

BENTHIC OXYGEN DEMANDS
OF
HOUSTON SHIP CHANNEL SEDIMENTS

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ABSTRACT

The purpose of this research was to determine the benthic demand of the deposits in the Houston Ship Channel for use in modeling the channel for dissolved oxygen. The scope of the study included: (1) collection of bottom samples; (2) determining characteristics of the sludge such as biochemical oxygen demand (BOD), heavy metals, etc.; (3) use of galvanic oxygen cells in determining oxygen uptake rates in grams of oxygen per hour per square meter, or other units; (4) determination of benthic demands at different temperatures to obtain a demand versus temperature correlation; and (5) the determination of mixing effects.

Mud and sludge deposits in the channel are laid down and impounded over a long period of time since currents are too slow to prevent settling or to scour the bottom. If the overlaying waters contain dissolved oxygen aerobic conditions are maintained at the surface of the accumulating organic debris. Diffusion of the oxygen within the deposits is normally too slow to carry enough oxygen to deeper strata to keep them from becoming anaerobic.

The benthic demands were determined using electrolytic biochemical oxygen demand cells and the sludges were placed in the cells within 24 hours after collection. Nine sludge samples were taken from the entire 24 mile reach of the channel and benthic demands were determined at 32°C. Correlations were made relating benthic demand to the five-day biochemical oxygen demand of the sludges. Benthic demands versus temperature were studied for a sample from Mile 20 (Morgans Point is Mile 0) and a correlation of benthic demand versus temperature was made. This allows

the benthic demand at other temperatures to be determined and will be useful in modeling since the temperature of the channel varies during the year.

The water in the cells was recirculated to the extent that the sludge surface was scoured to determine if a scoured condition increased the benthic demand over that of a quiescent condition. Also some tests were made using a level of mixing that caused a complete suspension of the entire sludge to determine the increase in benthic demand for this condition.

Mass transfer fundamentals were used to determine the benthic demand as a function of ultimate benthic demand, time, and molecular diffusivity.

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LIST OF SYMBOLS

A	= Cross section area, normal to flux; surface area
a	= Current flow in amperes
BOD	= Biochemical oxygen demand
BOD ₅	= Five-day biochemical oxygen demand
c	= Benthic oxygen demand, mg/l
c	= Dissolved oxygen concentration, organic matter concentration
C	= Dissolved oxygen concentration, organic matter concentration
C _A	= Dissolved oxygen concentration of the water
C _t	= Organic material concentration at time, t
C _o	= Organic material concentration at time, t = 0
c _o	= Benthic oxygen demand in mg/sludge volume
D	= Diffusion constant, cm ² /hr, cm ² /sec
D _B	= Net rate of benthic oxygen demand
F	= Flux
K	= Reaction rate constant
K	= Reaction rate constant for bio-oxidation
L	= BOD of the water
L	= BOD remaining at t = 0
L _a	= BOD added to the water
L _T	= BOD remaining at time, t
m	= Volatile material concentration, kgm/m ²
n	= Upstream point
n + 1	= Downstream point
R	= Reaction rate in mg/l-hr
R	= Benthic oxygen demand, gm/hr-m ² , gm, mg, gm/m ² , or gm/gm
R'	= Benthic oxygen demand, mg/hr

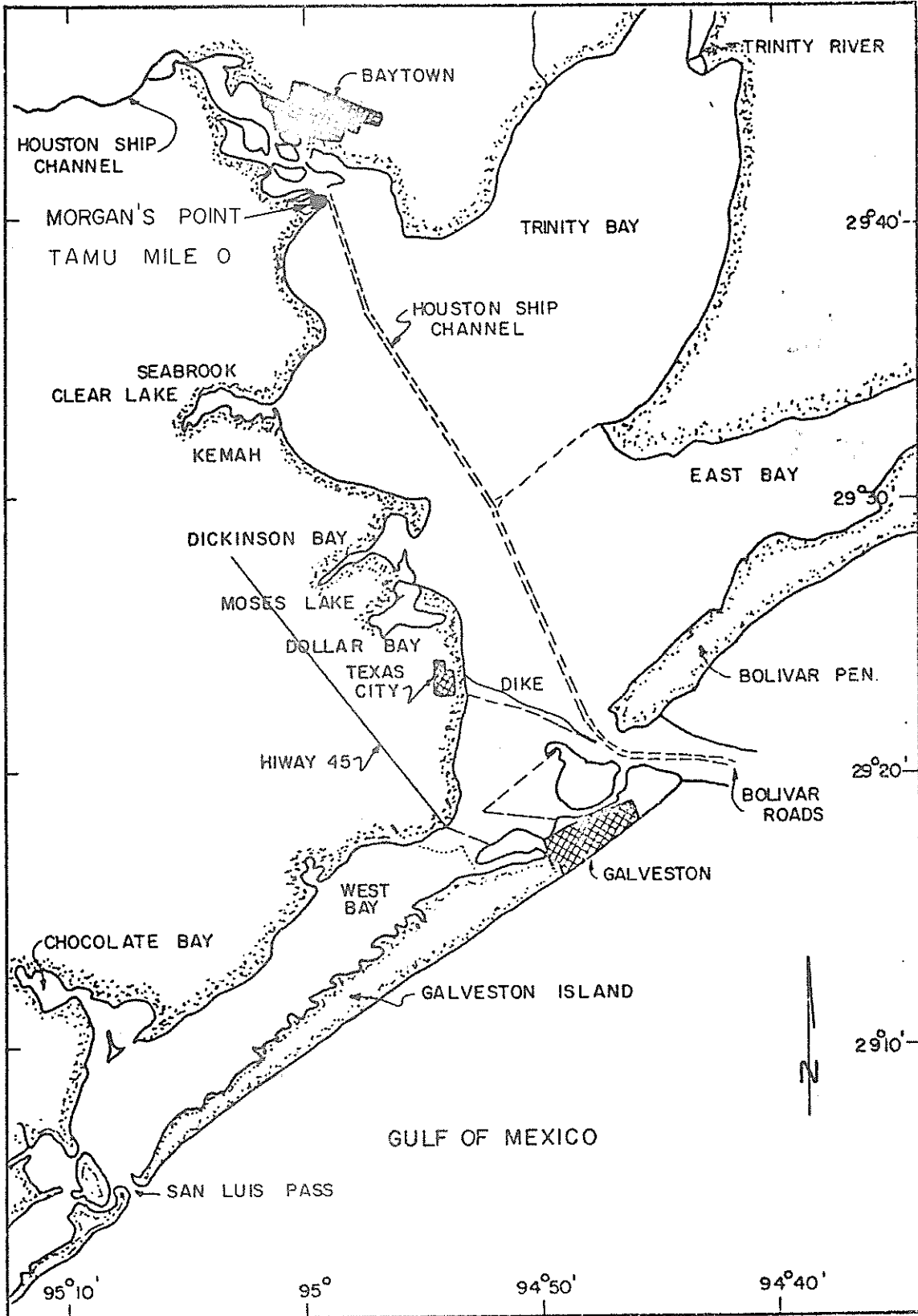
R_1	= Benthic oxygen demand at temperature T_1 , °C
R_2	= Benthic oxygen demand at temperature T_2 , °C
r	= Distance in the radial direction
T	= Detention time, days
T_1	= Degrees Centigrade
T_2	= Degrees Centigrade
t	= Time
v	= Velocity
V_r	= Volume within which the reaction occurs
X	= Depth
y	= Biochemical oxygen demand satisfied at time, t
y	= Depth of sludge in cm.
y	= Benthic oxygen demand in mg/day-m^2 , mg or gm
Y_{So}	= Initial benthic oxygen demand rate, gm/day-m^2
z	= Distance in the z direction
θ	= Temperature correction value, angular displacement

CHAPTER I

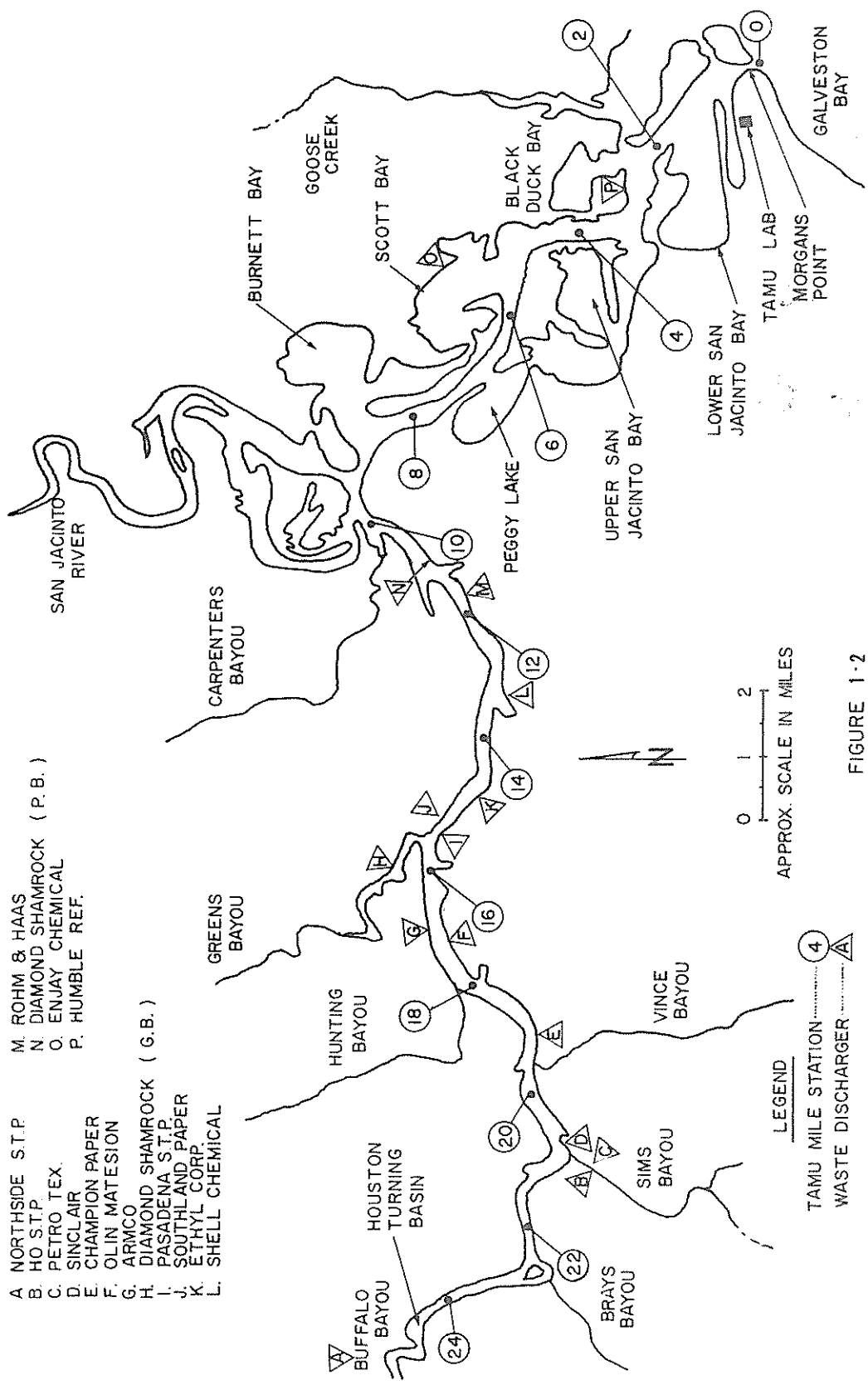
INTRODUCTION

The Houston Ship Channel is an estuary, modified by man, which traverses a distance of 55 miles from Galveston Harbor through Galveston Bay and inland to the port of Houston. The waterway is a modification of Buffalo Bayou and the San Jacinto River. Figure 1-1 shows the Galveston Bay area with the lower portion of the ship channel and Figure 1-2 shows the upper 24 miles of the Houston Ship Channel. The banks of the channel are broken by 12 bayous, the San Jacinto River, several tidal flats, and small shallow bays. First modifications of the estuary originated in March 1905, when channel bends were widened and pile dikes were constructed along the channel. Dredging work on the channel began in 1906, when the city of Houston started developing a 16-foot-deep channel. The turning basin and the slips at Houston were excavated between December 1906 and May 1910.

Two years later, in 1912, a contract was made to provide a 25 foot channel from the Gulf, across 25 miles of fast-shoaling Galveston Bay and 30 miles through Buffalo Bayou, to the turning basin. This contract required that the entire 55 miles of channel, in fully specified width and depth, be turned over at one time to the United States Army Corps of Engineers. In the years from 1919 to 1925, the waterway was deepened to 30 feet, widened, and the Houston Turning Basin was enlarged. Bends were realigned and the inland portion of the channel from Morgans Point to Baytown was widened during the period from 1930 to 1935. The main channel was widened and the depth



**FIGURE 1-1
GALVESTON BAY AREA**



- M. ROHM & HAAS
- N. DIAMOND SHAMROCK (P. B.)
- O. ENJAY CHEMICAL
- P. HUMBLE REF.

- A. NORTHSIDE S.T.P.
- B. HO S.T.P.
- C. PETRO TEX.
- D. SINCLAIR
- E. CHAMPION PAPER
- F. OLIN MATESSION
- G. ARMCO
- H. DIAMOND SHAMROCK (G. B.)
- I. PASADENA S.T.P.
- J. SOUTHLAND PAPER
- K. ETHYL CORP.
- L. SHELL CHEMICAL

FIGURE 1-2
 LOCATION OF DOMESTIC AND INDUSTRIAL DISCHARGES ON THE
 HOUSTON SHIP CHANNEL

LEGEND
 TAMU MILE STATION 4
 WASTE DISCHARGER A

APPROX. SCALE IN MILES
 0 1 2

was lowered to 34 feet in the 1935-1945 period. After 1945, further widening of the channel was carried out until 1948. In 1948, a ten-year deepening and widening project was initiated, which called for a channel 36 feet deep. In 1958 and 1959, the channel depth was increased to 40 feet in all sections except that portion of the waterway from Sims Bayou to the turning basin. Since 1960, the Corps of Engineers sponsored improvements have included realignment of bends and depth increases to 42 feet in the lower reaches of the waterway. Today, the bottom width of the channel ranges from 150 feet in the Houston Turning Basin to 1000 feet at some locations along the channel.

Since the end of World War II, the Houston Ship industrial complex has undergone tremendous expansion, and as a result, the channel now receives large pollution loadings comprised of both domestic and industrial wastes. In 1968, the biochemical oxygen demand (BOD_5) going into the channel was approximately 450,000 lbs. per day. Since then many wastewater treatment plants have been built by industries and municipalities. The BOD_5 loading has been reduced to about 100,000 to 125,000 lbs/day at the present, (1972). Although the waste loads have been reduced appreciably, the present load together with the sluggish flow characteristics of the waterway overload the natural purification capability of the estuary resulting in a severe pollution problem. During the majority of the time the channel, from Mile 10 to Mile 24, has no dissolved oxygen in it and is anaerobic.

As a result a number of research grants have been awarded by both federal and state agencies. These studies are to examine the channel with the goal being to develop effective water quality management techniques

for the system. A most important tool in quality management is the development of a mathematical dissolved oxygen model capable of predicting a water's dissolved oxygen concentrations under a number of different conditions. However, because of the complexity of an estuarine system such as the Houston Ship Channel, key parameters and their effects on the quality of waters within the system must be evaluated before an effective mathematical model can be developed.

Biochemical oxygen demand (BOD), salinity, dissolved oxygen, and temperature are recognized as key parameters in the evaluation of any polluted estuarine system. In the Houston Ship Channel, the benthic loadings have also been shown to represent a significant portion of the overall waste load.

The purpose of this research was to determine the benthic oxygen demand of the deposits in the Houston Ship Channel for use in modeling for dissolved oxygen in the Channel. The scope of the study included: (1) collection of bottom samples, (2) determining characteristics of the sludge such as BOD_5 , etc., (3) use of electrolytic oxygen cells in determining oxygen uptake rate in grams of oxygen per hour per square meter or other units, (4) benthic demands at different temperature to obtain a demand versus temperature correlation and (5) effect of mixing.

Mud and sludge deposits are composed of solids that have been laid down and impounded, generally over long periods of time. If the overriding waters contain dissolved oxygen aerobic conditions are maintained at the surface of the accumulating organic debris. Diffusion of oxygen into the deposits is normally too slow to carry enough oxygen to the deeper strata to keep them from becoming anaerobic.

The sludge-water interface is by no means static. During periods of sedimentation, settling solids form new surface layers. During periods of scour, the deposits are churned up. Gases of decomposition are produced within the sludge under anaerobic conditions. If they are released in sufficient volume, they may buoy some of the sludge into the supernatant water (and even to the water surface). Hydrography determines the degree of deposition as well as the rate of scour, whereas temperature establishes the intensity of decomposition of sludge activity. Because the processes of decomposition in deep deposits are largely anaerobic, their rate of stabilization is normally much slower than that of the suspended and dissolved polluttional load.

Since benthic deposits do represent an oxygen sink it is necessary to know quantitatively the rate of benthic oxygen demand in order for dissolved oxygen modeling to be done for the Houston Ship Channel.

CHAPTER II
LITERATURE REVIEW

Benthic deposits have long been recognized as having effects on the quality of overlying waters (1, 2, 3). As early as 1925 when Streeter and Phelps (4) published their oxygen sag profile method of stream analysis, they recognized the fact that their assumption of no stream water interaction with the bottom was at best tenuous. Streeter (5) later stated that this assumption caused a 40% error in a study of the Illinois River. Other investigators, Schropfer (2) and Hayes and MacAulay (6), have indicated that benthic deposits may contribute as much as 50% of the total oxygen requirement of the river. Camp (7) states that the assumption that the biochemical oxygen demand (BOD) removed from the overlying waters by the sludge is equal to the BOD contributed to the water by the sludge is rarely acceptable, and causes typically low estimates.

Because of the error encountered in neglecting the effects of the benthic oxygen demand on stream quality, numerous investigators have attempted to characterize the effects of the sludge in such a way as to incorporate benthic demand into stream oxygen balance equations (5, 8, 9, 10, 11, 12). None of the analyses thus proposed have been sufficiently encompassing to gain widespread acceptance (1). The primary reason for this is that the interaction between sludge and the overlying water is too complex to lend itself to either simple or comprehensive

solutions. These interactions may be summarized as follows:

1. Oxygen-demanding substances are desorbed from sludge particles into overlying waters. (9, 13)
2. Oxygen-demanding substances are adsorbed onto clay particles in the sediments. (1, 14)
3. Scouring resuspends oxygen-demanding particulates. (5, 15)
4. Oxygen-demanding particulates in times of low flow may settle. (1)
5. Decomposition products of anaerobic activity (i.e., H_2S ; CH_4) may desorb from sediment layers to be stabilized by the oxygen in the overlying waters. (13, 16, 17, 18)
6. Oxygen may be absorbed into the sediment for aerobic stabilization in the benthic system. (1)

To compound the difficulties in characterization, each of these interactions is a function of such parameters as turbulence (1, 19, 20, 21, 22), temperature (23), dissolved oxygen (D.O.) (24, 25, 26), sludge depth (13, 27), pH (17), and sludge physical and chemical characteristics (17, 24, 7).

Some attempt has been made by investigators to study the interaction of the sludge and water under controlled conditions to isolate the effect of individual parameters in an attempt to produce a comprehensive model using the sum total of the effects of the individual parameters. Baity (13) conducted a study in which he attempted to determine the effect of depth on oxygen uptake of sludge at a constant temperature. Using depths of 0.1 to 4.0 cm the following empirical depth-demand relationship was determined:

$$y = 2,700 X^{0.485} \dots \dots \dots (2-1)$$

where:

X = depth of sludge in cm

y = rate of oxygen demand in $mg/day-m^2$ of sludge surface.

Fair et al. (27), using methods somewhat more refined than Baity, and sludge depths of 1.5 to 10.2 cm, proposed the following equation:

$$Y_{So} = 2.45 mX^{0.485} \quad (2-2)$$

where:

Y_{So} = initial rate of oxygen demand, gm/day-m²

m = concentration of volatile matter, kgm/m²

X = depth of sludge in cm.

The results of Fair and Baity, although seemingly accurate for the quiescent systems, were found not to be valid in systems which were of sufficient turbulence to cause slight erosion of the mud surface.

Edwards and Rolley (20) and Hanes and Irvine (1), in independent studies of the effect of mud erosion on oxygen consumption of river muds, found that oxygen requirements were independent of sludge depth. They did determine, however, that oxygen uptake was a function of the extent of erosion of sludge by the turbulence of overlaying water. The oxygen uptake rate in a sample in which the top 0.5 cm of sludge was eroded was 6 times that in which no erosion occurred.

Knowles (28) made a similar observation, but found that the effects of mixing on sludge oxygen uptake rate varied with the dissolved oxygen in the overlying water. Variation in the dissolved oxygen concentration was also a factor in oxygen uptake rates in quiescent sludge systems in which the overlying water was relatively quiescent also.

McKeown (21) determined that at sludge depths greater than one foot the surface area rather than depth controlled oxygen uptake rates. He also observed the increase in oxygen uptake rates for stirred samples to be twice that in unstirred samples.

Carey (22) observed an increase of 1.6 to 8.3 mg/hr-m² between essentially no mixing and what he termed standard mixing, and he observed an increase of 8.3 mg/hr-m² to 27.8 mg/hr-m² between standard mixing and mixing.

Hanes and Irvine (23) made a determination of the effects of temperature on quiescent oxygen uptake rates by covering sludge with aerated water and allowing the supernatant to be totally depleted. Their data indicated the increase in oxygen uptake rates from 20°C to 25°C was more than triple (from 0.042 to 0.133 gm/hr-m²) and an increase from 15°C to 20°C from 0.026 to 0.042 gm/m²-hr. Kramer (29) in preliminary studies on the Houston Ship Channel, indicated that temperature could be as important if not a more important parameter than mixing. Using an electrolytic benthal respirometer apparatus, he measured rates at 35°C which showed an increase of four times over the 20°C rate. No attempt was made to correlate mathematically temperature versus uptake rate.

Several authors have attempted to produce mathematical expressions which could be used within the oxygen sag curve to make possible the inclusion of benthic demand. Ogunrombi and Dobbins (30), using material balance techniques, developed a set of equations assuming that benthic oxygen demand was composed of two separate reactions: (1) the BOD desorbed from the sludge to the overlying water and (2) the oxygen absorbed into the sludge for benthic stabilization. The two equations they derived are as follows:

$$L_a = \left[\frac{L_{n+1} - L_n}{t} \right] + \left[\frac{1}{T} + \frac{K_{n+1} + K_n}{2} \right] \left[\frac{L_{n+1} + L_n}{2} \right] \dots \dots \dots (2-3)$$

where:

L_a = BOD added to the stream

L = BOD of the water

t = time

T = detention time (days)

K = reaction rate for biological oxidation

n = upstream point

$n+1$ = down stream point

and

$$D_B = \frac{1}{T} \left[\left(\frac{C_{A,n+1} + C_{A,n}}{2} \right) - \left(\frac{C_{n+1} + C_n}{2} \right) \right] - \left[\left(\frac{K_{n+1} + K_n}{2} \right) \left(\frac{L_{n+1} + L_n}{2} \right) \right] - \left[\frac{C_{n+1} - C_n}{t} \right] \dots \dots \dots (2-4)$$

where:

D_B = net rate of removal of dissolved oxygen by benthic deposit

C_A = dissolved oxygen content of the water

C = dissolved oxygen content of water

These equations, although valuable since they are derived from theory, are highly limited in practical application. Unless one uses a synthetic sludge, as Ogunrombi and Dobbins did, (30), K_n and K_{n+1} are not truly constant and are extremely difficult to determine; and if a first order reaction rate is assumed, as they did, simple arithmetical averages are not sufficient to give accurate mean values of K , L , and C .

From the literature cited above, it appears that the most important aspect of sludge characterization is an understanding of the effects of temperature, reaction rate, diffusion and scouring. This investigation attempts to quantitatively ascertain the effects of each of these parameters on benthic deposits.

CHAPTER III
METHODS AND PROCEDURES

Sampling and Analytical Procedures

In this investigation, samples were taken from the entire length of the Houston Ship Channel. Samples consisted of sludge taken with an Eckman Dredge, composed of sediments from the top three inches of the Ship Channel bottom. Water was taken from one to two feet above the solid liquid interface at the same point the sludge was taken.

The samples were enclosed in sealed containers and refrigerated. The tests were initiated within 24 hours of the sampling time, providing conditions within the bottle which were similar to those actually encountered in the Ship Channel.

Some sludges were analyzed for total organic carbon (TOC) and chemical oxygen demand (COD) before and after test runs. The COD analyses were according to the procedure outlined in Standard Methods (44). A representative sample was tested for heavy metals, total solids, and volatile solids. The analyses for heavy metals were made using an atomic absorption spectrophotometer (AA). The samples were examined for aerobic biological activity and macroscopic invertebrate content. The results of these analyses are shown in Table 3-1.

Experimental Apparatus and Theory of Operation

In determining the benthic oxygen demand the electrolytic respirometer system developed by Clark (32, 33) was used. Figure 3-1 shows the cell set up for a BOD experiment. Figures 3-2 and 3-3 give more detail

TABLE 3-1
 SLUDGE ANALYSES*
 Mile 20

<u>Analysis</u>	<u>Pretest Concentration</u>	<u>Post Test Concentration</u>
BOD	28,000 mg/kgm	0 mg/kgm
COD	354,000 mg/kgm	350,000 mg/kgm
Total Solids	22.5%	22.5%
Heavy Metals		
Hg	846 μ gm/kgm	
As	6.5 mg/kgm	
Pb	203 mg/kgm	
Zn	217 mg/kgm	
Cu	50 mg/kgm	
Cr	122 mg/kgm	
Ni	24 mg/kgm	
Mn	120 mg/kgm	
Fe	4.3 mg/kgm	
Ag	4.3 mg/kgm	
MPN		
without Hg ⁺⁺		39 x 10 ⁶ bact/sample
with Hg ⁺⁺ (600 mg/l)		131 x 10 ⁵ bact/sample
Volatile Solids**	10.0%	10.0%
Macroscopic Invertebrate Content	0	0

* Reported on dry weight basis

** Percent of total solids

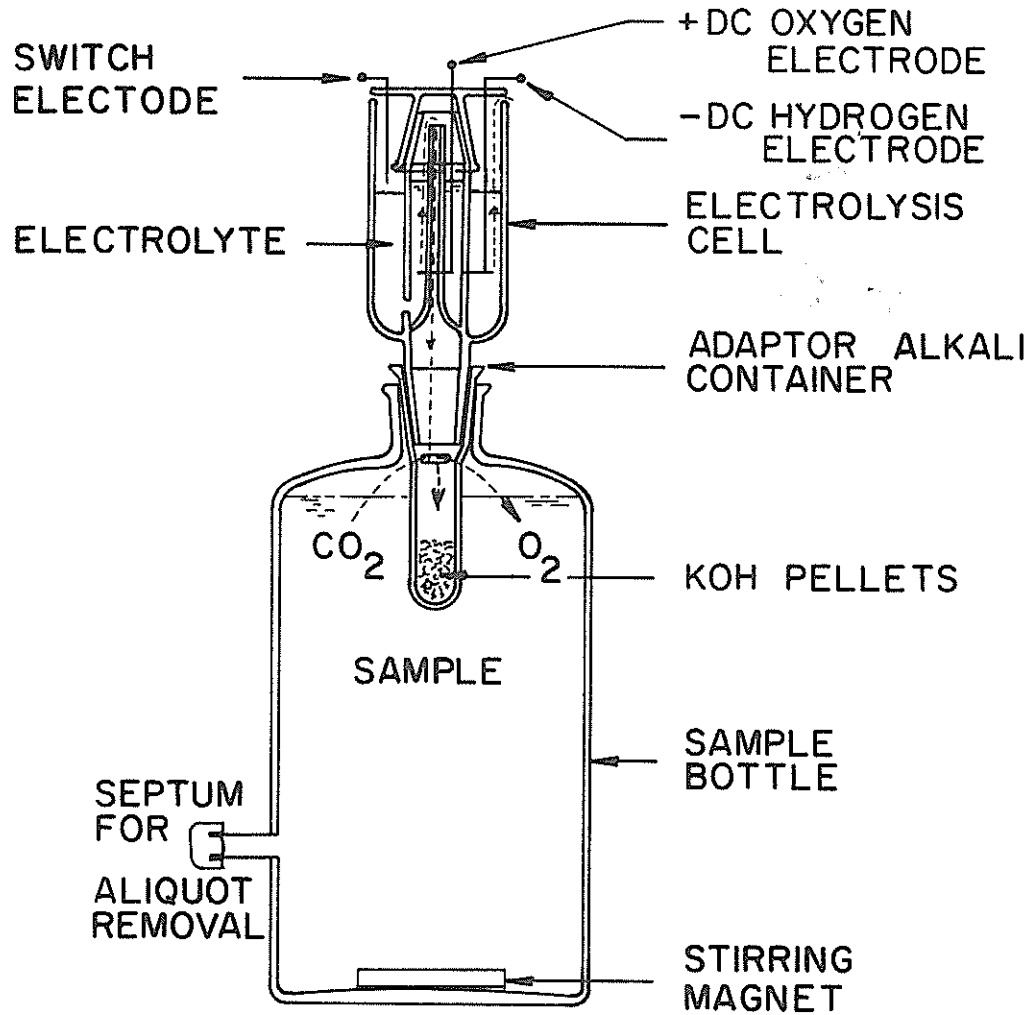


FIGURE 3-1
SCHEMATIC DIAGRAM SHOWING THE BASIC
OPERATION OF THE ELECTROLYSIS SYSTEM
FOR MEASURING BOD OF A LIQUID

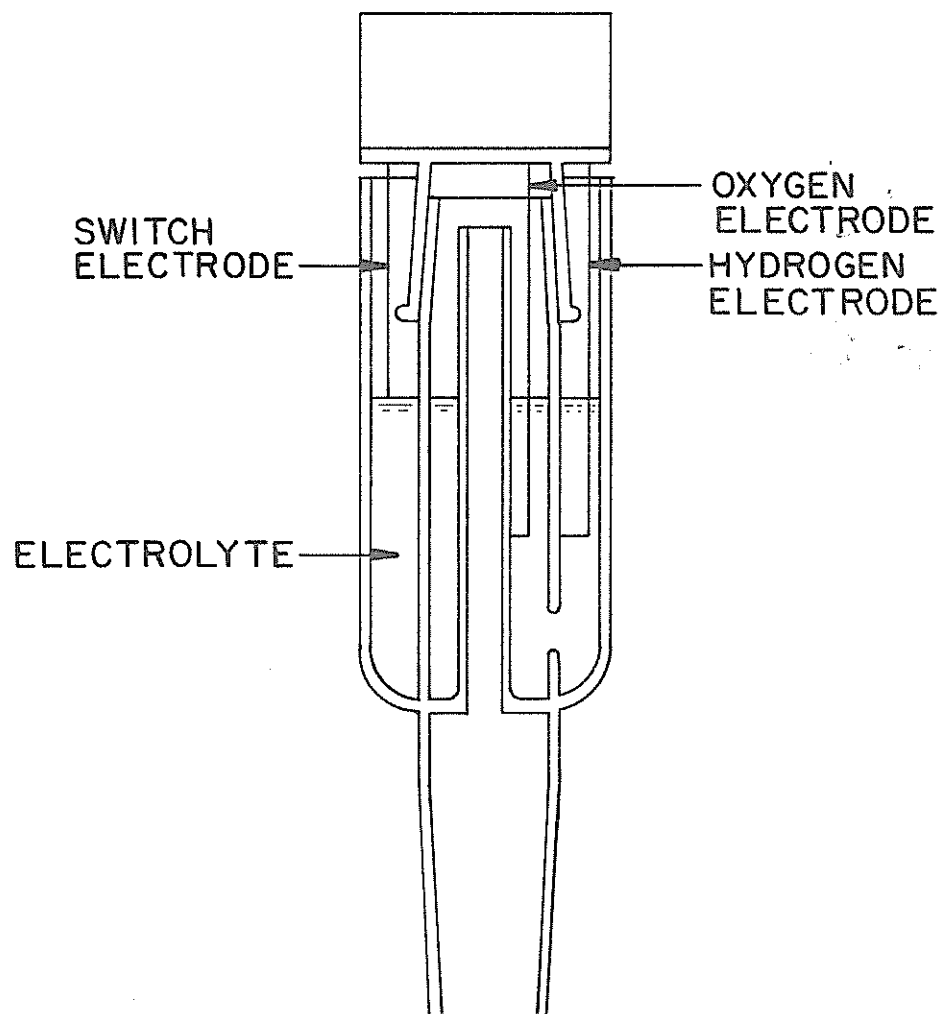


FIGURE 3-2

SWITCH ELECTRODE IN CONTACT WITH
ELECTROLYTE OXYGEN GENERATOR OFF

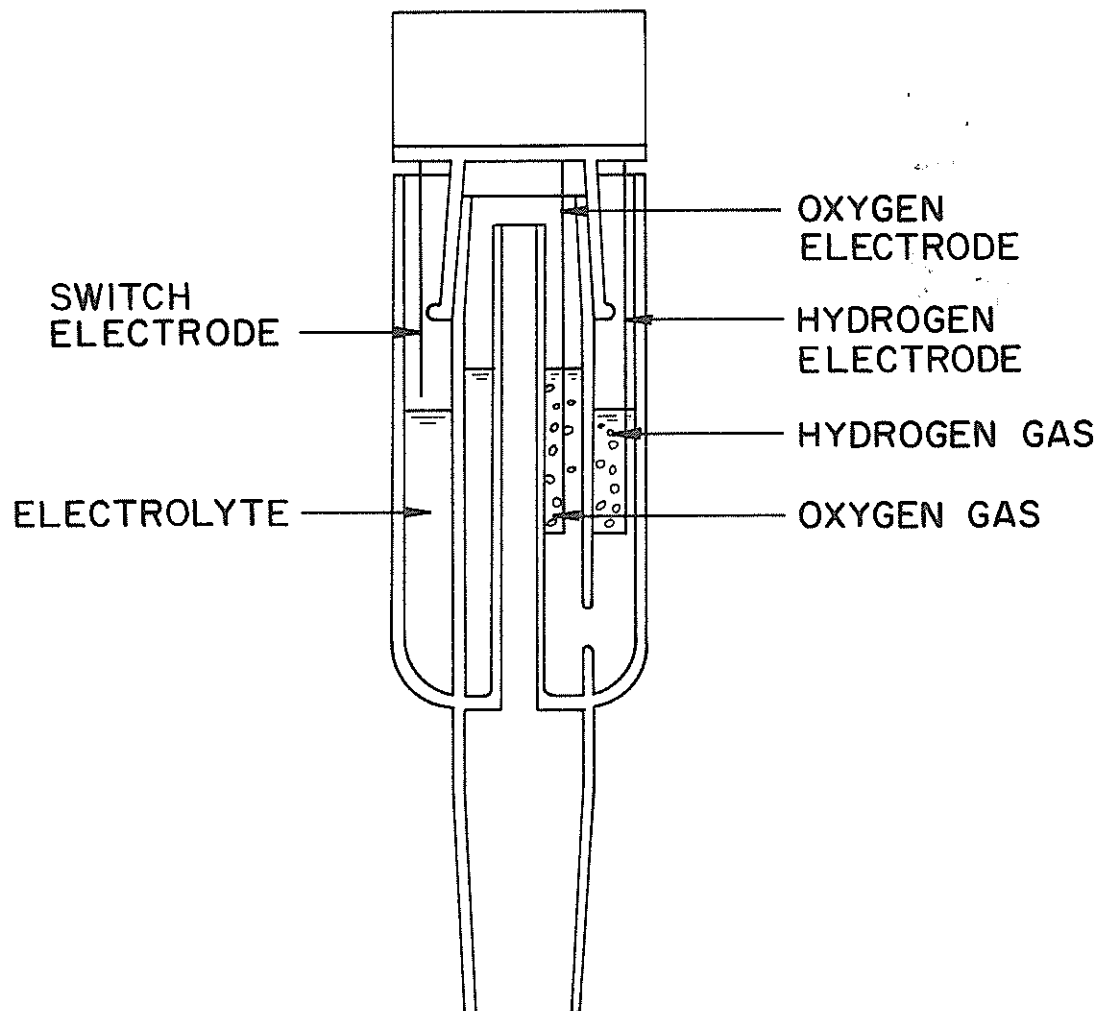


FIGURE 3-3
SWITCH ELECTRODE NOT IN CONTACT
WITH ELECTROLYTE

on the unit. Figure 3-4 shows a cell set up for the biochemical oxygen demand of a water sample. A brief description of the unit is as follows.

Biochemical oxygen demand (BOD) has been successfully evaluated by the use of this electrolysis manometric technique and has been reported in the literature (29, 32-43). Basically, the system continuously replaces oxygen used in the sample by a manometrically triggered electrolysis reaction.

The electrodes in Figure 3-2 are connected to a switching and counting circuit. As oxygen is chemically or biologically removed from the sample (the CO_2 which is released as a metabolic end product is removed from the air space by a KOH solution), a slight vacuum in the air space is produced. This causes a rise of electrolyte in the inner tube of the cell and a fall in electrolyte in the annular space below the switch electrode. When contact with the switch electrode is broken, Figure 3-3, oxygen gas is generated to fill the partial vacuum until the pressure deficit has been satisfied. At such time the electrolyte again makes contact with the switch electrode. The time during which the electrolysis cell was generating oxygen to the sample and the current supplied during that time are converted electronically to milligrams of oxygen.

Milligrams of oxygen supplied by the cell are related to Faraday's law, which states that 96,500 coulombs of electricity will deposit one gram-equivalent of an element. In theory the milligrams of oxygen produced are:

$$\text{mg O}_2 = \left(\frac{8000 \text{ mgO}_2}{\text{gm-equiv}} \right) \left(\frac{1 \text{ gm}}{96,500 \text{ amp-sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) (a) (t) \dots (3-1)$$

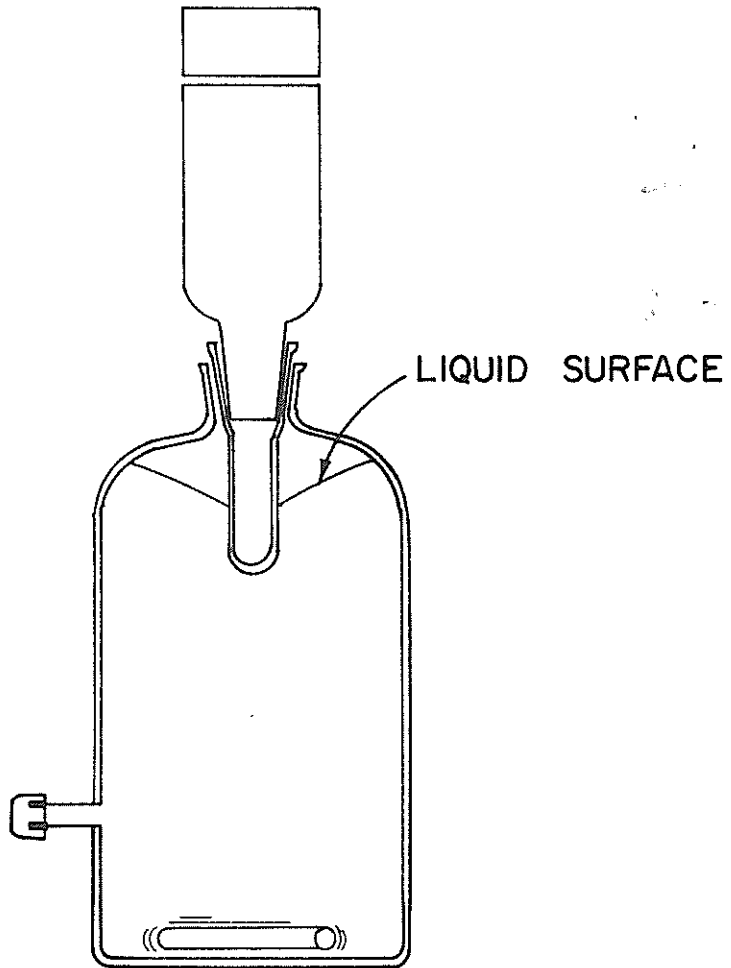


FIGURE 3-4
ELECTROLYTIC CELL MIXING WITH
LIQUID AND MAGNA-MIX BAR

where:

mg O₂ = mg oxygen

a = current flow in amps

t = time in minutes

The BOD unit set up in Figure 3-1 is for a liquid. The water must be slowly mixed by the magna-mix bar in order for the unit to work, Figure 3-4. Figure 3-5 shows a cell set up for benthic oxygen demand. In order to circulate the liquid, the gas above it was recycled to create the mixing effect required for oxygen circulation. The surface area for the sludge in the 3 3/4" I.D. bottle was $7.12 \times 10^{-3} \text{ m}^2$.

Experimental Procedure

This investigation consisted of experiments designed to give:

- (1) Benthic oxygen demand for samples from the entire length of the Channel,
- (2) Correlation of benthic demands to BOD₅ of the sludges,
- (3) Relationships between benthic demands and temperature,
- (4) Benthic demand for quiescent, scoured, and completely suspended conditions,
- (5) Depth of the aerobic layer,
- (6) Kinetics of benthic uptake and
- (7) Flux theory and equations.

The experiments on benthic demands in quiescent systems involved the following procedures. Two hundred or 250 ml of sludge from the Ship Channel equaling 64 and 80 grams dry weight, respectively, was placed in the bottom of each of the electrolysis cells and 800 ml and 750 ml of Ship Channel water was added to each and allowed to settle for 24 hours. Blanks were prepared with 1000 ml of Ship Channel water to permit the subtraction of the BOD of the Channel water itself. The blanks were stirred by a magna-mix, Figure 3-1. The bottles with the sludge, Figure 3-5, were

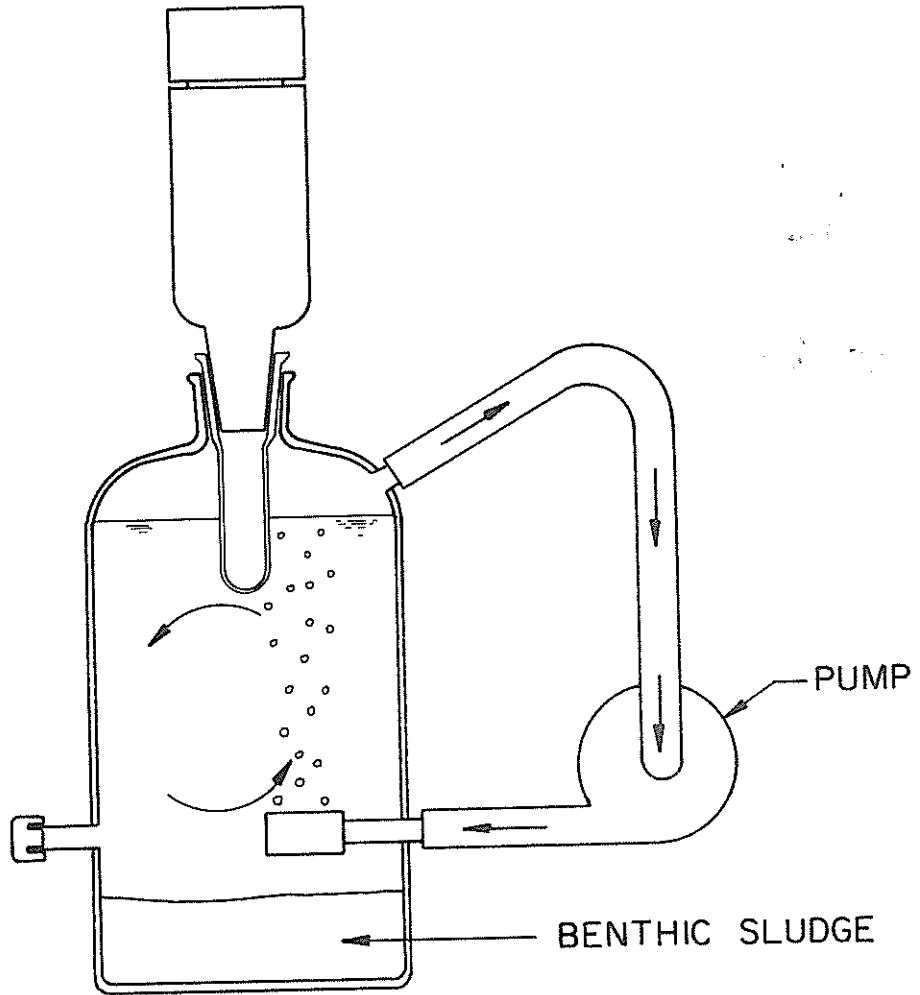


FIGURE 3-5
SLUDGE BENTHIC PUMPING OPERATION

operated so that the air flow rate was enough to mix the water but not enough to scour the sludges. The oxygen demand versus time was recorded and the data reduced to give the demand expressed as grams or milligrams of oxygen per hour-m². Correlations of benthic demand with BOD₅ of the sludges were made using BOD₅ values as determined by Standard Methods for Water and Wastewater, 13th edition, 1971.

The relationships between benthic demand and temperature used electrolysis cells set up as described previously with the cells set in incubators of constant temperature. The temperatures used were 15°C, 20°C, 32°C, and 35°C and the air flow rate was kept low enough to prevent scour of the sludge surface. The range in temperatures span the temperature range found in the channel from past studies. Measurements were made to determine the depth of the aerobic layer within the sludge. The depth of aerobic activity in the sludge was measured by a ruler by observing the point at which the black coloring (probably caused by FeS) changed to light brown.

The tests to determine benthic demands were for three systems which were: (a) a quiescent condition, (b) a scoured condition and, (c) a completely mixed condition. The quiescent system used a low air flow rate and was described on page 19. The scoured system had an air flow rate which was great enough to scour the sludge surface. The completely mixed system was stirred by a magna-mix to an agitation level where the entire sample was suspended. The kinetics of uptake flux theory and equations were derived by reducing the data to determine the necessary variables.

One experiment was done to compare the benthic demand to the natural chemical demand. Completely mixed samples, that is, samples in which the stirring was by magna-mix at a rate which kept the sludge in suspension,

were used. One sample was the control, one had one gram of HgCl_2 and another had 5 grams HgCl_2 per liter. The HgCl_2 was added to inhibit microbial activity.

CHAPTER IV

RESULTS AND DISCUSSIONS

Benthic Demand For The Entire Channel Length Under Quiescent Conditions

The quiescent, non-scoured system is modeled as illustrated in Figure 4-1. The material in the reaction vessel can be seen as being divided into separate areas; supernatant or water layer, aerobic sludge layer and the anaerobic sludge. Even with the simplified model the diffusion-reaction transport equilibrium is still extremely complex. Reaction most probably occurs in both the supernatant and the aerobic sludge at different rates. There is a change in the rate of diffusion of oxygen-demanding substances out of the sludge both at the aerobic-anaerobic interface and at the solid-liquid interface, and oxygen diffuses into and through the aerobic layer.

Figure 4-2 shows two typical oxygen uptake plots for a sample from Mile 22 and Mile 12 under quiescent conditions at 32°C. It can be noted that the Mile 22 sample had more oxygen demand than Mile 12. This was as expected since a large portion of the sludges in the upper channel come from municipal wastewater. Since the sludge water interface was 7.12×10^{-3} sq. meters the demand is

$$\text{Demand(Mile 20), } R = \left(1.4 \frac{\text{mg}}{\text{hr}}\right) \left(\frac{\text{gm}}{1000 \text{ mg}}\right) \left(\frac{1}{7.12 \times 10^{-3} \text{ m}^2}\right) = 0.20 \text{ gm/hr-m}^2$$

and

$$\text{Demand(Mile 12), } R = \left(0.9 \frac{\text{mg}}{\text{hr}}\right) \left(\frac{\text{gm}}{1000 \text{ mg}}\right) \left(\frac{1}{7.12 \times 10^{-3} \text{ m}^2}\right) = 0.13 \text{ gm/hr-m}^2$$

Table 4-1 and Figure 4-3 show the benthic demand, R , in gm/hr-m^2 for sludges from the entire channel length under quiescent conditions at 32°C.

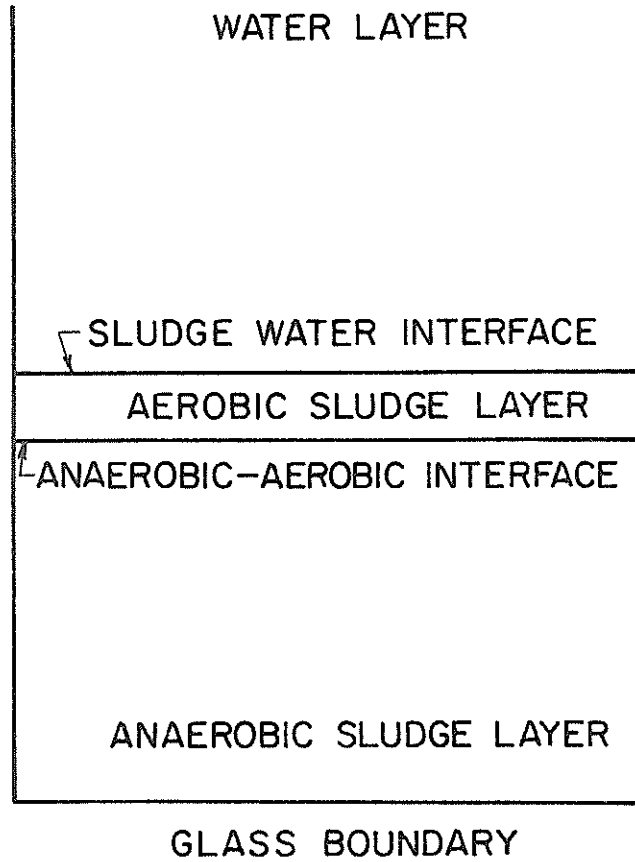


FIGURE 4-1
DIAGRAM OF QUIESCENT SYSTEM

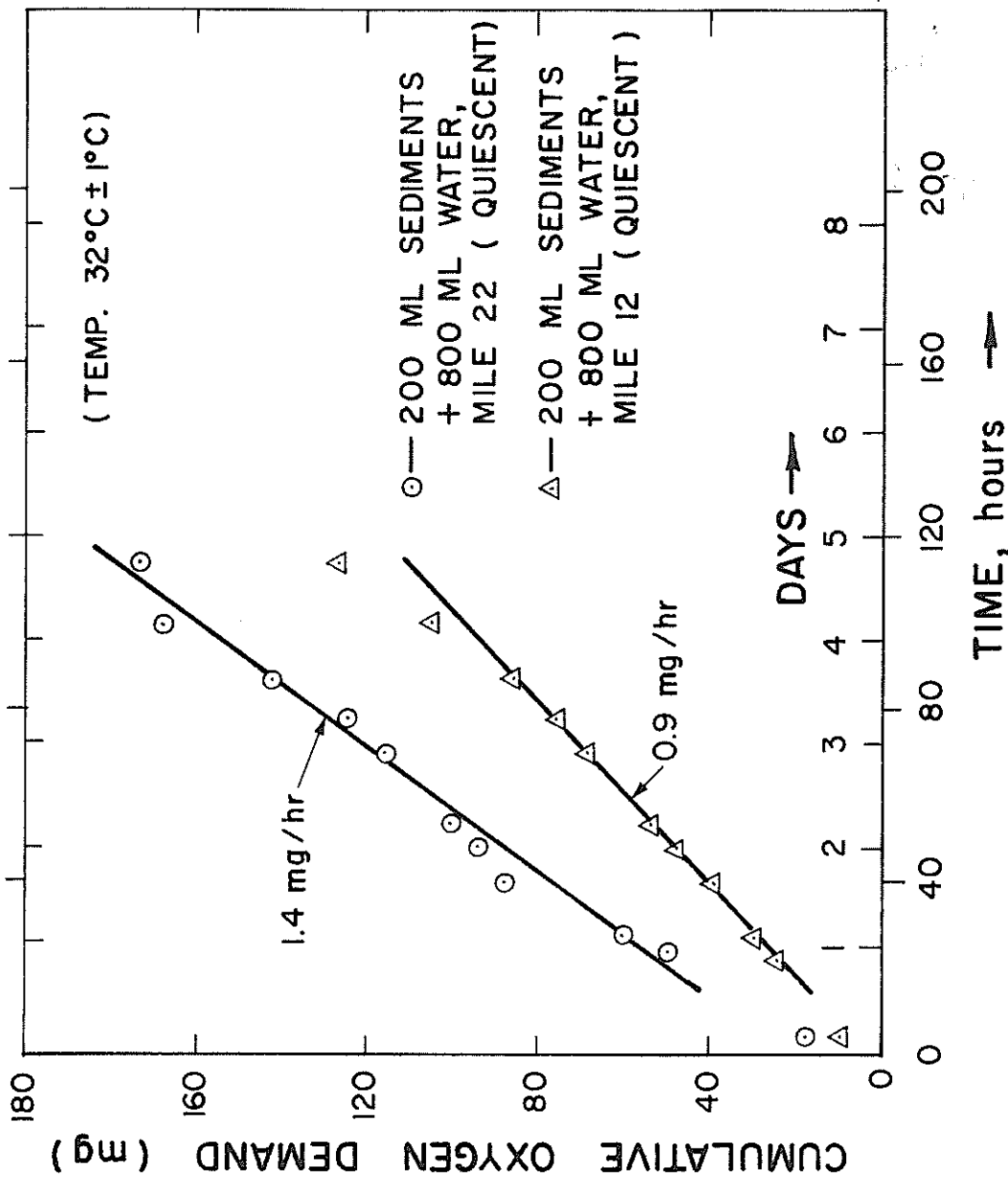


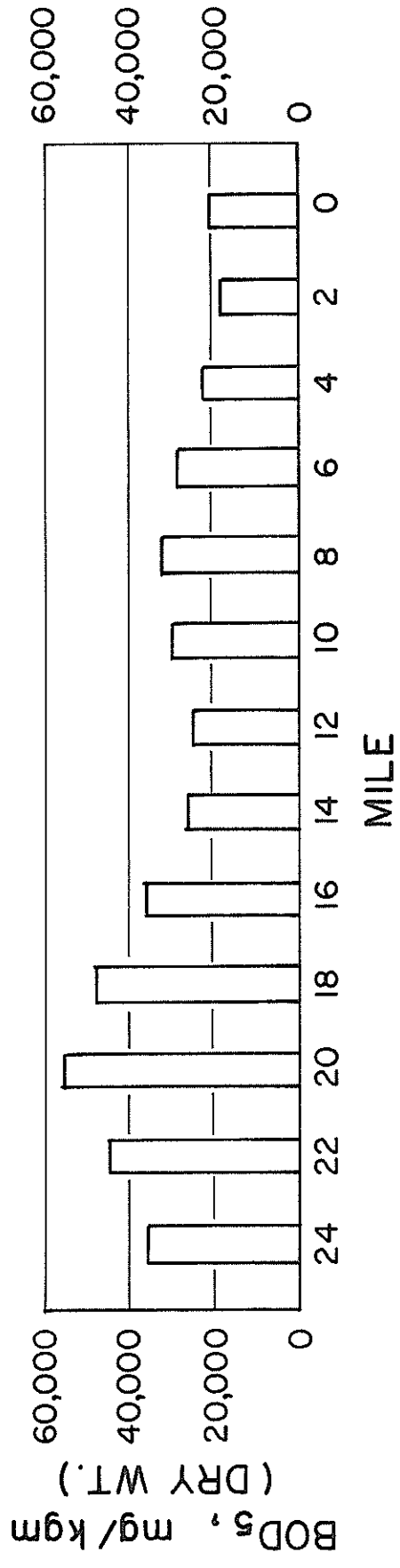
FIGURE 4-2

HOUSTON SHIP CHANNEL BOTTOM SEDIMENTS OXYGEN DEMAND

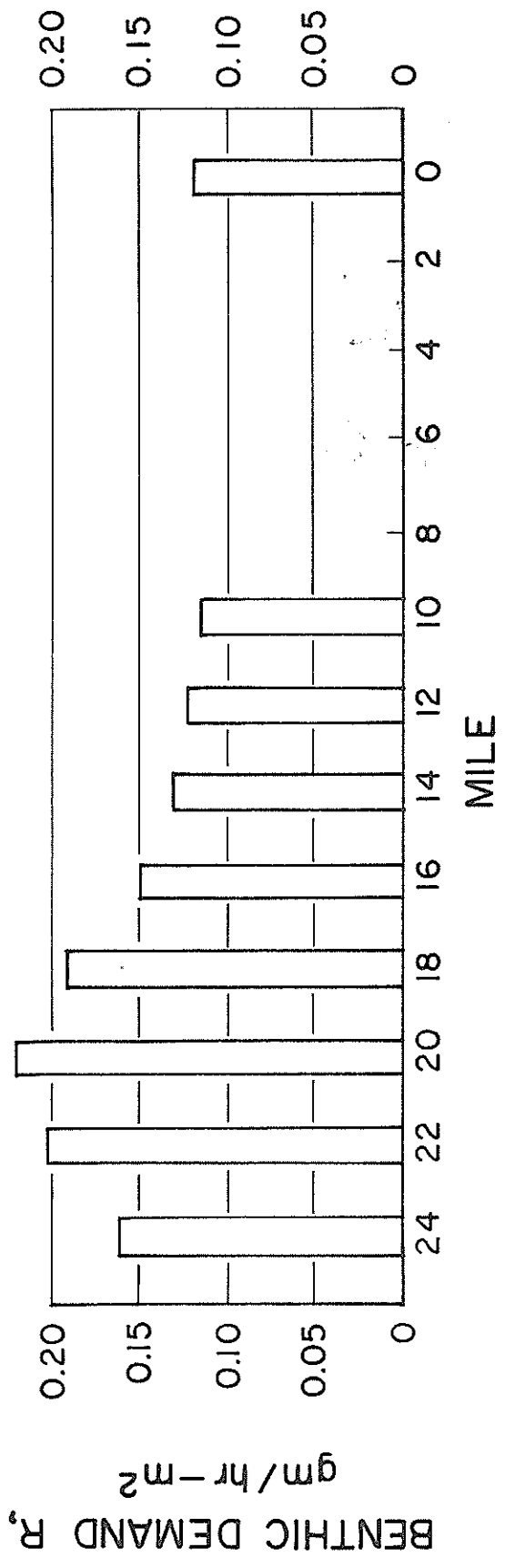
TABLE 4-1

BENTHIC OXYGEN DEMANDS AND BOD₅ VALUES FOR
HOUSTON SHIP CHANNEL STATIONS
(Miles Upstream from Morgan's Point)

<u>Mile</u>	<u>BOD₅ mg/kgm (dry wt.)</u>	<u>Oxygen Demand at 32°C gm/hr-m²</u>
24	35,000	.16
22	45,000	.20
20	55,000	.22
18	47,000	.19
16	35,000	.15
14	25,000	.13
12	25,000	.125
10	30,000	.12
8	32,000	-
6	29,000	-
4	22,000	-
2	14,000	-
0	21,000	.12



BOD₅ PROFILE



BENTHIC DEMAND PROFILE

FIGURE 4-3
BENTHIC DEMAND AND BOD₅ PROFILES

Also shown are BOD₅ values of the sludges as reported in previous work (47). It can be seen that there is a relationship between the BOD₅ and the benthic demand. Figure 4-4 shows the relationship as a linear plot of a straight line. This is a straight line with a slope of the general type,

$$y = b + mx$$

Inserting values from the graph gives

$$R = 0.035 + 3.45 \cdot 10^{-6} \cdot \text{BOD}_5 \quad \dots \dots \dots (4-1)$$

Where:

R = benthic oxygen demand, gm/hr-m² at 32°C

BOD₅ = mg/kgm (dry wt.), 20°C

The reason for the higher benthic demands and higher BOD₅ values in the sludge in the upper one-half of the Channel is that the industrial complex is greater in this area and also because there are several large municipal wastewater treatment plants in this region. The municipal plants discharge into tributaries which, in turn, flow into the Ship Channel.

It must be remembered that these demands are for the sludge in a quiescent state and for a temperature of 32°C (Conversion to other temperatures can be made using Equation 4-3.) The rate of sludge accumulation and other physical characteristics of the sediments has been reported in a prior report (27).

Temperature Effects on Benthic Demands

One series of tests was run at three different temperatures with no mixing of the sludge with overlaying water to determine the effects of temperature and the effects of diffusion in the sludge on oxygen uptake rate. In accordance with information presented in the literature, the sludge was allowed to settle for 24 hours and become compacted before

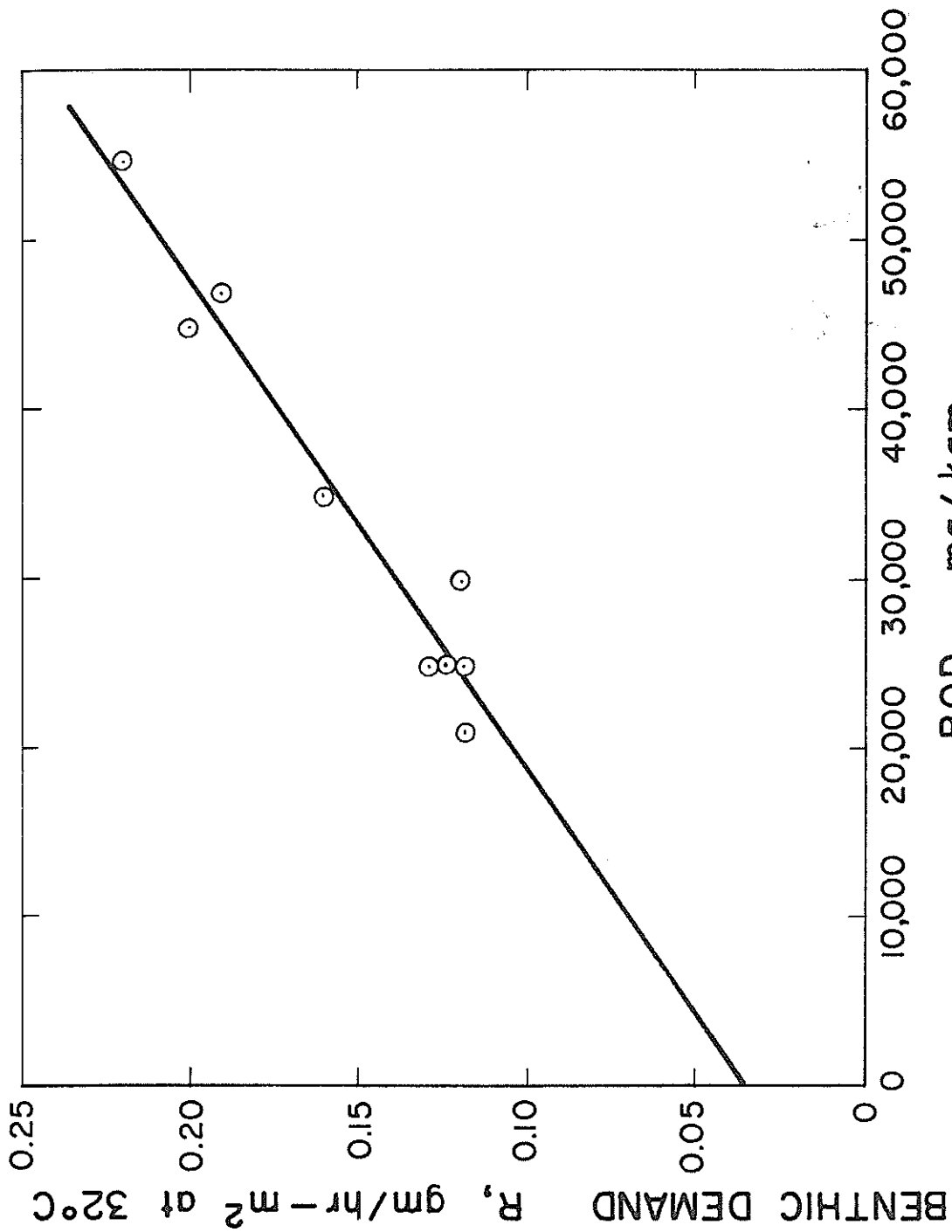


FIGURE 4-4
 BOD_5 VS BENTHIC DEMAND

the results would be independent of the depth used in the sample (21).

All quiescent systems were similar in that each showed an initial rapid oxygen uptake period in which the suspended oxygen demand was stabilized, followed by a period of constant rate oxygen uptake. Oxygen uptake as a function of time is shown in Figure 4-5 and Figure 4-6 gives the benthic demand as a function of temperature. Table 4-2 shows the data for the tests. It can be seen that as the temperature increases the benthic demand gets greater. The benthic demands, expressed in gm/hr-m², are in keeping with the values found in the literature.

Temperature - rate correlations in biological processes are commonly made by the following type of equation.

$$R_2 = R_1 \theta^{(T_2 - T_1)} \quad \dots \dots \dots (4-2)$$

This is an equation derived from the Van't Hoff-Arrhenius equation. The θ value found in this study was 1.055, which agrees well with literature values. Thus the temperature correction equation is:

Mile 0 to Mile 24:

$$R_2 = R_1 \cdot 1.055^{(T_2 - T_1)} \quad \dots \dots \dots (4-3)$$

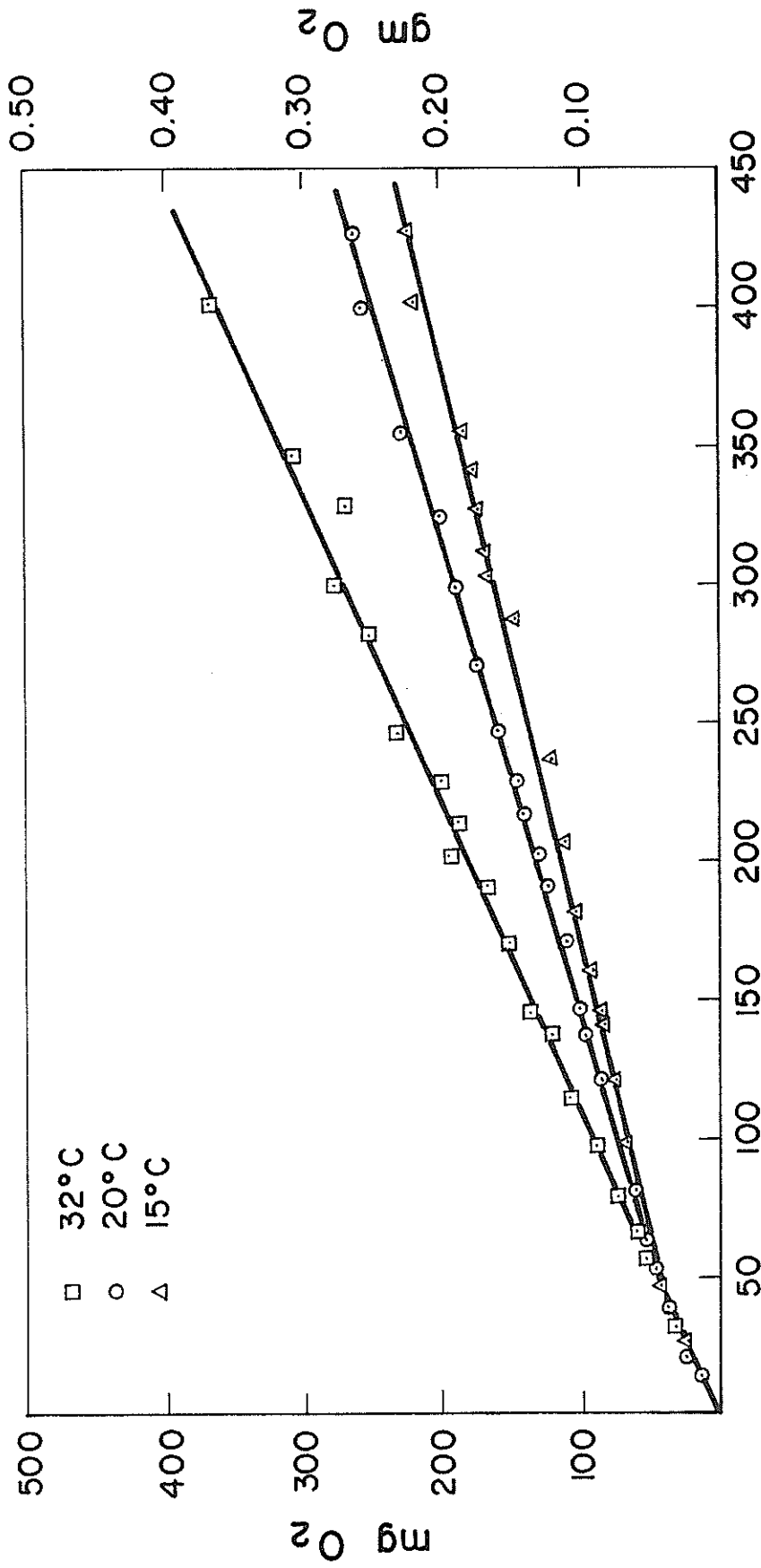
Where:

R_1 = Benthic demand, gm/hr-m² at T_1

R_2 = Benthic demand, gm/hr-m² at T_2

T_1, T_2 = Temperature in Centigrade

Equation 4-3 and the Figure 4-6 show that the biological activity increases 1.75 times with a 10°C rise in temperature. This compares well with the generalization that biological activity doubles for every 10°C rise in temperature.



RUN TIME (HR)
 OXYGEN UPTAKE AT VARIOUS TEMPERATURES, MILE 20

OXYGEN UPTAKE AT VARIOUS TEMPERATURES, MILE 20

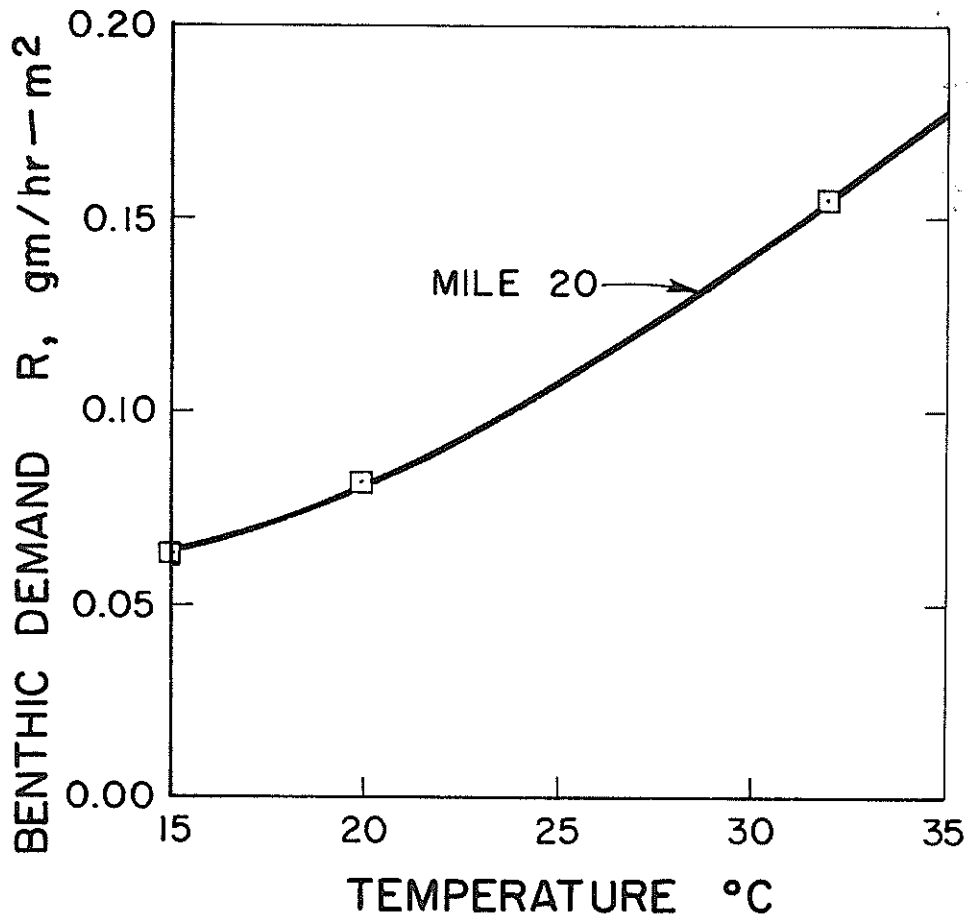


FIGURE 4-6

BENTHIC DEMAND Vs TEMPERATURE,
MILE 20

TABLE 4-2

BENTHIC OXYGEN DEMANDS FOR HOUSTON SHIP
CHANNEL AT VARIOUS TEMPERATURES

<u>Location</u>	<u>Temp. C°</u>	<u>Benthic Demand, R, mg O₂/hr</u>	<u>Benthic Demand, R, gm O₂/hr-m²</u>
Mile 20	15	0.45	0.063
Mile 20	20	0.57	0.082
Mile 20	32	1.10	0.154

Benthic Demand For Scoured Conditions

A benthic demand test was run on a sample from Mile 20 under quiescent and scoured conditions at 20°C. The results of these tests were then compared to determine the effect of increased suspended material and to determine what effect slight scouring of the sediment surface might have in a system. The results of these tests are shown in Figure 4-7.

The findings of the comparison between scoured and unscoured systems were somewhat unexpected when compared to the literature (1, 19, 20, 21, 22). The scoured system had essentially the same oxygen uptake rate as the quiescent system as can be seen in Figure 4-7. There was a slight initial increase probably due to the fact that there were more suspended particles in the scoured system, but after a short period both tests gave virtually the same results.

The oxygen demands were 0.079 gm/hr-m^2 for the scoured sample and 0.084 gm/hr-m^2 for the quiescent sample. The slight difference is probably due to experimental inaccuracy. The aerobic zone in the sludge of the scoured system was twice the thickness of that in the unscoured system, Table 4-3, but this apparently had no bearing on the benthic demand.

It is possible that the scouring used in this test was not sufficient to cause changes in the oxygen uptake rate. Results reported in the literature showed that a minimum of 5 mm of sludge was eroded in the tests which were used to determine the effect of scour. In the test in this investigation only 1 to 2 mm was scoured, which may have been insufficient to give a change of rate.

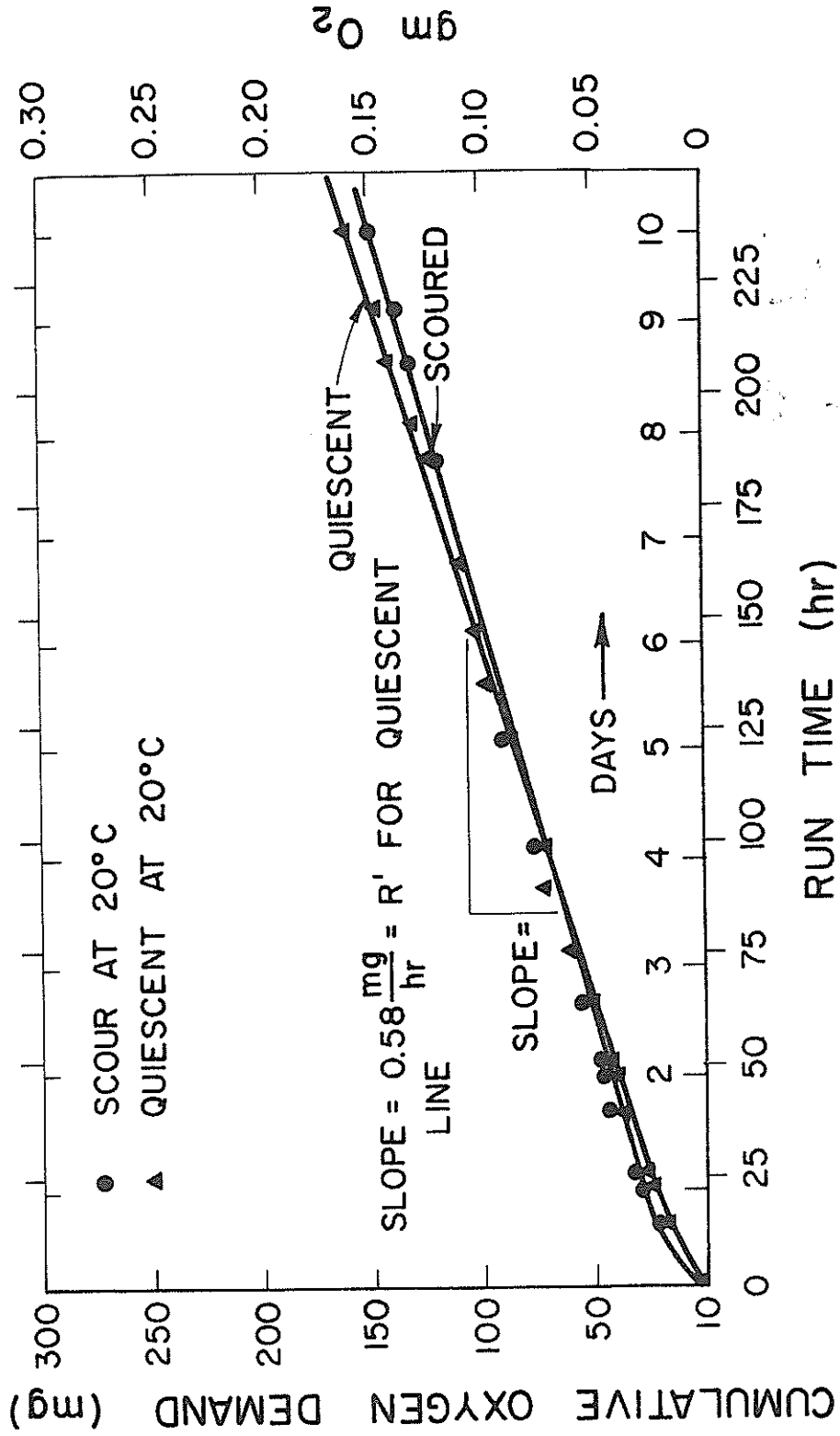


FIGURE 4-7

COMPARISON BETWEEN SCOURED AND QUIESCENT SYSTEMS AT 20°C, MILE 20

TABLE 4-3

DEPTH OF AEROBIC LAYER IN QUIESCENT AND
SCOURED SLUDGES, MILE 20

<u>Temperature</u>	<u>Depth</u>	<u>Condition</u>
15 ^o C	2 mm	Quiescent
20 ^o C	4 mm	Quiescent
20 ^o C	8 mm	Scoured
32 ^o C	4 mm	Quiescent

Benthic Demand For a Completely Suspended Condition

Two tests were run using a high degree of mixing that completely suspended all of the sludge in the electrolysis cells. The sludge came from Mile 20. Figure 4-8 shows the benthic demand on the two samples at 20°C. It can be seen in comparing Figure 4-8 to Figure 4-7 that a suspended condition created a much greater benthic demand than a scoured or quiescent condition. For instance, after 5 days, the suspended test used 1300 to 1440 mg oxygen demand, whereas in a scoured or quiescent state, only 84 mg of oxygen was utilized. Thus complete mixing of the sludge created a demand 15 to 17 times as great as quiescent or scoured conditions.

The plots in Figure 4-8 appear to be pseudo - first order reactions that are dependent upon the substrate concentration. The substrate is assumed to be represented by the oxygen demand to stabilize it biochemically. For a pseudo - first order reaction the rate is

$$\text{Rate} = - \frac{dC}{dt} \propto C$$

or

$$\text{Rate} = - \frac{dC}{dt} = KC$$

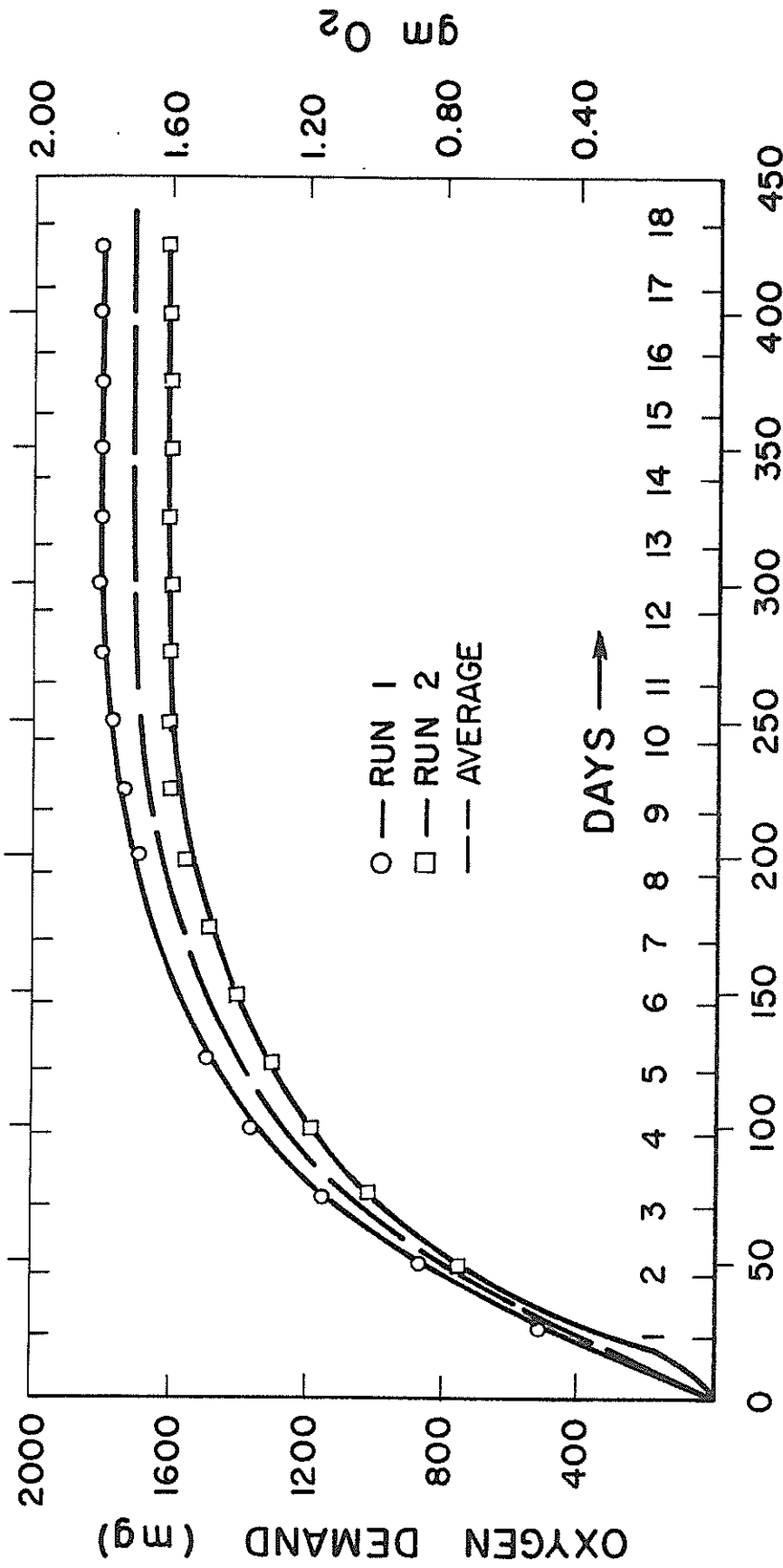
Where C is the organic matter present and dt = time increment.

Transposing,

$$- \frac{dC}{C} = Kdt$$

Setting for integration,

$$\int_{C_0}^{C_t} \frac{dC}{C} = -K \int_0^t dt$$



RUN TIME (hr)
 DAYS →
 O — RUN 1
 □ — RUN 2
 - - - AVERAGE
 FIGURE 4-8
 OXYGEN DEMAND FOR COMPLETELY SUSPENDED SYSTEMS, 20°C, MILE 20

Integrating,

$$\ln \frac{C_t}{C_0} = -Kt$$

$$\ln \frac{C_t}{C_0} = -Kt$$

The amount of organic matter is proportional to the oxygen required to stabilize the organic material aerobically. Therefore,

$C_t \propto L_T$ where L_T is the biochemical oxygen demand remaining at time, t .

$C_0 \propto L$ where L is the biochemical oxygen demand remaining at $t = 0$

Substituting values for C gives

$$\ln \frac{L_T}{L} = -Kt$$

$$\ln L_T = \ln L - Kt \quad \dots \dots \dots (4-4)$$

$$\frac{L_T}{L} = e^{-Kt}$$

The biochemical oxygen demand satisfied at t is y , where

$$y = L - L_T$$

$$y = L(1 - e^{-Kt}) \quad \dots \dots \dots (4-5)$$

A plot of L_T values versus time is given in Figure 4-9. It can be seen that it is a straight line plot so the reaction is pseudo-first order. The slope represents K and is 0.35 day^{-1} or 0.0146 hr^{-1} , and $L = 1675 \text{ mg}$ or 1.675 gms . This is for 20°C .

The equation for the benthic oxygen demand, R , is

$$R = y = 1675 \text{ mg} \left(1 - e^{-0.0146t} \right) \quad \dots \dots \dots (4-6)$$

or

$$R = y = 1.675 \text{ gm} \left(1 - e^{-0.0146t} \right) \quad \dots \dots \dots (4-7)$$

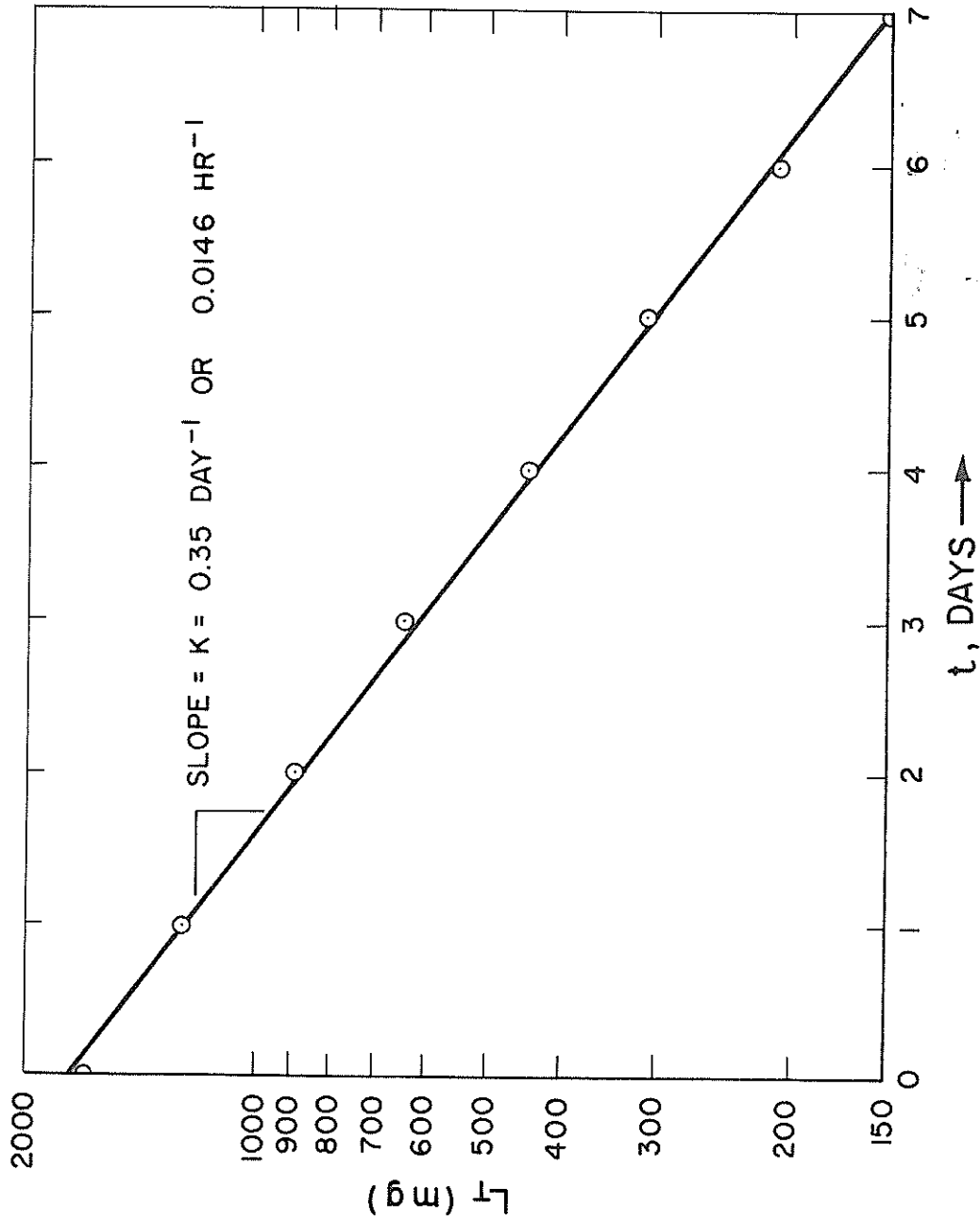


FIGURE 4-9
 L_T Vs t FOR SUSPENDED TEST AT 20°C, MILE 20

Where:

t = hours

R = y = benthic demand at time t

The rate constant of $K = 0.35 \text{ day}^{-1}$ (base e) is 0.15 day^{-1} (base 10) which compares favorably with values found in the literature of 0.10 to 0.35 day^{-1} (base 10) at 20°C .

It may be desirable to express the benthic demand in terms of grams per square meter, which for an area of $7.12 \times 10^{-3} \text{ m}^2$ is

$$R = 235 \frac{\text{gm}}{\text{m}^2} \left(1 - e^{-0.0146t} \right) \dots \dots \dots (4-8)$$

Also, it may be desired to express the benthic demand in terms of dry weight of sediment; since 80 grams (dry wt.) were used, the equation is

$$R = 2.09 \times 10^{-2} \frac{\text{gm}}{\text{gm}} \left(1 - e^{-0.0146t} \right) \dots \dots \dots (4-9)$$

Both Equations 4-8 and 4-9 are for 20°C , and for complete suspension.

In order to determine the effects of mercury upon the benthic demand, completely suspended tests were run using 600 mg/l Hg^{++} and 30,000 mg/l Hg^{++} . Mercury was used since it is toxic and is one of the most common heavy metals found in the Ship Channel sludges, see Table 3-1. The tests with mercury had essentially the same benthic demand as those without mercury. This was not as suspected and the probable reason is that the mercury was adsorbed by the clays present. The clays are a montmorillonite which has a rather high cation exchange capacity and the heavier the atomic weight the more preference the clay has for the cation, thus the mercury ion would easily be adsorbed by ion exchange.

Theoretical Development of Diffusion and Flux

If the quiescent, non-scoured system is modeled as shown in Figure 4-1, the material in the reaction vessel can be seen as being divided into separate areas; (1) supernatant, (2) aerobic sludge, and (3) anaerobic sludge. Even with the simplified model shown, the diffusion-reaction transport equilibrium is still extremely complex. Reaction most probably occurs in both the supernatant and the aerobic sludge at different rates. There is a change in the rate of diffusion of oxygen-demanding substances out of the sludge both at the aerobic-anaerobic interface and at the solid-liquid interface, and oxygen diffuses into and through the aerobic layer.

The system is too complex to characterize mathematically, and simplifying assumptions have to be made. The first assumption is that it may be possible to ignore the transport of oxygen into the sludge as being insignificant when compared to the rate of reaction of oxygen with oxygen-demanding substances. This entails also the assumption that the aerobic zone can be ignored, which is probably justified in that it comprises only 5 percent of the total volume of sludge.

A second assumption is that all oxygen-demanding substances may be considered as a single compound diffusing through the sludge creating a two component diffusion system.

Assuming the above, it is possible to apply the continuity equation as developed by Bird, Stewart, and Lightfoot (45) to the system, which for constant density and diffusivity in cylindrical coordinates is:

$$\frac{\partial c}{\partial t} + \left[v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r} \frac{\partial c}{\partial \theta} + v_z \frac{\partial c}{\partial z} \right] =$$

$$D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \frac{1}{r^2} \cdot \frac{\partial^2 c}{\partial \theta^2} + \frac{\partial^2 c}{\partial z^2} \right] + R \quad \dots \dots \dots (4-10)$$

where:

c = the concentration of benthic oxygen demand in the sludge in mg/l

t = time in hours

v = velocity in cm/hour

r = distance in radial direction

z = distance in axial direction

θ = angular displacement

D = the diffusion constant in cm^2/hour or $\text{cm}^2/\text{second}$

R = the reaction rate in mg/l-hr within the diffusion media

Since there is no sludge transport across the glass boundary and there is no circular motion of the sludge, v_r , v_θ , and v_z are zero. Neither is there any appreciable dependence of the variables in either the r or θ direction. In addition, according to the first assumption, all reaction takes place at or outside the boundary of the sludge, and the equation of continuity for the sludge becomes:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad \dots \dots \dots (4-11)$$

It is assumed that for the time period of the test the bottom of the reaction vessel has no effect on the diffusion, which seems possible from the literature reviewed (21), and that the initial condition and boundary conditions are given by

$$\text{IC} \dots c(z,0) = c_o \quad \dots \dots \dots (4-12)$$

$$\text{BC1} \dots c(\infty,t) = c_o \quad \dots \dots \dots (4-13)$$

$$\text{BC2} \dots D \frac{\partial c}{\partial z} \Big|_{z=0} = - \frac{KcV_r}{A} \quad \dots \dots \dots (4-14)$$

where: A = surface area

V_r = volume within which the reaction takes place

A solution for Equation 4-11 has been reported in the literature by both Dobbins (8) and Crank (45) as

$$c = c_o \left[1 - \operatorname{erfc} \frac{z}{\sqrt{4Dt}} - e^{hz+h^2Dt} \operatorname{erfc} \left(\frac{z}{\sqrt{4Dt}} + h \sqrt{Dt} \right) \right] \quad (4-15)$$

where:

c_o = the concentration of benthic oxygen demand at $t = 0$ in mg/l

h = a constant equal to $\frac{KV_r}{DA}$, expressed in cm^{-1}

Now

$$F = -D \frac{\partial c}{\partial z} \quad (4-16)$$

where:

F = the flux across the solid-liquid interface at any time t .

F may be defined by observing that for the duration of the reported test results the reaction rate, R' , in mg. oxygen per hour, was a constant and would have to be equal to the flux times the area of the interface, A . Expressed in equation form this becomes

$$R' = FA \quad (4-17)$$

or for a pseudo-first order reaction,

$$R' = FA = KcV_r \quad (4-18)$$

Rearranging Equation 4-18 gives,

$$F = \frac{KcV_r}{A} \quad (4-19)$$

where c is defined at the interface ($z=0$) and it is assumed that the reaction takes place throughout the supernatant at the same concentration, c . The value of c at $z=0$ may be determined from Equation 4-15 and is

$$c = c_o \left[1 - \operatorname{erfc} (0) - e^{h^2Dt} \operatorname{erfc} \left(0 + h \sqrt{Dt} \right) \right] \quad (4-20)$$

From Equation A-2 in the Appendix, the value of erfc (0) is one. Thus Equation 4-20 becomes,

$$c = c_o \left[-e^{h^2 Dt} \operatorname{erfc} \left(h \sqrt{Dt} \right) \right] \dots \dots \dots (4-21)$$

Substituting Equation 4-21 into Equation 4-19 for c gives,

$$F = \frac{KV_r}{A} \left\{ c_o \left[-e^{h^2 Dt} \operatorname{erfc} \left(h \sqrt{Dt} \right) \right] \right\} \dots \dots \dots (4-22)$$

Since $h = \frac{KV_r}{DA}$, substitution with Equation 4-22 gives,

$$F = \frac{KV_r}{A} c_o \left[-e^{\frac{K^2 V_r^2}{D^2 A^2} Dt} \operatorname{erfc} \left(\frac{KV_r}{DA} \sqrt{Dt} \right) \right] \dots \dots \dots (4-23)$$

Letting $x = \frac{KV_r}{DA} \sqrt{Dt}$ in Equation 4-23 yields,

$$F = -\frac{KV_r}{A} \left[c_o \left(e^{-x^2} \operatorname{erfc} x \right) \right] \dots \dots \dots (4-24)$$

It can be shown in the Appendix that for large values of x, $e^{-x^2} \operatorname{erfc} x$ approximates $\frac{1}{x\sqrt{\pi}}$, from Equation A-8. Substituting into Equation 4-24 gives,

$$F = -\frac{KV_r}{A} c_o \cdot \frac{1}{x\sqrt{\pi}} \dots \dots \dots (4-25)$$

Substituting for $x = \frac{KV_r}{DA} \sqrt{Dt}$ into Equation 4-25 yields,

$$F = -\frac{KV_r}{A} c_o \cdot \frac{DA}{KV_r \sqrt{Dt} \sqrt{\pi}} \dots \dots \dots (4-26)$$

Canceling terms and simplifying yields,

$$F = -c_o \frac{\sqrt{D}}{\sqrt{\pi t}} = -c_o \sqrt{\frac{D}{\pi t}} \dots \dots \dots (4-27)$$

The evaluation of F for Eq. 4-27 is difficult from the experimental data because potentially suitable data for F as a function of time can only be obtained for a very short period at the beginning of the test. That data, however, is the least reliable because results are masked due to the oxygen demand exerted by suspended particulates.

The flux after approximately 60 hours is dependable enough to use in the evaluation of D from Equation 4-27, but is not easily described as a function of t . F , after 60 hours, can be assumed to be approximately constant and can be used to give an approximate value for D . Assuming F constant and choosing a mean value of t for the test, the parameters needed for the evaluation of Equation 4-27 at 20°C are:

$$R' = 0.58 \text{ mg/hr, From Figure 4-7,}$$

$$A = 71 \text{ cm}^2 \text{ (Area of 3 3/4" ID cell)}$$

$$F = \frac{R}{A} = 0.58 \frac{\text{mg}}{\text{hr}} \cdot \frac{1}{71 \text{ cm}^2} = 0.0082 \frac{\text{mg}}{\text{hr-cm}^2}$$

Since the total amount of oxygen used was 1700 mg and the volume of sludge was 250 ml the value of c_o is,

$$c_o = \frac{1700 \text{ mg}}{0.250 \text{ l}} = 6800 \text{ mg/l} = 6.8 \frac{\text{mg}}{\text{cm}^3}$$

and $t = 100$ hours. Thus from Equation 4-27

$$D_{20^{\circ}\text{C}} = \frac{F^2}{c_o} \cdot \pi t \quad \dots \dots \dots (4-28)$$

Substituting

$$D_{20^{\circ}\text{C}} = \frac{(8.2 \times 10^{-3} \text{ mg/hr-cm}^2)^2 (3.14) (100 \text{ hr}) (\text{hr})}{(6.8 \text{ mg/cm}^3)^2 (3600 \text{ sec})} = 1.27 \times 10^{-7} \text{ cm}^2/\text{sec} \quad \dots \dots \dots (4-29)$$

Having obtained D , it is possible to use it to calculate F as a function of t . By comparing F values obtained using Equation 4-27 with the observed values for F it is possible to estimate the error encountered in assuming F constant. Calculated and observed values for F are plotted in Figure 4-10. This plot shows a 30 percent deviation between observed and calculated values from 60 to 200 hours. This deviation in F can easily be within the error of the test itself. Values of F observed for duplicate samples in the same test varied as much as 30 percent.

An uncertainty of 30 percent in F causes a much larger uncertainty in D since D varies as F^2 . Using the maximum and minimum values of F to calculate D , it was found that D_{20} is between 5.07×10^{-8} and 2.53×10^{-7} cm^2/sec . The value of the flux, F , is the same as the benthic oxygen demand, R .

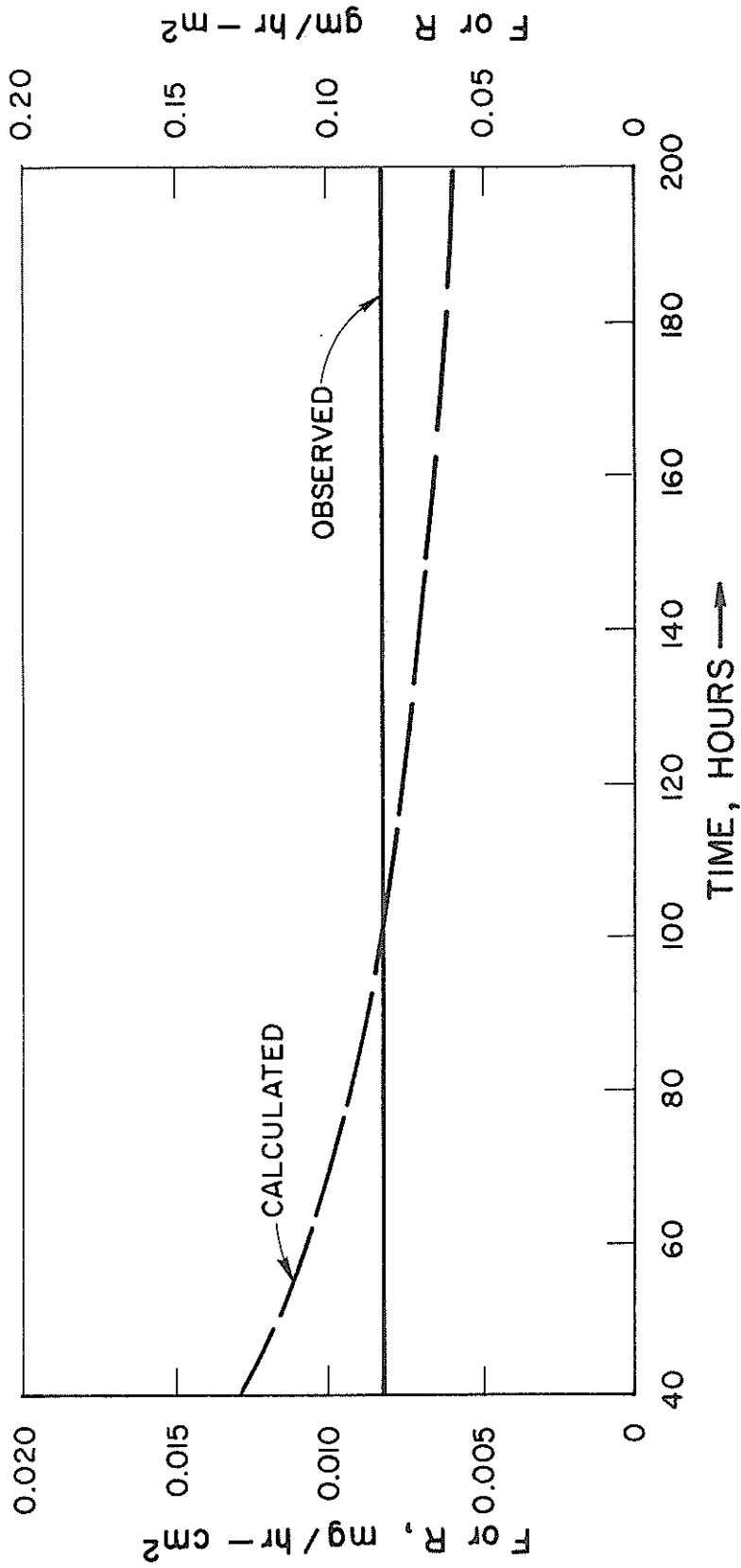


FIGURE 4-10
CALCULATED VS OBSERVED FLUX VALUES, MILE 20

CHAPTER V
CONCLUSIONS

1. The benthic oxygen demands of the sediments for quiescent conditions from the entire channel length of 24 miles varied from 0.12 to 0.22 gm/hr-m² at 32°C.
2. The BOD₅ values for the sludges varied from 14,000 to 55,000 mg/kgm.
3. The benthic oxygen demand for quiescent conditions, R, was related to the BOD₅ values as follows,

$$R = 0.035 + 3.45 \times 10^{-6} \cdot \text{BOD}_5$$

where

R = benthic oxygen demand, gm/hr-m² at 32°C

BOD₅ = five-day biochemical oxygen demand, mg/kgm(dry weight), 20°C

4. The benthic oxygen demand was related to temperature by the equation

$$R_2 = R_1 \cdot 1.055^{(T_2 - T_1)}$$

where

R₂ = benthic oxygen demand in gm/hr-m² at T₂

R₁ = benthic oxygen demand in gm/hr-m² at T₁

T₂ = temperature, C°

T₁ = temperature, C°

5. The benthic oxygen demand for a scoured condition was the same as for a quiescent condition. A scoured condition was when the overlaying water was mixed to the extent that erosion was occurring at the sludge-water interface.

6. The benthic oxygen demand for a completely suspended condition was 15 to 17 times that of a quiescent or scoured condition. For a completely suspended condition mixing had to be vigorous enough to keep the 200 ml of sludge in suspension.
7. The benthic oxygen demand for the completely suspended condition was a pseudo-first order reaction, and the describing equation is,

$$R = 235 \frac{\text{gm}}{\text{m}^2} \left(1 - e^{-0.0146t} \right)$$

where

R = benthic oxygen demand, gm/m² up to time t at 20°C

t = time in hours

8. The benthic oxygen demand for quiescent conditions was related to the total benthic demand, the time and the diffusion coefficient by,

$$F(\text{or } R) = - c_o \sqrt{\frac{D}{\pi t}}$$

where

F(or R) = the benthic oxygen demand or flux

c_o = total benthic oxygen demand

D = diffusion coefficient

t = time

9. The diffusion coefficient, D, for 20°C, varied from 5.07 x 10⁻⁸ cm²/sec to 2.53 x 10⁻⁷ cm²/sec.
10. Although there was an appreciable content of heavy metals in the sludges, there was apparently no inhibition of benthic organisms since the benthic demand values compared favorably with the literature. The aggregate sum of mercury, arsenic, lead, zinc,

copper, chromium, nickel, and silver was 628 mg per kilogram (dry weight) on the sample from Mile 20. The clays present in the sediments are expanding layer montmorillonites which have appreciable cation exchange capacities. Since the heavier metallic ions are preferred by the clays, it is believed they are adsorbed by the clays and are rendered non-toxic to benthic organisms.

11. In studying the completely suspended condition, addition of up to 30,000 mg/l mercury ion did not cause any reduction in benthic oxygen demand. Apparently, the mercury ions were adsorbed by the clay.

APPENDIX

Development of simplified approximation of e^{x^2} erfc x. e^{x^2} and erfc x may both be expressed in the form of a series expansion of x. The series expansion of e^{x^2} has been recorded in literature as:

$$e^{x^2} = 1 + \frac{x^2}{1!} + \frac{x^4}{2!} + \frac{x^6}{3!} + \frac{x^8}{4!} \dots \frac{x^{2n}}{n!} \dots \dots \dots \text{A-1}$$

and erfc x may be derived from the definition of the error function:

$$\text{erfc } x = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-a^2} da \dots \dots \dots \text{A-2}$$

which may be expressed as:

$$\text{erfc } x = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \left[1 - a^2 + \frac{a^4}{2!} - \frac{a^6}{3!} + \frac{a^8}{4!} + \dots (-1)^n \frac{a^{2n}}{n!} \right] da \dots \text{A-3}$$

integrating:

$$\text{erfc } x = 1 - \frac{2}{\sqrt{\pi}} \left[x + \frac{x^3}{3} - \frac{x^5}{5 \cdot 2!} + \frac{x^7}{7 \cdot 3!} - \frac{x^9}{9 \cdot 4!} \dots \frac{(-1)^n x^{2n-1}}{(2n-1)(n-1)!} \right] \dots \dots \dots \text{A-4}$$

It may be noted that $\frac{1}{x} e^{-x^2}$ has a similar series expansion to that of erfc x:

$$\frac{1}{x} e^{-x^2} = 1 - x + \frac{x^3}{2!} - \frac{x^5}{3!} + \frac{x^7}{4!} - \frac{x^9}{5!} \dots \frac{x^{2n-1}}{n!} (-1)^n \dots \dots \dots \text{A-5}$$

If, term by term, Equation A-4 is subtracted from Equation A-5 multiplied by $\sqrt{\pi}$, the result is:

$$\sqrt{(\pi)} \operatorname{erfc} x - \frac{1}{x} e^{-x^2} \sum_{n=1}^{\infty} \left[\frac{x^{2n-1}}{(2n-1)(n-1)!} - \frac{x^{2n-1}}{n!} \right] (-1)^n \dots \text{A-6}$$

As x grows large only the n th terms of Equation A-6 become important and as n grows large $2n-1$ equals $2n$. The limit of Equation A-6 is:

$$\lim_{x \rightarrow \infty} \sqrt{(\pi)} \operatorname{erfc} x - \frac{1}{x} e^{-x^2} = \frac{x^{2n-1}}{2n!} - \frac{x^{2n-1}}{n!} = 0 \dots \text{A-7}$$

$$x \rightarrow \infty$$

$$n \rightarrow \infty$$

Thus e^{-x^2}/x , equal to $\sqrt{\pi} \operatorname{erfc} x$ in the limiting case, becomes an approximation of $\sqrt{\pi} \operatorname{erfc} x$ at $x < \infty$:

$$e^{x^2} \operatorname{erfc} x \simeq \frac{e^{x^2} e^{-x^2}}{x\sqrt{\pi}} = \frac{1}{x\sqrt{\pi}} \dots \text{A-8}$$

To determine the minimum value for x for which the approximation would be acceptable, the calculated values were tabulated with observed values from literature (45, 46).

Table A1

x	$\frac{1}{x\sqrt{\pi}}$	$e^{x^2} \operatorname{erfc}$
1	0.565	0.428
2	0.283	0.255
3	0.188	0.179
5	0.113	0.110
10	0.0565	0.0563

From Table A1, it is assumed that for x greater than 3 the assumption is justified.

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