RESULTS

Table A-1

Laboratory Sediment Column Analysis

Sample location	Sediment density gm (dry)/ml	% organic carbon	Organic carbon density gm/ml	Overlying water		
				alkalinity mg/ℓ $CaCO_3$	pH TSOD columns	colour (CSOD columns) Co-Pt units
STN # 270	0.29	7.3	0.021	150	7.0-8.3	1,150
STN # 258	0.24	13.7	0.033	150	7.0-8.3	950
Composite	0.24	12.1	0.029	85	7.0-8.3	2,000
Blue Chalk	0.06	31.5	0.019	<10	6.5-6.8	2,750
Chub	0.05	44.0	0.024	<10	6.5-6.8	14,000
Red Chalk	0.06	48.6	0.030	<10	6.5-6.8	7,000

APPENDIX B

UWHAUS PROGRAM LISTING AND TYPICAL OUTPUT

```
                                MAIN

0001                EXTERNAL MODEL
0002                DIMENSION SCRAT(300)
0003                DIMENSION TH(2),SIGNS(2),DIFF(2)
0004                COMMON x(30),Y(30)
0005                READ(5,11) NUMBER
0006             11 FORMAT(I2)
0007                DO 89 J=1,NUMBER
0008                APROB=J
0009                NP=1
0010              3 READ(5,4) NOB,TH(1)
0011              4 FORMAT(I3,F10.4)
0012                DO 12 I=1,NOB
0013                READ(5,1000) X(I),Y(I)
0014           1000 FORMAT(2F10.4)
0015                WRITE(6,10) X(I),Y(I)
0016             10 FORMAT(2F9.5)
0017             12 CONTINUE
0018                WRITE(6,8) NOB,TH(1)
0019              8 FORMAT(I3,F10.4)
0020                WRITE(6,9) NUMBER
0021              9 FORMAT(20X, 10HPROBLEM NUMBER, I3)
0022                SIGNS(1)=0.0
0023                DIFF(1)=.01
0024                EPS1=1.0E-5
0025                EPS2=1.0E-5
0026                CALL UNIANS(APROB,MODEL,NOB,X,NP,TH,DIFF,SIGNS,EPS1,EPS2,
                   610,.01,10.,SCRAT)
0027             89 CONTINUE
0028                STOP
0029                END
```

UMMAUS

```
0001                SUBROUTINE UMMAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
                   1  MIT,FLAM,FNU,SCRAT)
0002                DIMENSION SCRAT(1),TH(1),DIFF(1),SIGNS(1),Y(1)
0003                IA=1
0004                IB=IA+NP
0005                IC=IB+NP
0006                ID=IC+NP
0007                IE=ID+NP
0008                IF=IE+NP
0009                IG=IF+NOB
0010                IH=IG+NOB
0011                II = IH + NP * NOB
0012                IJ = IH
0013                CALL MAUS80(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT
                   1  ,FLAM,FNU,SCRAT(IA), SCRAT(IB), SCRAT(IC), SCRAT(ID),
                   2  SCRAT(IE),SCRAT(IF),SCRAT(IG),SCRAT(IH),SCRAT(II),
                   3  SCRAT(IJ) )
0014                RETURN
0015                END
```

MODEL

```
0001                SUBROUTINE MODEL (NPROB, TH,F,NOB,NP)
0002                COMMON X(30),Y(30)
0003                DIMENSION TH(1),F(1)
0004                DO 10 I=1,NOB
0005             10 F(I)=TH(1)*0.907**(20.0-X(I))
0006                RETURN
0007                END
```

```
                                    HAUS59

0001            SUBROUTINE HAUS59(NPROB, MODEL, NOB,Y,NO,TH,DIFZ,SIGMS,EPIS,EPSS,
                1 PHI,TB,F,P,A,D,IFLZ)
                C
0002            DIMENSION TH(1),DIFZ(1),SIGMS(1),Y(1),G(1),P(1),E(1),
                1 PHI(1),TB(1),F(1),P(1),A(1),D(1),IFLZ(1)
0003            ACOS(X)=-ATAN(SQRT(1.0/X**2-1.0))
0004            NP = NO
0005            NPROB = NPROB
0006            NOB = NOB
0007            EPS1=EPIS
0008            EPS2 = EPSS
0009            NPSQ=NP*NP
0010             NSCRAC = 5*NP+NPSQ + 2*NOB+NP*NOB
0011            PRINT 1000, NPROB, NOB, NP, NSCRAC
0012            PRINT 1001
0013            CALL GASSAD(1, NP, TH, TEMP, TEMP)
0014            PRINT 1002
0015            CALL GASSAD(1,NP,DIFZ,TEMP,TEMP)
0016            IF(MINO(NP-1,50-NP,NOB-NP,MII-1,999-MIT)) 99,15,15
0017         15 IF(SENSW(1,0)) 99, 99, 16
0018         16 CONTINUE
0019            DO 19 I=1,NP
0020            TEMP = ABS(DIFZ(I))
0021            IF(AMIN1(1.0-TEMP,ABS(TH(I)))) 99,99,19
0022         19 CONTINUE
0023            CALL CLEAR
0024            MIT =1
0025            LABS = 0
0026            IF(EPS1) 5,70,70
0027          5 EPS1=0
0028         70 SSQ = 0
0029            CALL MODEL(NPROB, TH, F, NOB, NP)
0030            DO 90  I= 1, NOB
0031            R(I) = Y(I) - F(I)
0032         90 SSQ=SSQ+R(I)*R(I)
0033            PRINT 1003, SSQ
                C
                C                       BEGIN ITERATION
```

```
      100  GA = GA/FNU
           INTCNT = 0
           PRINT 1004, NIT
      101  JS = 1 + NOB

           DO 130 J=1,NP
           TEMP = TH(J)
           P(J)=DIFZ(J)+TH(J)
           TH(J)=TH(J)+P(J)
           B(J)=0
           JS = JS + NOB
           CALL MODEL(NPNOB, TH, DELZ(JS), ANS, NP)
           IJ=JS-1
           DO 120 I = 1, NOB
           IJ = IJ + 1
           DELZ(IJ) = DELZ(IJ) - F(I)
      120  B(J) = B(J) + DELZ(IJ) * P(I)
           H(J)= H(J)/P(J)
C                                        G=X1-B (STEEPEST DESCENT)
      130  TH(J) = TEMP

           IF(LAUS) 131,131,919
      131  DO 150 I= 1, NP
           DO 151 J=1,1
           SUM = 0
           KJ = NOB*(J-1)
           KI = NOB*(I-1)
           DO 160 K= 1, NOB
           KI = KI + 1
           KJ = KJ + 1
      160  SUM = SUM + DELZ(KI) * DELZ(KJ)
           TEMP = SUM/(P(I)*P(J))
           JI = J + NP*(I-1)
           B(JI) = TEMP
           IJ = I + NP*(J-1)
      151  B(IJ) = TEMP
      150  E(I) = SQRT(B(JI))
      666  CONTINUE
           DO 153 I = 1, NP
           IJ = I*NP
```

```
0071                  DO 153 J=1,I
0072                  IJ =IJ + NP
0073                  A(IJ) = A(IJ) / (E(I)*E(J))
0074                  JI = J + NP*(I-1)
0075            153   A(JI) = A(IJ)
                C                    A= SCALED MOMENT MATRIX
0076                  II = II + NP
0077                  DO 155 I=1,NP
0078                  P(I)=Q(I)/E(I)
0079                  PHI(I)=P(I)
0080                  II = NP + I + II
0081            155   A(II) = A(II) + GA
                C
0082                  I=1
0083                  CALL MATI(A,NP,P,I,DET)
                C                    P/E = CORRECTION VECTOR
0084                  STEP=1.0
0085                  SUM1=0.
0086                  SUM2=0.
0087                  SUM3=0.
0088                  DO 234 I=1,NP
0089                  SUM1=P(I)*PHI(I)+SUM1
0090                  SUM2=P(I)*P(I)+SUM2
0091                  SUM3= PHI(I) * PHI(I) + SUM3
0092            241   Q(I) = P(I)
0093                  TEMP = SUM1/SQRT(SUM2*SUM3)
0094                  IEMP = AMIN1(TEMP,1.0)
0095                  IEMP = 57.295*ACOS(IEMP)
0096                  PRINT 1041, DET, IEMP
0097            170   DO 220 I = 1, NP
0098                  P(I) = PHI(I) *STEP / E(I)
0099                  TB(I) = TH(I) + P(I)
0100            220   CONTINUE
0101                  PRINT 7000
0102          1 7000  FORMAT(1HONEXT ST P(I)+1 PARAMETER VALUES )
0103                  PRINT 2006, (TB(I), I = 1, NP)
0104                  DO 221 I = 1, NP
0105                  IF(SIGNS(I)) 221, 221, 222
0106            222   IF(SIGN(1.0,TH(I))*SIGN(1.0,TB(I))) 223, 221, 221
0107            221   CONTINUE
0108                  SUM=0
```

```
0109                CALL MODEL(NPROB, TH, F, NOB, NP)
0110                DO 230 I=1,NOB
0111                R(I)=Y(I)-F(I)
0112          230   SUMB=SUMB+R(I)*R(I)
0113                PRINT 1003, SUMB
0114                IF(SUMB - (1.0+EPS1)*SSQ) 270, 270, 265
0115          663   IF( AMIN1(TEMP-30.0, GA)) 665, 665, 664
0116          665   STEP=STEP/2.0
0117                INTCNT = INTCNT + 1
0118                IF(INTCNT - 36) 170, 2700, 2700
0119           664  GA=GA+FNU
0120                INTCNT = INTCNT + 1
0121                IF(INTCNT - 36) 666, 2700, 2700
0122          662   PRINT 1007
0123                DO 669 I=1,NP
0124          669   TH(I)=TH(I)
0125                 CALL GASSOO(I, NP, TH, TEMP, TEMP)
0126                PRINT 1000, GA, SUMB
0127                IF(EPS2) 229,229,225
0128          229   IF(EPS1) 270,270,265
0129          225   DO 240 I = 1, NP
0130                IF(ABS(P(I)/(1.E-20+ABS(TH(I)))-EPS2) 240,240,241
0131           241  IF(EPS1) 270,270,265
0132          240   CONTINUE
0133                PRINT 1009, EPS2
0134                GO TO 280
0135          265   IF(ABS(SUMB - SSQ) - EPS1*SSQ) 280, 280, 270
0136          266   PRINT 1010, EPS1
0137                GO TO 280
0138          270   SSQ=SUMB
0139                NII=NITT
0140                IF(NII - NITT) 100, 100, 280
0141          2700  PRINT 2710
0142          2710  FORMAT(//,15H0****THE SUM OF SQUARES CANNOT BE REDUCED TO THE SUM
                    1OF SQUARES AT THE END OF THE LAST ITERATION - ITERATING STOPS  /)
                C
                C                       END ITERATION
                C
```

```
0163          280  PRINT 1011
0164               PRINT 2001, (F(I), I = 1, NOB)
0165               PRINT 1012
0166               PRINT 2001, (H(I), I = 1, NOB)
0167               SSQ = SUMB
0168               IDF=NOB-NP
0169               PRINT 1015
0170               I=0
0171                CALL MATIN(D, NP, P, 1, DET)
0172               DO 7692 I=1,NP
0173               II = I + NP*(I-1)
0174          7692 E(I)=SQRT(D(II))
0175               DO 340 I=1,NP
0176               JI = 1 + NP*(I-1) - 1
0177               IJ = 1 + NP*(I-2)
0178               DO 340 J = 1, NP
0179               JI = JI + 1
0180               A(JI) = D(JI) / (E(I)*E(J))

0181               IJ = IJ + NP
0182          340  A(IJ) = A(JI)
0183               CALL GASSO0(3, NP, TEMP, TEMP, A)
0184               PRINT 1016
0185               CALL GASSO0(1, NP, E, TEMP, TEMP)
0186               IF(IDF) 341, 910, 341
0187          341  SDEV = SSQ / IDF
0188               PRINT 1040, SDEV, IDF
0189               SDEV = SQRT(SDEV)
0190               DO 391 I=1,NP
0191               P(I)=TH(I)+2.0*E(I)*SDEV
0192          391  TH(I)=TH(I)-2.0*E(I)*SDEV
0193               PRINT 1039
0194               CALL GASSO0(2, NP, TH, P, TEMP)
0195               LAOS = 1
0196               GO TO 101
0197          410  DO 415 K = 1, NOB
0198               TEMP = 0
0199               DO 420 I=1,NP
0200               DO 420 J=1,NP
```

```
0181              ISUB = K+NOB*(I-1)
0182              DEBUG1 = DFLZ(ISUB)
                C     DEBUG1 = DELZ(K + NOB*(I-1)
0183              ISUB = K+NOB*(J-1)
0184              DEBUG2 = DFLZ(ISUB)
                C     DEBUG2 = DFLZ(K + NOB*(J-1))
0185              IJ = I + NP*(J-1)
0186              DEBUG3 = D(IJ)/(B1F2(I)*B1F2(J)*SDEV(I)*SDEV(J))
0187        420   TEMP = TEMP + DEBUG1 * DEBUG2 * DEBUG3
0188              TEMP = 2.0*SQRT(TEMP)*SDEV
0189              R(K)=F(K)+TEMP
0190        415   F(K)=F(K)-TEMP
0191              PRINT 1008
0192              IE=0
0193              DO 425 I=1,NOB,10
0194              IE=IE+10
0195              IF(NOB-IE) 430,435,435
0196        430   II=NOB
0197        435   PRINT 2001, (R(J), J = I, IE)
0198        425   PRINT 2000, (F(J), J = I, IE)
0199        410   PRINT 1033, OPROB
0200              RETURN
0201        99    PRINT 1039
0202              GO TO 410
0203        1000FORMAT(35H1NON-LINEAR ESTIMATION, PROBLEM NUMBER   I5,// I5,
                1  14H OBSERVATIONS,  I5,  11H PARAMETERS   I10,  12H SCRATCH VECTOR[60]
0204        1001 FORMAT(/25H0INITIAL PARAMETER VALUES )
0205        1002 FORMAT(/52H0PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS )
0206        1003 FORMAT(25H0INITIAL SUM OF SQUARES =    E12.4)
0207        1006 FORMAT(////////5X,10(1H1)/5X,10(1H1)/5X,10(1H1)/5X,10(1H1))
0208        1007 FORMAT(/35H0PARAMETER VALUES VIA  REGRESSION )
0209        1008 FORMAT(////5H0PARAMETER,3X,23H CORRECTION FACTOR LINUS FOR EACH FUNCTION VAL
                1UE    )
0210        1009FORMAT(/A2H0ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LE
                1SS THAN   E12.4)
0211        1010FORMAT(/A2H0ITERATION STOPS - RELATIVE CHANGE IN SUM OF SQUARES LE
                1SS THAN   E12.4)
0212        1011 FORMAT(22H0FINAL FUNCTION VALUES )
```

```
0213          1012 FORMAT(////10HORESIDUALS )
0214          1014 FORMAT(//23HDEGREES OF FREEDOM OF RESIDUALS =  ,I12,8X,7H,I4,
                  120H DEGREES OF FREEDOM   )
0215          1015 FORMAT(////19HDEFORMATION MATRIX  )
0216          1016 FORMAT(////21HNONORMALIZING ELEMENTS  )
0217          1033 FORMAT(//A1,9HEND OF PROBLEM NO.,I3)
0218          1034 FORMAT(//16HUPARAMETER ERROR  )
0219          1039 FORMAT(//31HDIAGONAL ELEMENT OF DIFFERENCE MATRIX FOR PARAMETER ,I3,1
                  1NEAR HYPOTHESIS)  )
0220          1040 FORMAT(/4HOLAMDA=,E10.3,40X,33HSUM OF SQUARES AFTER REGRESSION =
                  1E15.7)
0221          1041 FORMAT(1H0,5HTHETA=,E12.8,8X,20H ANGLE IN SCALED COORD. =
                  1   F5.2, 8HDEGREES   )
0222          1043 FORMAT(23H0INCREMENT SUM OF SQUARES =  ,E12.4)
0223          2001 FORMAT(/10E12.4)
0224          2006 FORMAT(10F12.8)
0225               END
```

GASS60

```
0001            SUBROUTINE GASS60(ITYPE, NO, A, B, C)
0002            DIMENSION A(NO),B(NO),C(NO,NO)
0003            NP=NO
0004            NR=NP/10
0005            LOW = 1
0006            LUP = 10
0007      10    IF( NR )1a,20,30
0008      1a    RETURN
0009      20    LUP=NP
0010            IF(LOW.GT.LUP) RETURN
0011      30    PRINT 500, (J,J=LOW,LUP)
0012            GO TO (40,60,80),ITYPE
0013      40    PRINT 600,(A(J),J=LOW,LUP)
0014            GO TO 102
0015      60    PRINT 600, (B(J), J=LOW,LUP)
0016            GO TO 40
0017      80    DO 98 I=LOW,LUP
0018      98    PRINT 720,I,(C(J,I),J=LOW,I)
0019            LOW2=LUP+1
0020            IF(LOW2.GT.NP) GO TO 102
0021            DO 95 I=LOW2,NP
0022      95    PRINT 720,I,(C(J,I),J=LOW,LUP)
0023      102   LOW = LOW + 10
0024            LUP = LUP + 10
0025            NR = NR - 1
0026            GO TO 10
0027      500   FORMAT(/18,9I12)
0028      600   FORMAT(10E12.4)
0029      720   FORMAT(1H0,I3,1X,F7.0,9F12.4)
0030            CONTINUE
0031            RETURN
0032            END
```

MATIN

```
0001            SUBROUTINE MATIN(A, NVAR, N, NP, DET)
0002            DIMENSION A(NVAR, 1), B(NVAR, 1)
0003            COMMON/GASPAR/DUMILS(7), PIVMIN
0004            PIVMIN=A(1,1)
0005             DET = 1.0
0006            DO 550 ICOL = 1, NVAR
0007             PIVOT = A(ICOL, ICOL)
0008            PIVMIN = AMIN1(PIVOT, PIVMIN)
0009             DET = PIVOT * DET
                C
                C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
                C
0010             A(ICOL, ICOL) = 1.0
0011            PIVOT = AMAX1(PIVOT, 1.E-20)
0012             PIVOT = A(ICOL, ICOL)/PIVOT
0013            DO 350 L=1,NVAR
0014        350  A(ICOL, L) = A(ICOL, L)*PIVOT
0015            IF(NB.EQ.0) GO TO 371
0016            DO 370 L=1,NB
0017        370  B(ICOL, L) = B(ICOL, L)*PIVOT
                C
                C     REDUCE NON-PIVOT ROWS
                C
0018        371  DO 550 L1=1,NVAR
0019             IF(L1 .EQ. ICOL) GO TO 550
0020             T = A(L1, ICOL)
0021             A(L1, ICOL) = 0.
0022            DO 450 L=1,NVAR
0023        450  A(L1, L) = A(L1, L) - A(ICOL, L)*T
0024             IF(NB.EQ.0) GO TO 550
0025            DO 500 L=1,NB
0026        500  B(L1, L) = B(L1, L) - B(ICOL, L)*T
0027         550 CONTINUE
0028            RETURN
0029            END
```

```
SUBROUTINE INUMBR(X,Y,HEIGHT,NUM,THETA,FMT)
DIMENSION BCD(1)
ENCODE(10,FMT,BCD)NUM
CALL SYMBOL(X,Y,HEIGHT,BCD,THETA,10)
RETURN
END
```

```
      0.0000    12.1000
     7[illegible].0000     9.1500
   1[illegible]3.0000     5.4500
   1[illegible].0000     3.[illegible]00
   2[illegible].0000     2.1000
   241.0000     2.1500
   267.0000     1.3500
   2[illegible].0000      .7500
CSOD RATE CONSTANT (HR.**-1.0) = .00135
```

6 OBSERVATIONS, 2 PARAMETERS 46 SCRATCH REQUIRED

INITIAL PARAMETER VALUES

.5013E-01 .1302E+02

PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS

.1001E-01 .1001E-01

INITIAL SUM OF SQUARES = .2692E+01

ITERATION NO. 1

DETERMINANT = .4275E+03 ANGLE IN SCALED COORD. =30.36 DEGREES

TEST POINT PARAMETER VALUES

.4975E-01 .1302E+02

TEST POINT SUM OF SQUARES = .1751E+00

PARAMETER VALUES VIA REGRESSION

.4955E-01 .1302E+02

LAMBDA = .1000E-02 SUM OF SQUARES AFTER REGRESSION = .1750945E+00

ITERATION NO. 2

DETER-MINANT = .3668E+01 ANGLE IN SCALED COORD. = 49.32DEGREES

TEST POINT PARAMETER VALUES
.4461E-01 .1330E+02

TEST POINT SUM OF SQUARES = .1393E+03

PARAMETER VALUES VIA REGRESSION

.4461E-01 .1330E+02

LAMBDA = .1000E-03 SUM OF SQUARES AFTER REGRESSION = .1332946E+03

ITERATION NO. 3

DETER-MINANT = .3935E+01 ANGLE IN SCALED COORD. = 50.79DEGREES

TEST POINT PARAMETER VALUES
.4459E-01 .1330E+02

TEST POINT SUM OF SQUARES = .1383E+03

PARAMETER VALUES VIA REGRESSION

.4459E-01 .1330E+02

LAMBDA = .1000E-04 SUM OF SQUARES AFTER REGRESSION = .1332946E+03

ITERATION STOPS - RELATIVE CHANGE IN SUM OF SQUARES LESS THAN .1000E-02

.13366+02 .9187E+01 .5769E+01 .3773E+01 .2912E+01 .2114E+01 .1410E+01 .9323E+00

RESIDUALS

-.5764E-01 -.3734E-01 .1108E+00 -.7056E-01 .182-E+00 .254oE-01 -.1631E+00 -.1277E+00

XPRIME-X MATRIX

	1	2
1	.67+1E+05	
2	-.2935E+03	.3875E+01

CORRELATION MATRIX

	1	2
1	1.0000	
2	.7749	1.0000

VARIANCE OF RESIDUALS = .330FE-01, 6 DEGREES OF FREEDOM

INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (NON-LINEAR HYPOTHESIS)

1	2
.2927E+01	.1331E+02
.4297E+01	.1251E+02

APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VALUE

.1331E+02 .9346E+01 .6595E+01 .3903E+01 .2066E+01 .1537E+01 .1093E+01 .8212E+00
.1321E+02 .9026E+01 .5943E+01 .3603E+01 .2278E+01 .1393E+01 .1212E+00

APPENDIX C

DISSOLVED OXYGEN VERSUS TIME DATA FOR CSOD, TSOD AND MSOD

CHEMICAL SEDIMENT OXYGEN DEMAND (C.S.O.D.) OXYGEN VERSUS TIME DATA

SEDIMENT SAMPLE— 270

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	12.80
53.00	11.10
142.00	9.00
217.00	8.15
293.00	7.35
363.00	6.70
459.00	6.05
536.00	5.65
627.00	5.20

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.60
77.00	7.40
172.50	6.00
241.00	5.10
336.00	4.50
414.00	3.75
480.00	3.10
554.00	2.65
648.00	2.35

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	10.75
70.00	7.50
143.00	5.45
218.00	4.15
311.00	3.15
385.50	2.50
648.00	0.95

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	10.40
19.50	7.65
43.00	6.40
67.00	5.20
119.00	3.95
213.00	2.50
334.00	2.00
382.00	1.60
477.50	0.65
526.00	0.60

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	9.20
19.50	8.65
43.00	7.15
67.00	6.55
119.00	5.40
213.00	4.50
334.00	3.55

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	8.10
18.00	7.65
42.00	6.60
66.00	5.90
92.50	5.30
161.00	3.90
186.00	3.55
210.00	3.20
233.50	3.00
260.00	2.60

SEDIMENT SAMPLE-- COMPOSITE

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	12.40
53.00	11.30
145.00	9.70
217.00	9.15
293.00	8.50
361.00	7.90
457.00	7.80

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	11.80
77.00	9.60
172.50	7.80
241.00	7.35
336.00	6.80
414.00	6.55

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.95
70.00	8.45
143.00	6.35
218.00	5.05
385.50	3.20
648.00	1.90

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10.

TIME	DISSOLVED OXYGEN CONC.
0.0	8.10
18.00	6.90
42.00	5.70
66.00	4.70
92.50	3.90
161.00	2.10
210.00	1.55
233.50	1.40
259.00	1.20
305.50	0.70

SEDIMENT SAMPLE— 258

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.90
73.00	10.70
145.00	8.30
217.00	7.60
293.00	7.00
363.00	6.10
459.00	5.70
535.00	5.55
627.00	5.05

TEMPERATURE 8 DEGREES. NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	12.05
77.00	9.50
178.50	8.65
241.00	8.35
336.00	8.20
414.00	8.00
480.00	8.30
554.00	8.30
648.00	8.10

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	10.70
70.00	8.50
143.00	7.30
218.00	6.60
311.00	6.30
385.50	6.00
648.00	4.20

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.10
19.50	8.45
43.00	7.75
67.00	6.55
119.00	5.65
213.00	4.05
336.00	2.85
383.50	2.40
477.50	1.45
525.00	1.15

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	7.80
19.00	6.50
42.00	5.30
66.00	4.70
90.50	4.60
161.00	2.40
210.00	2.20
233.50	2.00
260.00	1.70
306.50	1.15

SEDIMENT SAMPLE— BLUE CHAU

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	12.20
53.00	11.50
149.00	10.40
217.00	9.70
292.00	9.15
363.00	8.60

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	11.95
77.00	10.30
173.50	9.20
241.00	8.60
338.00	8.45
414.00	7.90
490.00	7.65

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.75
70.00	9.60
143.00	8.20
213.00	7.60
335.50	6.60
648.00	4.90

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.65
19.50	8.85
43.00	8.20
67.00	7.60
119.00	6.60
211.00	5.65
335.00	4.60
382.00	4.45
477.50	3.65
526.00	3.50

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 12

TIME	DISSOLVED OXYGEN CONC.
0.0	7.90
18.00	7.70
43.00	7.10
66.00	6.60
92.50	6.40
161.00	4.75
186.00	4.65
210.00	4.30
233.50	4.00
260.00	3.50
306.50	2.80
330.00	2.60

SEDIMENT SAMPLE-- CHUB LAKE

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.10
53.00	11.15
149.00	9.90
217.00	9.25
293.00	8.85
363.00	8.60
459.00	8.40
552.00	8.00

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	12.30
77.00	7.90
172.50	5.80
241.00	4.75
336.00	3.50
414.00	3.10

TEMPERATURE 12. DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.50
70.00	8.00
143.00	6.00
213.00	4.70
285.50	2.45
643.00	0.90

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	9.15
19.50	8.30
43.00	7.45
67.00	6.20
119.00	4.65
213.00	2.30
336.00	0.65
382.00	0.35
477.50	0.20

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 12

TIME	DISSOLVED OXYGEN CONC.
0.0	8.00
18.00	7.10
42.00	5.90
65.00	4.90
92.50	4.05
161.00	2.30
186.00	2.00
210.00	1.35
233.50	1.30
260.00	0.90
306.50	0.55
330.00	0.40

SEDIMENT SAMPLE-- RED CHALK

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.80
53.00	11.10
149.00	9.90
217.00	9.50
293.00	9.05
363.00	8.95
459.00	8.55
552.00	8.35
648.00	8.25

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	9.80
59.00	8.70
154.00	8.00
248.00	7.25
308.00	6.95
365.00	6.30
648.00	6.05

TEMPERATURE 13 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.75
70.00	9.00
143.00	7.60
213.00	6.60
285.50	4.90
648.00	3.10

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	9.60
19.50	9.10
43.00	8.30
67.00	7.20
119.00	6.15
213.00	4.80
336.00	3.10
382.00	2.65
477.50	1.85
526.00	1.65
574.00	1.45

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	8.00
18.00	7.55
42.00	6.60
66.00	5.60
92.50	4.95
141.00	3.25
186.00	2.90
260.00	2.10
306.50	1.40
330.00	1.25
353.50	1.20

TOTAL SEDIMENT OXYGEN DEMAND DATA (T.S.O.D.)

SEDIMENT SAMPLE-- 270 (1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.00
71.00	6.15
143.00	5.55
191.00	3.70
215.00	3.10
241.00	2.15
267.00	1.45
289.00	0.75

TEMPERATURE 9 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	9.25
11.00	8.10
35.00	7.00
63.00	4.35
83.50	4.05
95.00	3.20
105.00	2.00
110.00	1.70
155.50	0.60
159.00	1.40
180.00	0.25

TEMPERATURE 13 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.40
24.00	8.70
51.50	6.50
75.00	2.15
95.50	0.50
147.50	0.30

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.20
1.00	9.80
23.50	5.50
24.50	4.60
47.50	3.15
51.00	0.60
72.00	0.30
75.00	0.60
99.00	0.30
144.00	0.30

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 14

TIME	DISSOLVED OXYGEN CONC.
0.0	9.00
1.50	8.30
4.80	6.70
5.30	5.30
9.70	4.90
10.70	3.80
12.50	3.10
14.00	2.70
15.00	1.75
16.50	1.75
17.00	1.30
19.50	1.00
21.30	0.45
23.00	0.30

SEDIMENT SAMPLE-- 270 (E)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	12.80
71.50	6.40
143.50	1.40
192.50	0.45
216.50	0.15
241.50	0.30

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.50
22.50	8.45
23.50	8.55
46.50	5.05
73.50	2.45
93.00	1.15
94.50	0.50
115.50	9.20
120.50	6.40

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	11.20
24.00	8.00
48.00	7.20
71.50	4.80
96.00	2.70
121.00	0.85
144.00	0.40
216.00	0.25

[illegible] 16 DEGREES NUMBER OF OBSERVATIONS

TIME	DISSOLVED OXYGEN CONC.
0.0	9.50
1.50	9.70
24.00	5.30
25.00	4.40
49.00	1.45
51.50	0.30
72.50	0.25
73.50	0.20
96.50	0.25
144.50	0.30

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS = 16

TIME	DISSOLVED OXYGEN CONC.
0.0	8.70
0.50	8.60
1.50	8.40
4.00	5.40
5.50	5.00
8.70	4.15
9.50	3.55
11.70	2.10
13.00	2.85
14.50	2.35
15.00	1.60
17.50	1.30
17.80	0.90
19.00	1.10
19.70	0.35
23.00	0.25

SEDIMENT SAMPLE-- 259 (1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	12.70
71.00	7.10
143.00	2.65
168.00	0.50
216.00	0.40
241.00	0.30

TEMPERATURE 6 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.25
22.50	9.15
30.00	8.40
54.00	4.65
71.00	3.35
93.50	2.20
104.00	0.70
120.00	0.40
170.00	0.20

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS

TIME	DISSOLVED OXYGEN CONC.
0.0	10.90
24.50	9.60
51.50	7.80
72.00	5.05
96.50	2.20
240.00	1.50

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 5

TIME	DISSOLVED OXYGEN CONC.
0.0	9.65
24.00	6.20
51.00	1.70
72.00	0.45
144.00	0.35

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	9.30
1.30	7.20
3.30	5.65
5.00	5.70
8.00	3.40
10.50	2.15
13.20	1.25
15.80	0.75
17.00	0.45
18.70	0.30
25.30	0.25

SEDIMENT SAMPLE-- 258 (2)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	12.60
71.00	6.50
143.00	1.65
170.00	0.75
192.00	0.30
216.00	0.30
241.00	0.20

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	11.40
12.50	9.60
22.50	8.65
38.50	6.70
63.50	4.60
86.50	2.50
92.50	2.45
105.50	1.55
120.00	0.70
168.00	0.50
[illegible]	0.25

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS = 8

TIME	DISSOLVED OXYGEN CONC.
0.0	10.40
24.50	9.30
50.50	7.90
75.00	6.05
99.50	4.05
120.00	2.00
147.50	0.45
168.50	0.40

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS = 6

TIME	DISSOLVED OXYGEN CONC.
0.0	9.75
24.00	5.25
45.00	1.50
51.00	0.60
72.00	0.20
144.00	0.20

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	8.20
2.00	6.20
3.20	5.45
5.20	4.90
7.50	2.95
10.70	1.60
12.00	1.50
14.00	0.80
15.50	0.30
19.00	0.30
1.1	0.20

SEDIMENT SAMPLE-- COMPOSITE(1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	13.90
72.00	6.15
143.00	5.35
192.00	2.50
216.00	1.75
240.00	1.05
267.00	0.50
290.00	0.45

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	11.30
22.50	10.20
93.50	6.80
120.00	4.95
155.50	3.40
190.00	2.45
217.00	1.50
240.50	0.90
261.00	0.55
289.00	0.45

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.40
24.50	8.35
51.50	5.70
75.00	3.65
95.50	1.95
147.50	0.35

TEMPERATURE 15 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.80
4.00	9.15
24.00	5.25
28.00	5.45
50.50	2.65
51.00	2.10
72.00	0.40
77.50	0.30
104.00	0.30
144.00	0.30

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 15

TIME	DISSOLVED OXYGEN CONC.
0.0	8.35
2.00	8.25
2.50	7.95
5.00	7.20
7.00	6.25
12.00	4.75
16.00	4.75
19.00	3.60
21.00	3.55
25.00	3.00
26.00	2.30
28.00	1.70
32.00	0.95
42.00	0.30
46.00	0.30

SEDIMENT SAMPLE-- COMPOSITE(2)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.70
72.00	9.45
143.00	4.90
192.00	2.45
216.00	1.70
240.00	1.15
267.00	0.70
290.00	0.35

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.05
33.50	9.65
82.50	6.15
130.00	4.55
165.50	2.70
190.00	2.05
217.00	1.10
240.50	0.70
261.00	0.35

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	10.80
24.50	9.35
51.50	6.00
75.00	4.25
95.50	3.75
147.50	2.95
169.00	1.50
217.00	0.30

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.45
24.00	7.30
28.00	6.20
48.00	5.45
52.00	4.55
73.50	3.60
79.00	2.05
100.00	1.90
101.00	0.70
176.00	0.25

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 14

TIME	DISSOLVED OXYGEN CONC.
0.0	8.40
1.00	8.30
4.50	7.85
13.00	6.80
18.00	5.45
20.00	5.55
25.00	4.75
27.00	3.80
31.00	3.10
37.00	2.55
44.50	1.35
48.00	1.05
68.00	0.80
73.00	0.50

SEDIMENT SAMPLE-- BLUE CHALK (1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	12.60
72.00	9.80
143.00	5.15
192.00	2.50
216.00	1.55
241.00	0.75
267.00	0.35

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	10.90
22.50	10.00
92.50	5.85
120.00	4.20
165.50	2.20
190.00	1.40
217.00	0.75
240.50	0.50
261.00	0.20

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 13

TIME	DISSOLVED OXYGEN CONC.
0.0	10.70
24.50	9.70
51.50	8.85
75.00	7.55
95.50	7.15
147.50	7.10
169.00	6.60
217.00	5.30
243.50	4.80
310.00	3.00
388.00	1.60
440.00	1.60
540.00	0.75

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	9.65
24.00	8.65
51.00	7.40
72.00	6.65
144.00	3.50
194.00	2.20
219.00	1.50
242.00	0.95
268.50	0.80

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	8.90
4.75	8.40
9.75	7.80
28.00	6.75
28.50	6.35
48.00	4.95
79.00	2.80
93.50	1.70
99.00	1.45
120.00	0.80
150.00	0.50

SEDIMENT SAMPLE-- BLUE CHALK (2)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	10.00
72.00	8.70
143.00	5.80
192.00	3.00
215.00	2.20
241.00	1.25
267.00	0.60
290.00	0.45

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	11.70
22.50	9.60
92.50	6.45
120.00	4.80
165.50	2.60
190.00	1.85
217.00	1.30
240.50	0.80
261.00	0.50

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 12

TIME	DISSOLVED OXYGEN CONC.
0.0	10.40
24.50	9.50
51.50	8.00
75.00	7.40
95.50	6.70
147.50	4.75
192.00	4.40
217.00	3.10
243.50	1.65
280.00	1.00
330.00	0.60
385.00	0.50

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	10.00
24.00	8.40
51.00	7.35
72.00	6.45
144.00	3.35
194.00	1.80
219.00	1.20
245.00	0.75
288.50	0.20

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	9.25
4.75	8.30
9.75	7.80
23.00	6.60
28.50	5.85
48.00	4.75
79.00	2.00
93.50	1.35
99.00	1.10
120.00	0.30
150.00	0.20

SEDIMENT SAMPLE-- CHUB LAKE (1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	12.70
72.00	11.00
143.00	9.05
192.00	5.00
216.00	3.85
241.00	2.65
267.00	1.65
290.00	1.35
400.00	0.50
450.00	0.25

TIME	DISSOLVED OXYGEN CONC.
0.0	11.45
22.50	10.09
93.50	4.60
120.00	3.35
166.00	1.70
190.00	1.00
217.00	0.60
240.50	0.25

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	10.60
24.50	9.05
51.50	7.85
75.00	6.25
95.50	5.95
147.50	4.30
169.00	3.50
217.00	1.35
243.50	1.20
300.00	0.70
450.00	0.30

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	9.50
24.00	8.40
51.00	7.10
72.00	6.15
144.00	3.20
194.00	1.35
219.00	0.65
242.00	0.25

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.25
4.75	8.30
9.75	7.80
23.00	6.65
28.50	6.10
48.00	4.40
79.00	2.10
93.50	1.30
99.00	0.95
120.00	0.20

SEDIMENT SAMPLE-- CHUB LAKE (2)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	12.30
72.00	9.50
143.00	4.50
192.00	2.25
216.00	1.60
241.00	0.85
267.00	0.40

TIME	DISSOLVED OXYGEN CONC.
0.0	10.35
22.50	10.35
93.50	5.30
120.00	3.50
166.00	2.00
190.00	1.25
217.00	0.70
240.50	0.40
261.00	0.35

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	10.70
24.50	9.30
51.50	7.00
75.00	6.70
98.50	5.75
147.50	3.25
169.00	2.30
217.00	1.25
243.50	0.50

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	9.75
24.00	8.40
51.00	7.05
72.00	5.85
144.00	2.85
194.00	1.20
219.00	0.60
242.00	0.30

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	8.90
4.75	8.30
9.75	7.85
23.00	6.15
28.50	5.65
48.00	4.65
79.00	1.85
93.50	1.15
99.00	0.80
120.00	0.20

SEDIMENT SAMPLE-- FED CHALK (1)

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.40
72.00	7.10
143.00	2.25
170.00	1.00
192.00	0.55
216.00	0.35
241.00	0.20
267.00	0.20

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 13

TIME	DISSOLVED OXYGEN CONC.
0.0	11.10
22.50	9.75
52.50	8.35
120.00	7.20
165.00	6.30
190.00	4.90
217.00	4.20
240.50	3.90
261.00	3.50
313.00	1.45
334.00	1.25
382.50	0.45

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	10.60
24.50	9.15
51.50	8.30
75.00	6.75
95.50	5.60
147.50	5.10
169.00	4.45
217.00	3.20
243.50	2.65
320.00	1.00
420.00	0.50

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.45
24.00	8.50
51.00	7.70
72.00	6.40
144.00	3.90
194.00	2.15
219.00	1.60
242.00	1.10
268.50	0.65
296.00	0.45

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.00
4.75	8.20
9.75	7.75
23.00	6.35
48.00	5.15
79.00	2.85
93.50	2.35
99.00	1.85
120.00	0.95
150.00	0.50

SEDIMENT SAMPLES FED ONLY

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	13.10
72.00	10.50
143.00	6.50
192.00	3.10
216.00	2.00
241.00	1.00
267.00	0.60

TEMPERATURE 8 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	10.50
70.50	8.70
97.00	7.80
143.50	5.00
168.00	5.30
195.00	4.10
218.50	3.35
239.00	2.50
291.00	1.40
311.50	1.80
360.00	0.35

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 11

TIME	DISSOLVED OXYGEN CONC.
0.0	10.80
24.50	9.50
51.50	8.50
75.00	7.40
95.50	6.60
147.50	5.10
169.00	4.40
217.00	2.90
243.50	2.55
310.00	1.00
420.00	0.45

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 12

TIME	DISSOLVED OXYGEN CONC.
0.0	9.65
24.00	8.65
51.00	8.10
72.00	7.25
144.00	4.90
194.00	3.00
219.00	2.50
242.00	2.00
268.50	1.45
290.00	1.25
340.00	0.60
420.00	0.35

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 10

TIME	DISSOLVED OXYGEN CONC.
0.0	9.10
4.75	7.85
9.75	7.35
23.00	6.20
48.00	4.45
79.00	1.95
93.50	1.45
99.00	1.20
120.00	0.40
156.00	0.30

MACROINVERTABRATE OXYGEN UPTAKE (M.I.O.U.) OXYGEN VERSUS TIME DATA

SEDIMENT SAMPLE-- 270

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.00
100.50	9.10
169.00	7.90
245.00	6.50
315.00	6.00
409.00	4.80
487.00	4.10
577.00	3.15

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.10
23.00	9.00
50.50	6.85
97.50	4.70
197.50	1.20
219.50	0.60

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	9.55
25.00	7.95
49.00	6.70
73.00	4.95
113.00	2.25
196.00	0.60
215.00	0.50

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	8.15
20.50	5.55
46.00	2.60
67.50	0.90
92.50	0.45
119.00	0.30

SEDIMENT SAMPLE-- 259

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 8

TIME	DISSOLVED OXYGEN CONC.
0.0	12.45
53.00	9.80
148.50	5.40
217.00	3.50
293.00	2.05
363.00	1.85
457.00	1.35
535.00	1.10

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.20
23.00	8.10
50.50	5.65
97.50	3.75
197.50	1.10
218.50	0.90

TEMPERATURE 14 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	9.50
25.00	6.85
48.00	5.10
73.00	3.35
118.00	1.75
192.00	0.45
215.00	0.40

TEMPERATURE 22 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	8.30
1.50	7.50
20.50	2.85
35.00	0.90
37.00	0.65
46.00	0.30

SEDIMENT SAMPLE-- COMPOSITE

TEMPERATURE 4 DEGREES NUMBER OF OBSERVATIONS 9

TIME	DISSOLVED OXYGEN CONC.
0.0	13.10
53.00	11.50
148.50	9.10
217.00	8.60
293.00	7.30
363.00	6.65
457.00	5.35
535.00	5.30
627.00	3.30

TEMPERATURE 12 DEGREES NUMBER OF OBSERVATIONS 6

TIME	DISSOLVED OXYGEN CONC.
0.0	10.30
23.00	8.80
50.50	6.85
97.50	5.20
197.50	1.70
218.50	1.20

TEMPERATURE 16 DEGREES NUMBER OF OBSERVATIONS 7

TIME	DISSOLVED OXYGEN CONC.
0.0	9.50
25.00	7.85
49.00	6.65
73.00	4.95
118.00	2.15
192.00	0.40
240.00	0.30

TEMPERATURE 23 DEGREES NUMBER OF OBSERVATIONS 5

TIME	DISSOLVED OXYGEN CONC.
0.0	8.30
20.50	5.50
44.00	2.35
67.50	0.45
92.50	0.40

APPENDIX D

ANOVA TABLE AND F STATISTICS

Table D-1

Analysis of Variance (ANOVA) Example Table

Column: 270, 4°C

Parameter Estimated: k_c, the first-order rate constant for dissolved oxygen-time data fit to the model:

$$D.O.(t) = D.O. \cdot e^{-kct}$$

Source of variation	Degrees of freedom	Sum of squares	Mean square
Regression	2	51.63	25.82
Deviations from regression	6	2.35	0.392

$F = 65.87$

$F_{2,6,1\%} = 14.54$ (from tables)

$\therefore$ regression is significant at the 1% level of significance.

Table D-2

F Values from Regressions

Parameter estimated	Column		F value	Degrees of freedom from	
				regression	deviations from regression
k_c (CSOD)	STN # 270,	4°	65.9	2	6
		8	54.6	2	6
		12	230.0	2	4
		16	135.0	2	7
		22	2596.0	2	7
	STN # 258,	4	67.0	2	6
		8	7.15	2	6
		12	25.8	2	4
		16	44.2	2	4
		22	1290.0	2	7
	Composite,	4	41.84	2	4
		8	18.54	2	3
		12	78.84	2	3
		16	609.0	2	7
		22	200.0	2	7
	Blue Chalk,	4	283.0	2	3
		8	29.3	2	4
		12	56.4	2	3
		16	150.0	2	7
		22	461.0	2	9
	Chub,	4	29.7	2	5
		8	54.2	2	3
		12	2510.0	2	3
		16	451.0	2	6
		22	1870.0	2	9

Table D-2 (Cont'd) F Values from Regressions

Parameter estimated	Column	F value	Degrees of freedom from	
			regression	deviations from regression
	16	690.0	2	7
	22	398.0	2	12
Composite, (2)	4	437.0	2	5
	8	5750.0	2	6
	12	244.0	2	5
	16	169.0	2	7
	22	56.9	2	11
Blue Chalk, (1)	4	185.0	2	4
	8	2100.0	2	6
	12	270.0	2	10
	16	1230.0	2	6
	22	1210.0	2	8
Blue Chalk, (2)	4	69.2	2	5
	8	743.0	2	6
	12	1540.0	2	9
	16	2180.0	2	6
	22	1020.0	2	8
Chub, (1)	4	91.9	2	7
	8	464.0	2	5
	12	1320.0	2	8
	16	645.0	2	5
	22	281.0	2	7
Chub, (2)	4	193.0	2	4
	8	603.0	2	6
	12	2250.0	2	6
	16	3490.0	2	5
	22	890.0	2	7
Red Chalk,	4	1770.0	2	5
	8	314.0	2	9

Table D-2 (Cont'd) F Values from Regressions

Parameter estimated	Column		F value	Degrees of freedom from regression	Degrees of freedom from deviations from regression
	Red Chalk,	4	30.0	2	6
		8	23.9	2	4
		12	111.0	2	3
		16	1360.0	2	8
		22	2070.0	2	8
$\hat{\mu}_{bmax}$ (BSOD)	STN # 270, (1)	4	2340.0	2	5
		8	184.0	2	8
		12	35.2	2	3
		16	112.0	2	7
		22	1150.0	2	11
	STN # 270, (2)	4	692.0	2	3
		8	1030.0	2	6
		12	182.0	2	5
		16	444.0	2	7
		22	612.0	2	13
	STN # 258, (1)	4	1470.0	2	3
		8	205.0	2	6
		12	17.7	2	3
		16	140.0	2	2
		22	429.0	2	8
	STN # 258, (2)	4	650.0	2	4
		8	111.0	2	8
		12	80.3	2	5
		16	181.0	2	3
		22	414.0	2	8
	Composite, (1)	4	756.0	2	5
		8	2210.0	2	7
		12	484.0	2	3

Table D-2 (Cont'd) F Values from Regressions

Parameter estimated	Column	F value	Degrees of freedom from regression	Degrees of freedom from deviations from regression
	12	623.0	2	8
	16	666.0	2	7
	22	775.0	2	7
	Red Chalk, 4	115.0	2	4
	8	335.0	2	8
	12	2150.0	2	8
	16	673.0	2	9
	22	692.0	2	7
$\hat{\mu}_{mmax}$	STN # 270, 4	192.0	2	5
	12	22.1	2	3
	16	100.0	2	4
	22	744.0	2	3
	STN # 258, 4	173.0	2	5
	12	368.0	2	3
	16	280.0	2	4
	22	129.0	2	3
	Composite, 4	508.0	2	6
	12	504.0	2	3
	16	1190.0	2	4
	22	217.0	2	2
$R_1(k_c$ vs. temp.)	STN # 270	104.0	1	3
	STN # 258	27.3	1	3
	Composite	160.0	1	3
	Blue Chalk	166.0	1	3
	Chub	212.0	1	3
	Red Chalk	110.0	1	3
$P_1(\hat{\mu}_{bmax}$ vs. temp.)	STN # 270(1)	13.4	1	3
	STN # 270(2)	15.7	1	3

Table D-2 (Cont'd) F Values from Regressions

Parameter estimated	Column	F value	Degrees of freedom from	
			regression	deviations from regression
	STN # 258(1)	11.1	1	3
	STN # 258(2)	12.3	1	3
	Composite (1)	65.9	1	3
	Composite (2)	24.6	1	3
	Blue Chalk (1)	1.90	1	3
	Blue Chalk (2)	3.23	1	3
	Chub(1)	2.72	1	3
	Chub(2)	1.11	1	3
	Red Chalk(1)	1.43	1	3
	Red Chalk(2)	2.22	1	3
$P_1(\hat{\mu}_{mmax}$ vs. temp.)	STN # 270	20.9	1	2
	STN # 258	7.83	1	2
	Composite	18.5	1	2

APPENDIX E

CONVERSION FACTORS FROM LABORATORY

Rates of oxygen uptake from laboratory columns had to be converted from volumetric to areal units. T is a record of the conversion factors for each column used in this study. Values differ due to differences in water depth.

Table E-1

Sediment column	f, $m \cdot hr \cdot day^{-1}$
CSOD	
STN # 270	6.8
STN # 258	8.3
Composite	7.1
Blue Chalk	7.7
Chub	8.0
Red Chalk	7.5
BSOD and MSOD	
STN # 270(1)	7.5
STN # 258(1)	7.5
Composite(1)	7.5
BSOD only	
STN # 270(2)	7.5
STN # 258(2)	7.5
Composite(2)	7.5
Blue Chalk(1)	7.1
Blue Chalk(2)	7.1
Chub(1)	5.9
Chub(2)	5.9
Red Chalk(1)	7.2
Red Chalk(2)	7.2

where,

$$\hat{\mu}_{b \text{ or } m}(gm \cdot m^3 \cdot hr^{-1}) \cdot f(m \cdot hr \cdot day^{-1}) = \hat{\mu}_{b \text{ or } m}(gm \cdot m^{-2} \cdot day^{-1})$$

$$k_c(hr^{-1}) \cdot f(m \cdot hr \cdot day^{-1}) = k_c(m \cdot day^{-1}).$$

APPENDIX F

MODEL DERIVATION

Derivation of Model

Formulation of mass balance for oxygen in water overlying the sediments yields:

$$\frac{\partial(V[O_2])}{\partial t} = \hat{\mu}_b \frac{[O_2]}{K_{\frac{1}{2}} + [O_2]} \cdot V_s - \hat{K}_c A_s \frac{\partial [O_2]}{\partial z}$$

BIOLOGICAL PART — CHEMICAL PART — sediment water interface

where V = volume of water

$[O_2]$ = oxygen concentration in water

$\hat{\mu}_b$ = maximum volumetric aerobic oxidation rate

$K_{\frac{1}{2}}$ = half-saturation constant

V_s = aerobic volume of sediments

$\hat{K}_c$ = diffusivity coefficient of oxygen penetration

A_s = cross-sectional area of sediment-water interface.

Steps

1. Divide both sides of equation A_s
2. Let $\hat{\mu}_b \cdot \frac{V_s}{A_s} = \hat{\mu}_{bmax}$
3. Let $\frac{\partial O_2}{\partial z} \simeq \frac{[O_2]_{water} - [O_2]_{sediment}}{\Delta z}$, Δz is thickness between $[O_2]_{water}$ and $[O_2]_{sediment}$
4. Let $[O_2]_{sediment} = 0$
5. Let $\hat{K}_c / \Delta z = K_c$

6. Let $\frac{V}{A_s} \cdot \frac{d[O_2]}{dt}$ = Total SOD (gm/m^2-day)

This gives simplified equation given in text. Note K_c is a mass transfer coefficient, units of a velocity, e.g., m/day.

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