AN ABSTRACT OF THE THESIS OF

___DUANE COLLINS MARTIN___ for the ___M.S.___
(Name of Student)   (Degree)

in ___CIVIL ENGINEERING___ presented on _____
(Major)   (Date)

Title: THE EFFECT OF MIXING ON THE OXYGEN UPTAKE RATE

OF ESTUARINE BOTTOM DEPOSITS

Abstract approved: _____

A study of the effect of mixing on the oxygen uptake rate of estuarine bottom deposits is presented. The method of study involved the mixing of samples of bottom deposits with the overlying water to result in concentrations of suspended matter in the same order as observed in the estuary. Some samples were kept in a quiescent state as a control and the others mixed to concentrations of 30 to 50 mg/l suspended matter.

The effect of depth and the non-biological oxygen demand are presented with a discussion of the source of biochemical oxygen demand.

Results of this study showed that:

1. Mixing has a pronounced effect on the oxygen uptake rate.

2. The results tend to confirm that the increase in oxygen uptake is due to the release of bio-degradable substances from the bottom.

3. The oxygen uptake of benthic gases appears to be small compared to the total oxygen uptake rate.

4, The depth of deposit has no effect on oxygen uptake between the depths of two and 12 inches.

5. The possibility of a material having a high decay rate coefficient being released from the bottom deposit warrants further investigation.

6. The change in concentration of matter suspended from the surface of deposits in the order of 100 mg per liter appears to have no apparent effect on the oxygen uptake rate of water overlying the deposits.

The Effect of Mixing on the Oxygen Uptake
Rate of Estuarine Bottom Deposits

by

Duane Collins Martin

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1969

APPROVED:

_____   _____
Assistant Professor of Civil Engineering
in charge of major

Head of Department of Civil Engineering   _____

_____   _____
Dean of Graduate School

Date thesis is presented _May 9, 1969_____

Typed by Opal Grossnicklaus for _____ DUANE COLLINS MARTIN

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THE EFFECT OF MIXING ON THE OXYGEN UPTAKE
RATE OF ESTUARINE BOTTOM DEPOSITS

INTRODUCTION

The impact of organic bottom deposits on the oxygen balance of overlying waters has long been recognized. Streeter and Phelps (20) acknowledged the disturbing effect of sedimentation on the attempted determination of the oxygen demand for a section of river. Streeter (17) later quoted a study of the Illinois River which indicated that 40 percent of the total oxygen demand of the river was exerted by sludge deposits. He noted that the lack of knowledge of the effects of sludge deposits prevented the formulation of any general method to determine the oxygen demand of sludge deposits, but proposed a relation based on the theory that the amount of BOD added to the deposit each day is substantially equal to the daily amount of BOD oxidized, shown as equation 1.

$$L_d = \frac{P_d}{2.3\, k'} (1 - 10^{-k't'})$$ (1)

where L_d = the cumulative BOD in pounds or kilograms;

P_d = the BOD added to the deposit in pounds or kilograms per day and

k' = specific rate of oxidation of the deposit (base 10).

Jansa and Akerlindh (9) and Velz (23) developed methods for determining the demand of bottom sludge on the oxygen of a stream

based on Streeter's (17) formulation.

Camp (3) reasoned that Streeter's assumption of a steady state could not be applied to an actual stream and that it is essential in oxygen balance studies to consider the effects of both the settling of BOD and the rate of oxygen demand of bottom deposits on the overlying water separately.

Several investigators have conducted studies to determine the rate of oxygen demand in the biodegradation of deposited solids. Baity (2) studied the effects of oxygen concentration in the supernatant water; and depth of deposit; light; temperature; salinity; and bacterial and protozoan life on the oxygen uptake rate. Fair, Moore and Thomas (6) essentially followed the methods of Baity with improvements and studied the effects of temperature and depth of sludge. Both Baity and Fair et al. proposed relationships giving a rate of oxygen demand in terms of weight of oxygen per unit area of sludge deposit per unit time.

Most recently, McKeown, Benedict and Locke (12) have studied the effects of area, depth, composition, pH and age of the deposits on the oxygen demand of sludge deposits.

PURPOSE AND SCOPE

The purpose of this research is primarily to determine the effect of mixing on the oxygen uptake rate of bottom deposits and to propose an explanation of how a benthic system is changed by mixing. The measured rates of oxygen uptake rate supplement the results of other investigators.

The scope of this study consists of determining the change of dissolved oxygen concentration in waters overlying bottom deposits. Rates of oxygen demand are measured using natural sediment with efforts made to not disturb the samples. The overlying water is mixed with the surface of the deposits in an attempt to reproduce natural mixing using suspended matter concentration as a parameter. The depth of sludge is measured to relate depth to oxygen uptake rate. Experiments are batch with respect to sludge deposits and overlying water.

LITERATURE REVIEW

The first notable study on the oxygen uptake rate of bottom

deposits found in the literature was by Baity (2) in 1937. The sludge

used was collected from a sewage treatment plant. The sludge was

deposited uniformly over the bottom of 20 liter carboys and clean

water was allowed to flow continuously and at uniform rates over the

sludge. The depletion of dissolved oxygen concentration in the super-

natant water was measured. The effect of depth was measured by

studying depths from 0.1 cm to 4.0 cm and a general relationship

at 22° C was proposed as shown in equation (2).

$$Y = 2700 \ X^{0.485} \tag{2}$$

Where X is depth of sludge in centimeters and Y is rate of oxygen

demand in milligrams per day per square meter of sludge surface.

Fair, Moore and Thomas (6) studied sewage sludge and river

mud using methods similar to Baity (2). Water was allowed to flow

over the sludge but the rate of flow was adjusted to establish meas-

urable differences in oxygen content. Inert material was added to

the sewage solids to weight the sludge to the bottom. Depths of

sludge from 1.5 cm to 10.2 cm were studied and equation (3) was

proposed.

$$Y_{so} = 2.45 \ m^{0.485} \tag{3}$$

Where Y_{so} = initial rate of oxygen demand in grams per day per square meter and m = areal concentration of volatile matter in kilograms per square meter.

Knowles, Edwards and Briggs (10) used natural river water and cores of 8 cm depth and mixed the overlying water with a rotary mixer at a constant rate. The oxygen uptake rate was shown to increase with mixing but it appeared that the mixing was not related to actual mixing in the river. Studies showed that oxygen consumption varied with DO concentration between 1 and 4 ppm.

Mohlman, Herrick and Swope (13) measured varying amounts of Chicago Canal sediment into bottles. The bottles mixed by inverting the bottles every 15 minutes for the first hour then at intervals of 30 minutes showed an increase in oxygen utilization over the unmixed bottles.

Edwards and Rolley (5) studied the effect of mud erosion on oxygen consumption of waters overlying core samples of river muds. Erosion of the top 0.5 cm of sludge was accomplished by a rotary mixer. When mixing at 50 revolutions per minute with no resulting erosion, the DO consumption rate was 0.2 gm/sq.m/hr. Mixing at 200 r.p.m. caused erosion of the bottom deposit to greater than 4000 mg per liter of suspended matter concentration and an oxygen uptake of 1.2 gm per square meter per hour. Results showed that oxygen consumption was independent of sludge depths between 4 and 17 cm.

Hanes and Irving (7) used a constant flow apparatus to study the oxygen demand in saline waters using a submersible unit. Stirring was included inside the unit to provide the necessary flow for a DO probe. Results indicated that depth of deposit had no effect on oxygen consumption.

Lardieri (11) studied the effect of temperature on the benthal uptake rate of a stock sludge. Mixing was accomplished with a magnetic stirring bar but a fine wire mesh was placed over the sludge.

Most recently, McKeown, Benedict and Locke (12) studied among other effects, depth and scouring and confirmed that oxygen uptake by benthal deposits is directly proportional to the surface area of the deposit. It was reported that depth does not influence the oxygen demand of a cellulosic deposit greater than 1.0 ft. and the critical depth may be significantly less. Two types of sludge were studied. One was a diluted paper mill vacuum filter cake and the other was the clarifier underflow from a plant treating paperboard mill wastes. The effect of mixing was investigated by adjusting the flow rate over the sludge. Laminar flow rates produced uptake rates of 0.8 gm O_2/day/sq.m. which was in the same order as rates observed when the water was not flowing. Magnetic stirrers were used to produce scouring. The oxygen consumption with no mixing, normal mixing and slight scour was studied. A screen was placed over the sludge

during normal mixing. The uptake rate increased from 2.7 g DO/ day/sq.m. with normal mixing to about 4.4 g DO/day/sq.m. as a result of partial scour. Scouring was defined as "visible evidence of resuspension of sludge as a result of vortex action at the center of the column . . ." McKeown et al. presented an excellent literature review of investigations of the DO uptake rate of bottom deposits that indicates oxygen demands from 0.55 to 6.17 g/m_2/day were recorded with and without mixing.

Cary (4) mixed the surface of a mud core with the overlying water using an apparatus similar to the one described in this study. The samples were left in the core sampler and mixing was induced by a reciprocating wire through a three inch stroke. Three magnitudes of mixing were described. Minimum was defined as no mixing until just prior to sampling, standard as a very rough approximation of the natural mixing by observation of the current velocities in the actual sampling area and maximum as vigorous stirring just below the velocity that stirred the sediment. The results of Cary's studies related to mixing are shown in Table 1.

The literature review seemed to indicate that most previous investigators neglected the effects of mixing or did not adequately simulate the natural mixing of bottom deposits caused by tides, currents, etc.

Table 1. Oxygen uptake with mixing. From Cary (4).

Mixing	Initial conc. DO, ml_1	Final conc. DO, ml_1	Length of exp. hrs	Volume water ml	Average uptake $ml/m^2/hr$
Maximum	6.18	0.72	2.0	85	27.8
Standard	6.48	6.27	2.0	85	8.3
Minimum	5.66	5.64	2.0	85	1.6

EQUIPMENT METHODOLOGY

Experimental Equipment

The apparatus consisted of a device which could produce mixing of the mud surface with the overlying water. Figure 1 shows the apparatus with removable sampling tubes in place. Mixing blades were immersed in each tube as shown in Figure 2. The height of the blades above the mud, their rate and length of oscillation were adjustable.

Ports were provided as shown in Figure 2 for extraction of water samples from the tubes and mineral oil was used to prevent atmospheric reaeration of the water.

The apparatus was shrouded against light and placed in a constant temperature room during the experiments.

Collection of Samples

The sampling tubes were removed from the mixer when collecting samples. A cap and gasket were bolted on the top of each tube and serum caps were placed over each sampling port except for the sample port in the top cap which was left open to allow air to escape as the tube penetrated the mud.

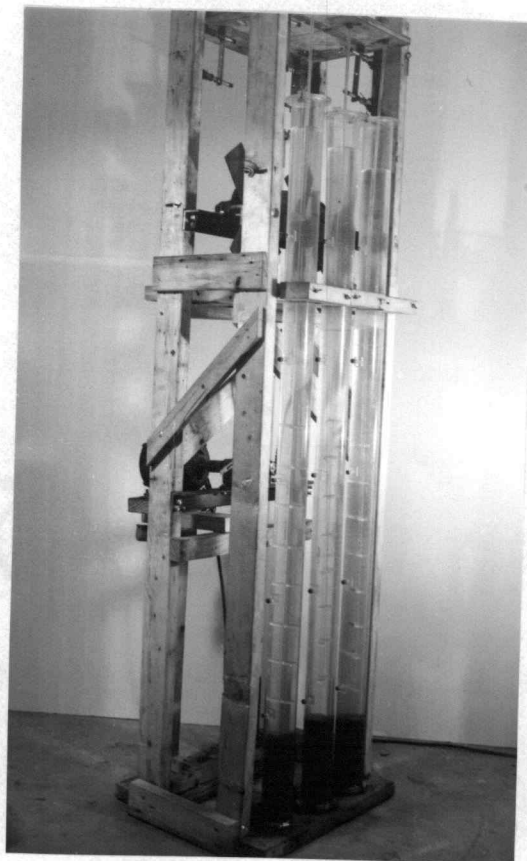Samples were collected in approximately five feet of water.

Figure 1. Mixing apparatus.

Figure 2. Mixing blades and sampling ports.

The time of sampling was near low tide so that no sample was taken in an area normally exposed at low tide. When extracting a sample, the tube was slowly lowered vertically until it touched the bottom. The tube was then slowly pushed straight down until it had penetrated from eight to 12 inches into the mud. After replacing the serum cap in the top cap, the tube was quickly raised and a cap placed over the bottom of the tube.

The depth of mud was adjusted by removing the bottom cap and allowing the mud to ooze out the opening. When the desired depth was attained, the bottom cap was replaced and tightened. A small amount of mud was observed to adhere to the inside of the tube. However, the mud was always from the upper aerobic layer as noted by the light tan color and it quickly settled to the surface of the sample when the overlying water was mixed.

The time taken to extract six samples was approximately one hour. During that time the remaining tubes were stored vertically in a small boat. The tubes were transported by boat for 15 minutes and then transferred to a truck. Each tube was kept in a vertical position at all times when being moved. The tubes were secured in the truck and moved to a 19 ° C constant temperature room within two hours.

Each tube was reaerated to saturation and a four inch layer of mineral oil was floated on the surface of the overlying water. The

tubes were placed in the mixing apparatus or if unmixed secured to a wall.

Adjustment of Mixer Speeds

Turbulence was not used to relate mixing in the tubes to mixing in the estuary because of the difficulty in reproducing in the laboratory the total situation found in the estuary. Instead, the concentration of suspended matter was used to relate mixing in the apparatus with mixing in the estuary. Many other factors influence the mixing in an estuary and the use of only suspended matter as a comparison is not complete but serves as a rough approximation.

Studies to find the range of concentration of suspended matter were made in the sampling area of the estuary. The change in concentration of suspended matter with tidal current velocity change from maximum flow to slack was measured by sampling for analysis of suspended matter over a period of time at a constant depth. A small pump was used to pump the water from the desired depth through rubber tubing which had been secured to a stake driven into the mud. The inlet end of the tubing was horizontal so that the possibility of sampling from another depth was reduced.

Tidal current velocity was measured simultaneously in the same area and depth as the suspended matter measurements. A propeller type current meter was positioned to measure velocity at the desired

depth and left in place during the entire experiment.

Tidal current velocity varied from maximum flow downstream across the sludge deposit at hour zero to maximum flow upstream across an area relatively clear of deposits easily resuspended at hour four. The geometric relationship as shown in Figure 3 explained the reduced concentration of suspended solids at hour four compared to the beginning of the experiment.

Current hours
2 1/2 to 5

Sludge
deposit

Sample
point

Current hours
0 to 2 1/2

Figure 3. Sample position.

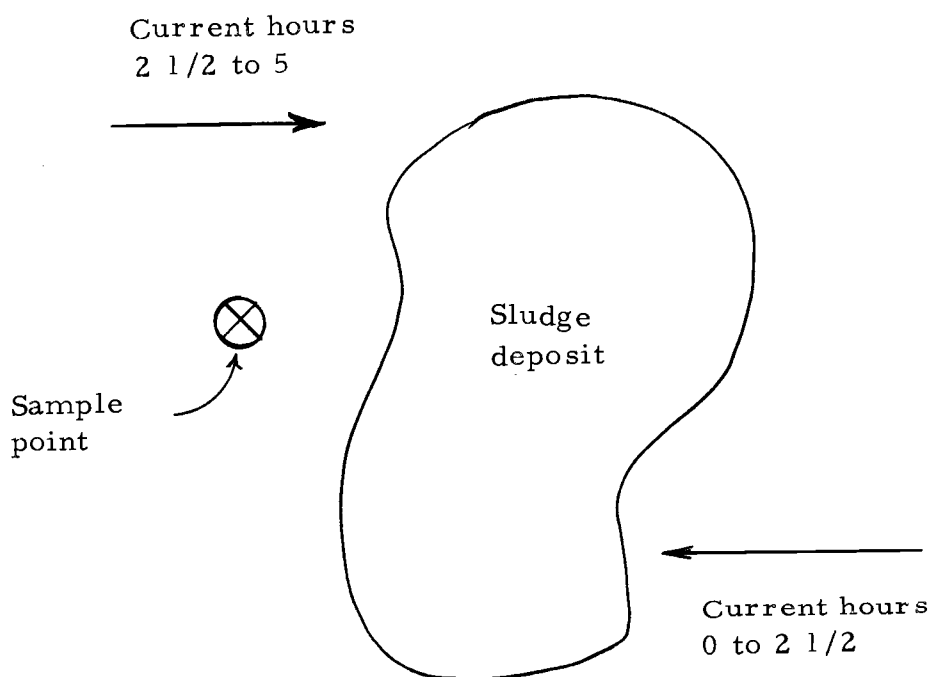Figure 4 shows the relationship of suspended solids concentration to tidal current velocity. The apparatus was tested for its capability to mix the overlying water with the top layer of the mud so that the resulting range of suspended matter was within the same order of magnitude as observed in the Yaquina Estuary. The distance between
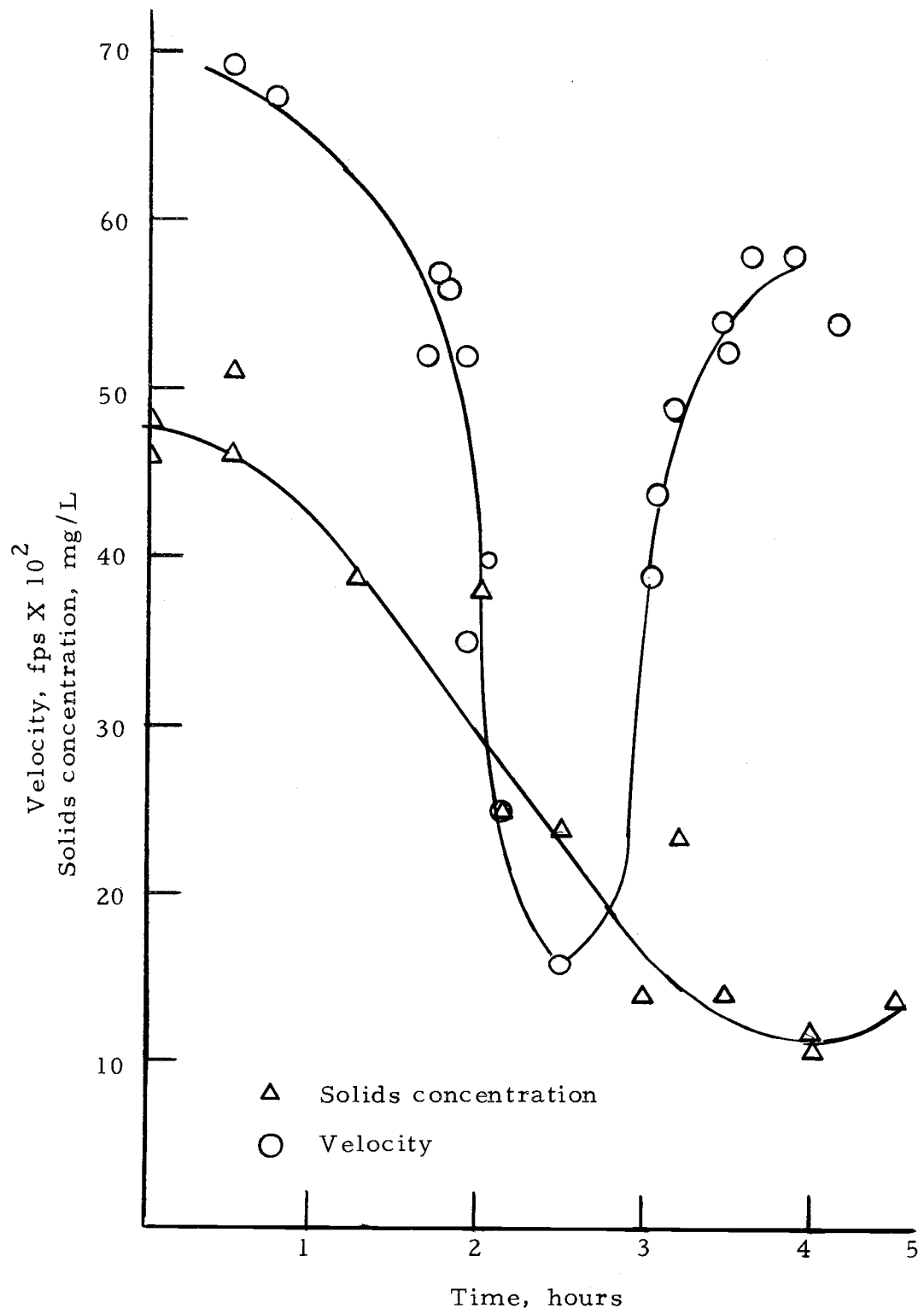
Figure 4. Suspended solids concentration vs. tidal velocity.

the mixing blades and the surface of the mud, the length of the mixing stroke of the blades and the speed of reciprocation were varied until a combination resulted in the desired concentration of suspended solids.

Forty complete strokes of two inches each direction at 2.6 strokes per minute resuspended matter to a level of concentration varying from 10 mg/l to 20 mg/l. However, continued mixing at that rate eventually scoured the bottom deposit resulting in 200 mg/l to 300 mg/l suspended matter in 15 minutes. A timer was used to turn the mixer on for 15 strokes every 90 seconds after an initial 40 strokes increased the suspended matter concentration to the desired level. The results of experiments using intermittent mixing showed that the concentration of suspended matter remained in the desired range.

The concentration of suspended matter seemed to vary during any mixing procedure depending upon the nature of the mud sample. Therefore, no attempt was made to vary the suspended matter concentration with time to compare with the observed change measured with time in the estuary.

Dissolved Oxygen Measurements

Micro-Winkler Technique

Dissolved oxygen was measured by modifying the azide

modification of iodometric method described in Standard Methods for the Examination of Water and Wastewater (1). A 30 ml syringe was used to extract 20 ml of overlying water through serum caps provided on the sampling tubes. The test is described in Appendix I.

The micro-Winkler technique was compared with the standard test using samples of estuary water and the two methods compared favorably to within 0.1 ppm dissolved oxygen. A calibration curve was prepared to account for the dissolved oxygen in the micro-Winkler reagents.

Mineral Oil

Experiments to test the effectiveness of the layer of mineral oil to reduce reaeration from the atmosphere were completed. Two of the sampling tubes were installed in the mixer and filled to within four inches of the top with distilled water. Mixing rods were inserted and nitrogen was bubbled through the water to reduce the concentration of dissolved oxygen in the water. When the dissolved oxygen had been reduced to 0.9 ppm, the nitrogen flow was stopped and a four inch layer of mineral oil was added to the tube.

Figure 5 shows the change in dissolved oxygen during the experiment over a period of 24 hours. The water in the tubes was completely mixed throughout the experiment after adjusting the stroke length of the mixing blades to two inches. Longer stroke lengths

greatly reduced the effectiveness of the mineral oil in preventing

reaeration.
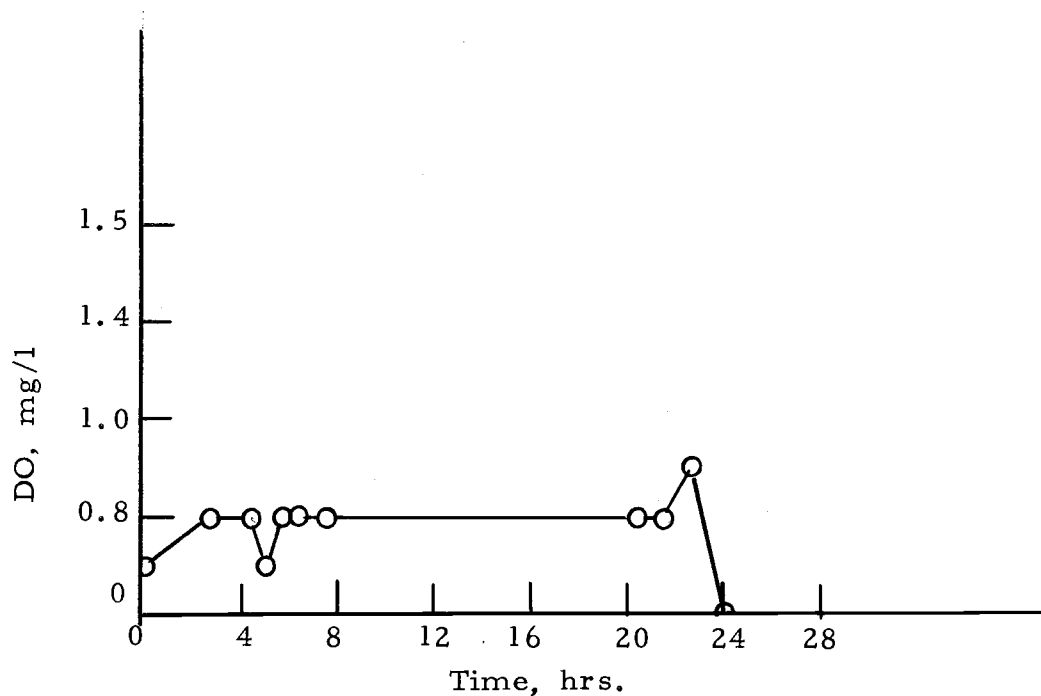
Figure 5.   Effect of mineral oil on reaeration.

Reaeration of Samples

The column of overlying water was reaerated to saturation at

the beginning of each experiment.   A compressed air source was

connected to the bottom sample port of the tube and the air flow was

regulated so that the mud sample was not disturbed.   When the dis-

solved oxygen concentration reached saturation, the air flow was

stopped and the mixing apparatus started.

The initial sample for measurement of dissolved oxygen

concentration was taken after the overlying water was completely mixed.

BOD and Suspended Matter

Samples for measurement of biochemical oxygen demand and suspended matter were taken from the water column through the sampling ports. The procedure used in performing the BOD analysis is outlined in Standard Methods for the Examination of Water and Waste Water (1).

The concentration of suspended matter was measured according to a method outlined by Wyckoff (24) using a glass fiber filter with a filter holder apparatus.

Experimental Procedure

Twenty-seven experiments were performed to study the effects of different levels of mixing and depth of bottom deposit on the oxygen uptake rate. Studies were made to try to determine the reason for the change in uptake rate with mixing.

The experiments were short term and batch with respect to bottom deposit and overlying water. The water column was reaerated during some of the experiments to determine the persistence of the DO uptake rate initially measured.

Table 2 is a tabulation of the general conditions of each

Table 2. Summary of experiments.

Experiment number	Date sampled	Depth of deposit inches	Length of exp, hrs.	DO uptake PPM:hrs	DO uptake mg/M^2-day	Mixing	Final susp. sol, mg/l
1	26 July	--	110	0.17:1	1.	Yes	--
2	26 July	--	110	0.05:1	1.	Yes	--
3	26 July	--	110	varied	1.	Yes	5
4	26 July	--	110	0.1:1	1.	Yes	7
5	31 July	--	19	0.87:1	1.	Yes	--
6	31 July	--	19	--	1.	Yes	31
7	31 July	--	19	0.91:1	1.	Yes	--
8	31 July	--	19	0.87:1	1.	No	--
9	31 July	--	19	0.06:1	1.	No	--
10	2 Aug	12	61	0.15:1	3220	Yes	3
11	2 Aug	11 1/4	79	0.1:1	3300	Yes	7
12	2 Aug	11 1/2	79	--	--	Yes	45
13	2 Aug	12	79	--	--	Yes	46
14	2 Aug	10	79	0.77:1	2640	No	
15	2 Aug	8 3/4	79	0.04:1	1250	No	2
16	10 Aug	8	195	0.12:1	3920	Yes	5
17	10 Aug	7 1/2	195	0.12:1	3880	Yes	3
18	10 Aug	6 1/4	195	0.12:1	3880	Yes	187
19	10 Aug	10 1/4	195	0.12:1	3880	Yes	33
20	10 Aug	10 1/2	195	0.06:1	2060	No	--
21	10 Aug	10 1/2	195	0.29:1	--	2.	--
22	20 Aug	6	88	0.98:1	3800	Yes	19
23	20 Aug	8 1/2	--	--	--	Yes	
24	20 Aug	7 3/4	147	3.	--	Yes	212
25	20 Aug	6 3/4	147	3.	--	No	
26	20 Aug	5	--	--	--	No	
27	20 Aug	8	147	0.05:1	1790	No	
28	28 Aug	6 3/8	68	0.77:1	3140	Yes	
29	28 Aug	7/8	68	0.8:1	3330	Yes	
30	28 Aug	2 5/8	88	0.8:11	3250	Yes	
31	28 Aug	4 1/4	62	4.	--	5.	
32	28 Aug	4 1/2	88	0.8:1	3150	Yes	

1. Leaks developed in the apparatus and total oxygen consumed per day could not be calculated.

2. Experiment 21 was mixed by mixing the water only by circulation. The bottom deposit was not disturbed.

3. Final slope. Experiments were dosed with $HgCl_2$ to study C.O.D.

4. Uptake rate increased with time.

5. Suspended matter increased to very high concentration with time.

experiment. The day the mud was sampled is noted because the DO

uptake rate appears to depend on factors that may have changed

between the times of sampling.

The depth of mud measured is an average because of the irregu-

larity of the mud surface. The highest part of the mud was always

within a half inch of the lowest.

The final concentration of suspended matter was measured as

noted in Table 2. The low concentration required such a large sam-

ple volume that no attempt was made to determine how the concentra-

tion varied during the experiment.

The rate of mixing was the same for each experiment that was

mixed which has been described previously in Adjustment of Mixer

Speeds. The experiments listed in Table 2 as not mixed were secured

to a wall, however, some small amount of turbulent diffusion may

have occurred in the overlying water when DO samples were taken.

The oxygen uptake rate was expressed as g/m^2-day. The

dissolved oxygen concentration of the overlying water was measured

intermittently during each experiment and plotted against time. The

slope of the concentration vs. time was adjusted as shown in equation

(1) to give the desired rate.

$$g/m^2\text{-hr} = (\text{slope DO-time, } g/L\text{-hr})(\text{Vol. Water, } L)$$

$$(1/\text{Area Mud, } m^2)(24 \text{ hrs/day}) \qquad (4)$$

The volume of overlying water varied during the experiments

because of the extraction of DO samples. The effect would be to

reduce the DO uptake, g/m^2-day with time assuming that the change

of concentration of DO remained constant with time. The volume of

the DO samples and their total number were small enough that the

change in volume resulted in a change of uptake rate of less than 5%.

The reported DO uptake rate expressed as g/m^2-day is based on the

average volume of water in the tubes during the experiment.

DISCUSSION OF RESULTS

Oxygen Uptake Rate

Effect of Mixing

The DO uptake rates measured during the experiments are tabulated in Table 2. Mixing produced average oxygen uptake rates of 3.4 grams per square meter per day ± 10%. When individual days were considered, the rates of DO uptake did not vary more than 3% from the average rate. The average unmixed oxygen uptake measured was 1.9 g/m^2-day ± 40% with the exception of experiment 14. Mixing appears to have caused the oxygen uptake rates to increase by nearly 80%.

Figure 6 is a composite of the rates of DO uptake during the mixed experiments and the rates of DO uptake during the unmixed experiments are shown in Figure 7. The figures show the reproducibility of the data and relatively higher uptake rate of the mixed experiments. The slopes of the lines in Figure 6 are approximately 1 mg/l DO per 10 hours while the slopes of the lines in Figure 7 are approximately 1 mg/l DO per 20 hours. These data are compared with the rates of oxygen uptake reported by others in Table 3.

Comparison of data is difficult because of the different methods of experiments. With the exception of McKeown et al. (12) none of
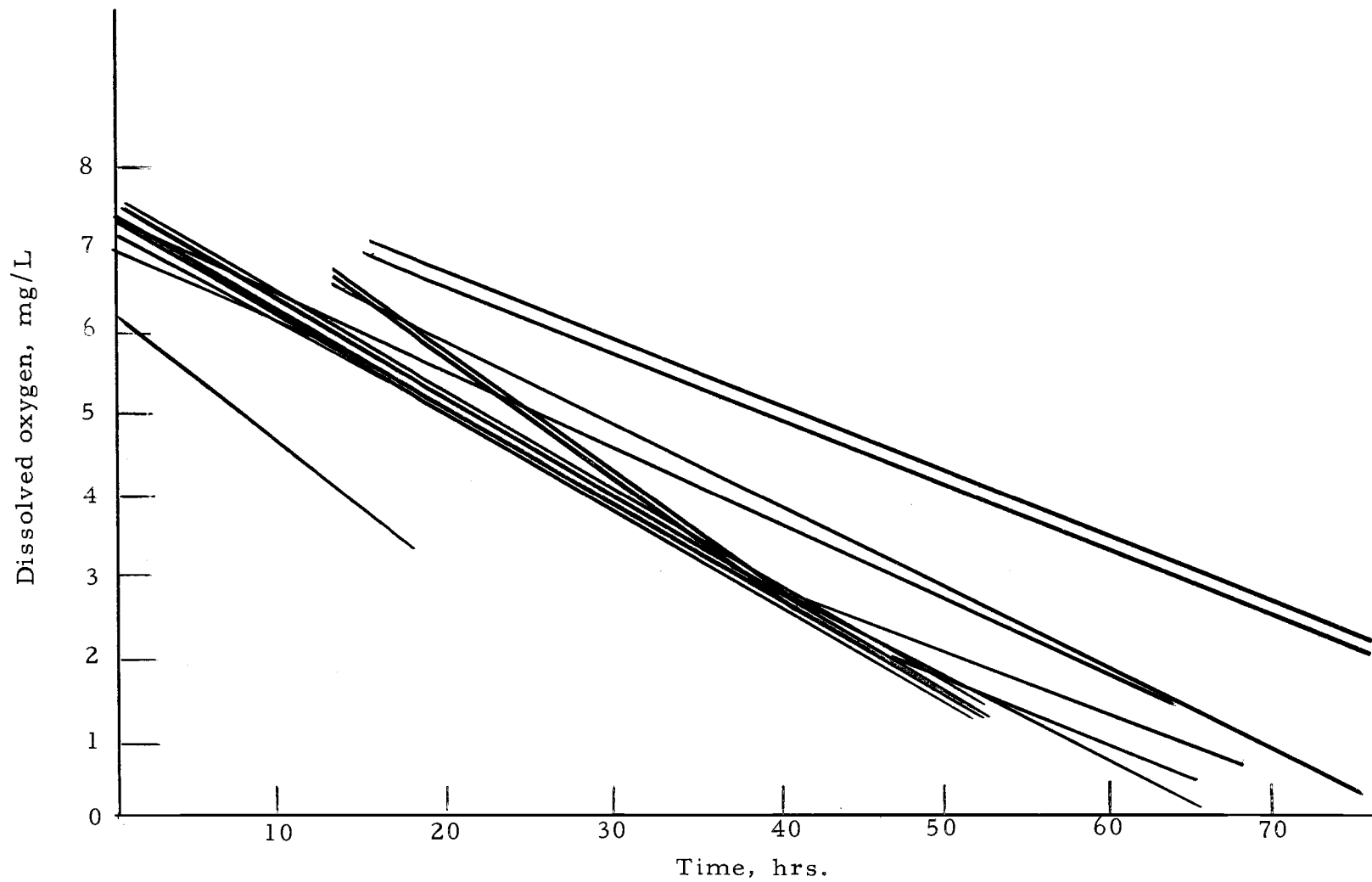
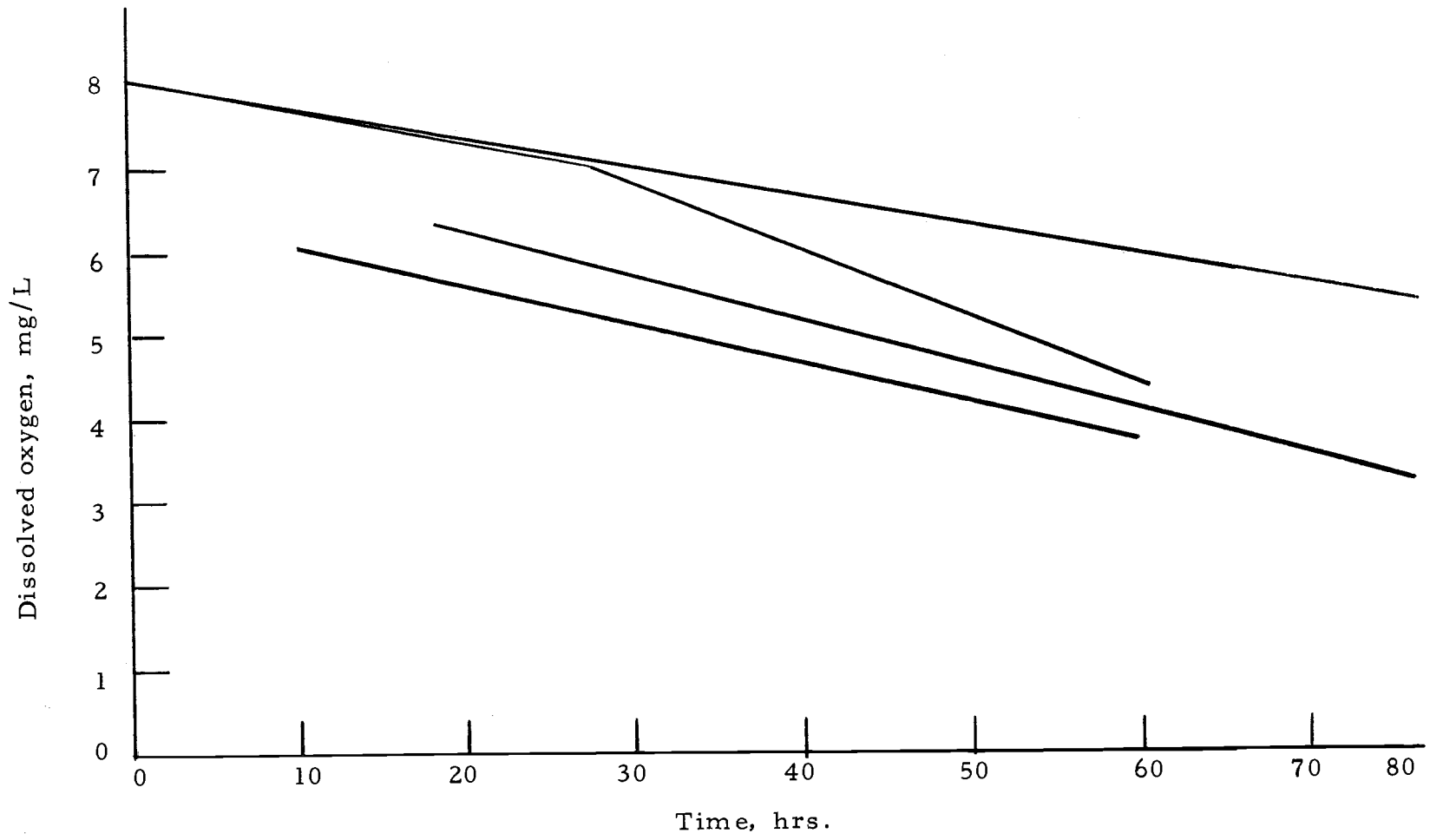Figure 6. Summary of DO uptake rate during mixed experiments.

Figure 7. Summary of DO uptake rate during unmixed experiments.

the previous investigators were studying the effect of mixing. However, in most cases the previous studies used an apparatus that allowed water to continuously flow over the sludge and some mixing may have occurred. The data in Table 3 indicates that mixing may have increased the rates of oxygen uptake during the past studies.

Table 3. Comparison of results with others.

Investigator	DO uptake, g/M^2-day	Remarks
Author	3.4	mixed
Author	1.9	unmixed
McKeown et al. (12)	2.7	mixed
McKeown et al. (12)	4.4	scoured
Baity (2)	1.8-5.4	water constant flow
Fair et al. (6)	1.2-4.6	water constant flow
Lardieri (11)	2.4-3.0	water constant flow
Hanes and Irving (7)	1.4-1.5	unmixed
Edwards and Rolley (5)	2.8-4.8	extremely scoured

A second type of mixing consisting of the recirculation of the overlying water was used in experiment 21. The water was pumped from the bottom of the water column to the top by an external pump at 120 ml per min. When the mixing was stopped, the oxygen uptake rate slowly adjusted to a slower rate approximated by the unmixed experiments as shown in Figure 8.

Mixing did have a positive effect on the oxygen uptake rate of estuarine bottom deposits and if these effects were neglected, the oxygen uptake rates were under-estimated.
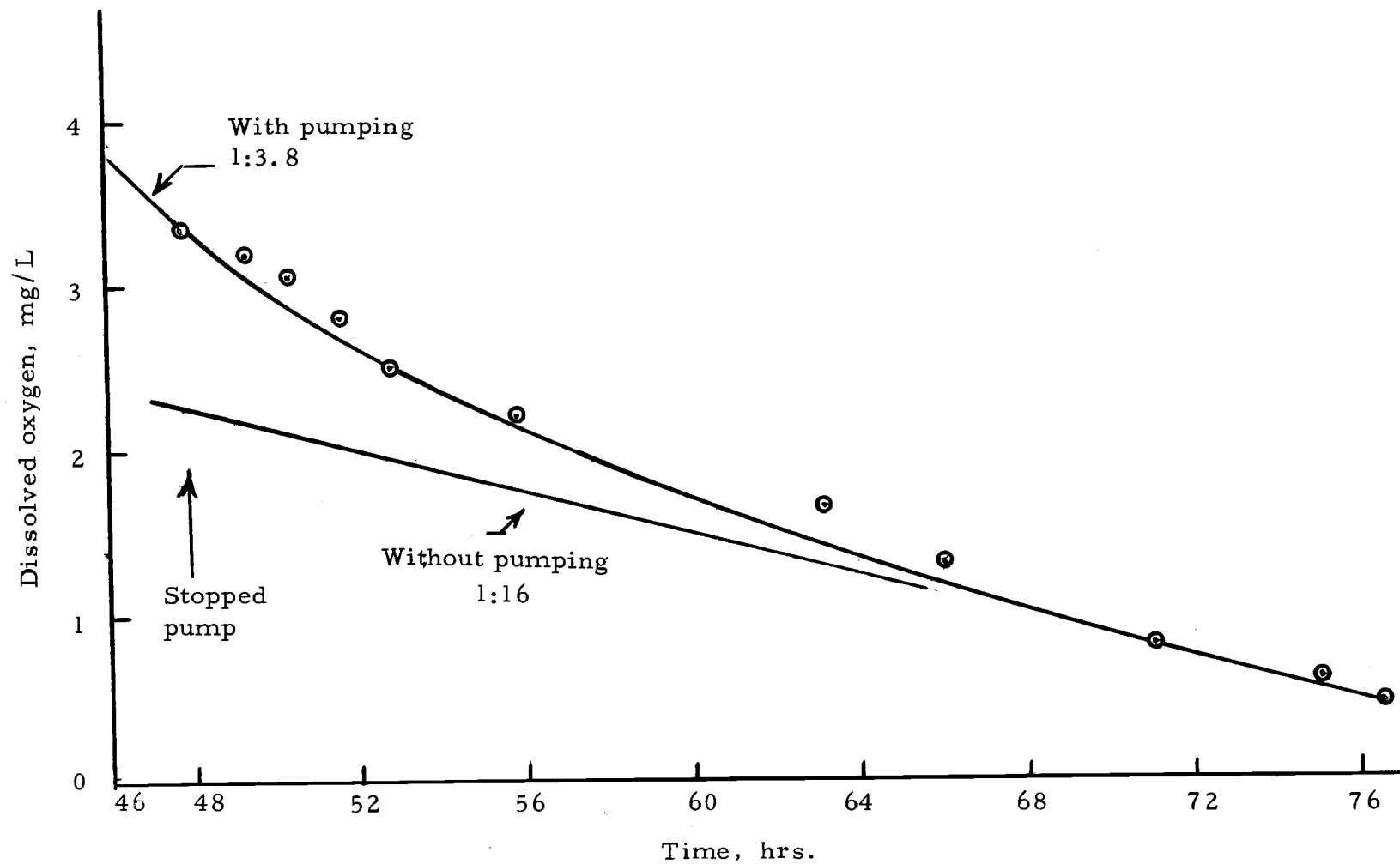
Figure 8. Effect of mixing without solids suspension.

Diffusion of Oxygen into Bottom Deposit

Camp (3) has stated that the oxygen demand on waters overlying bottom deposits by diffusion of dissolved oxygen from the water into the bottom is very small. This reasoning is based on the fact that the difference in BOD between the bottom deposit and the overlying water is much greater than the difference in dissolved oxygen concentration. Therefore, the transfer of oxygen demanding material from the bottom into the water will be at a higher rate than the transfer of oxygen from the water into the bottom deposit.

The results of experiments shown in Figure 6 tend to confirm Camp's reasoning. The uptake rate remained constant throughout the experiments but the dissolved oxygen varied over a wide range. As the DO in the column became less, the gradient between the overlying waters and the DO in the bottom deposits would be less if the diffusion or mixing of DO into the bottom was significant, and the oxygen transfer rate would be expected to decrease as the DO in the overlying layer decreased. However, the results shown in Figure 6 illustrate that the DO uptake rate was constant and did not decrease.

The results of experiment 21 also suggest that the oxygen uptake rate did not significantly depend on the diffusion of DO into the bottom deposit. Figure 8 shows when mixing in experiment 21 was stopped, the oxygen uptake rate changed slowly to an uptake rate

typical of the unmixed experiments. The change in uptake rate would have been more abrupt if the rate was dependent on diffusion. The slow change of uptake rate indicates that the oxygen demand was bio-chemical and was dependent on the bio-degradable material remaining in the supernatent due to the mixing.

Non-biological Oxygen Demand

The possibility of a non-biological oxygen demand was studied. Mercuric Chloride was used in experiments 24 and 25 to kill all bacterial metabolism in a mixed and an unmixed tube. Figure 9 shows that the apparent non-biological oxygen demand accounts for about one-third of the oxygen demand rate measured during the mixed experiments. The increase in apparent non-biological DO demand rate with mixing was approximately 0.25 mg/l DO per day.

The results indicate that the oxygen uptake rate is dependent on the biological system. The indicated rate of non-biological oxygen demand may be misleading, however, because the products of biological metabolism might have exerted a chemical oxygen demand. However, the resulting non-biological oxygen demand would depend upon the ability of the bacteria to produce the non-biological oxygen demand exerting materials and it is concluded that the DO uptake rate depends upon the biological system.
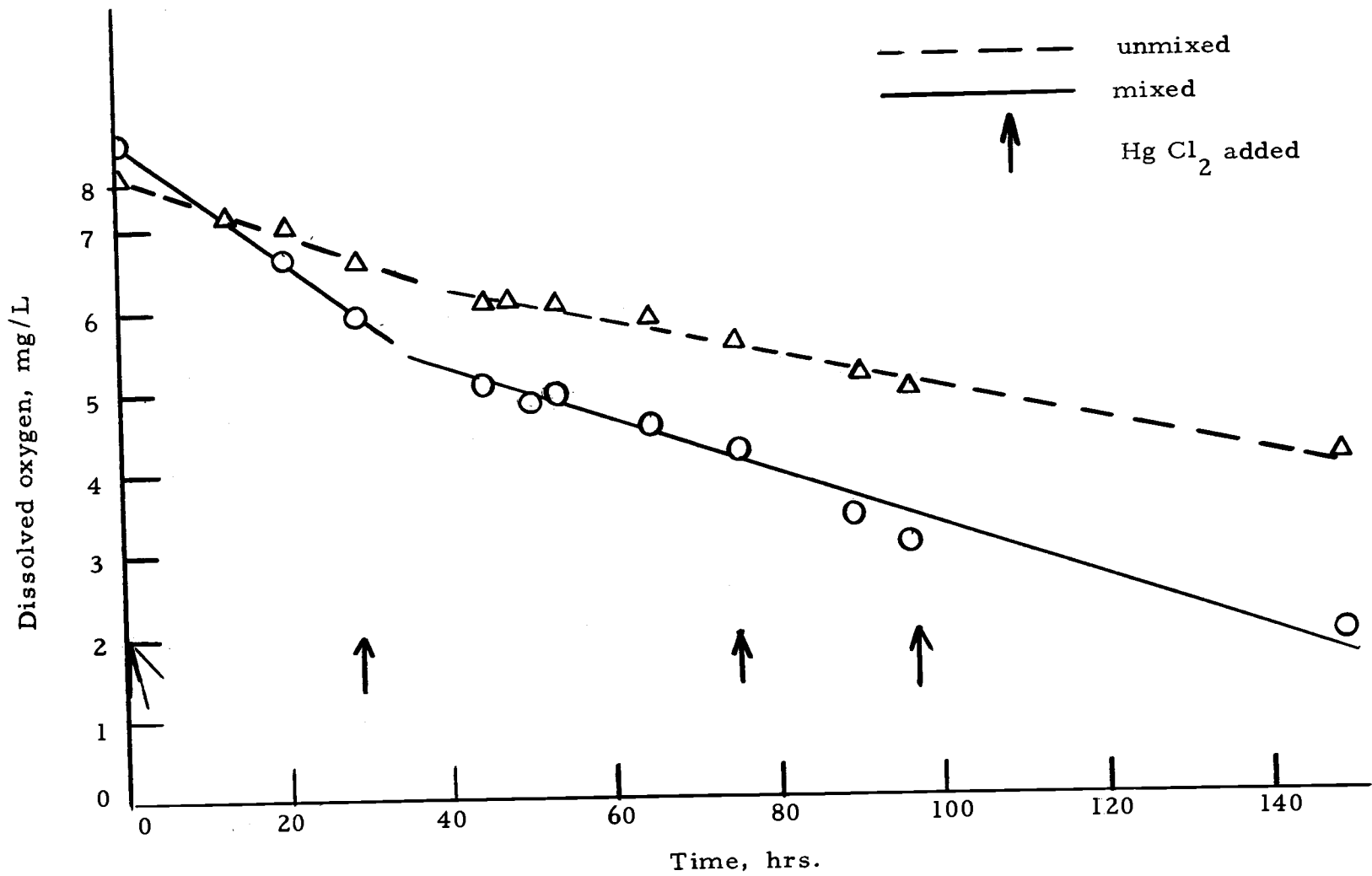
Figure 9. Non-biological oxygen demand of mixed and unmixed experiments.

Oxygen Demand by Benthic Gases

The gases produced from an anaerobic bottom deposit were discharged into the bottom of a mixed column of distilled water dosed with $HgCl_2$ to measure the transfer of dissolved DO by stripping. A schematic drawing of the system is shown in Figure 10. The distilled water was mixed during the last half of the experiment to break the gas bubbles into smaller sizes.
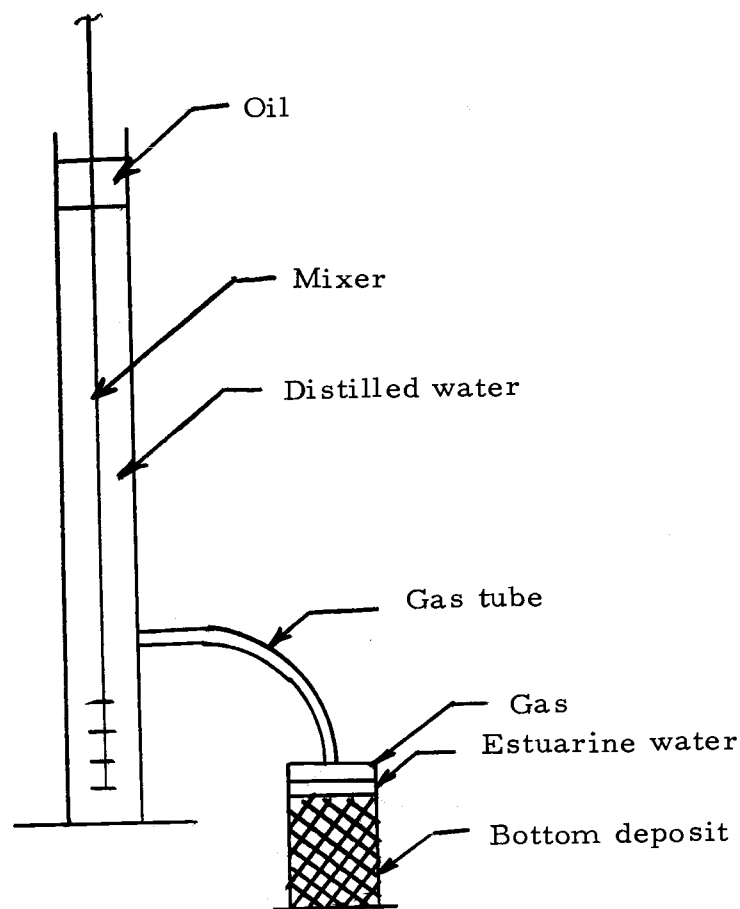

Figure 10. Apparatus for studying benthic gases.

The dissolved oxygen concentration in the distilled water was decreased 0.3 mg/l in three days by the anaerobic gases. No attempt was made to measure the flow of gas produced by the bottom deposit.

Biochemical Oxygen Demand Released
from Bottom Deposit

Introduction

Camp (3), Fair et al. (6) and Streeter (17) have agreed in separate discussions that the primary DO uptake is due to the diffusion of BOD exerting materials out of the bottom deposits rather than the diffusion of DO from the overlying water into the bottom.

Camp reasons that the BOD concentration gradient from bottom deposit to overlying water is much greater than the DO concentration gradient from water to deposit. Therefore, the transfer of DO down will be insignificant compared to the DO demand of materials transferred up into the water.

The BOD of the supernatent water from some typical mixed experiments were measured at one-day intervals for five days. The tests were conducted using incubation bottles without agitation according to Standard Methods (1).

The mixed experiments indicated an ultimate BOD of approximately 12 mg/l. This ultimate BOD would result in the measured oxygen uptake rate of 2.4 mg/l per day if the decay coefficient

K_1 was 0.2 per day. A number of BOD tests indicated substantially
lower ultimate BOD's. For example, a five-day BOD was measured
at 4 mg/l. Without a corresponding decrease in the oxygen uptake
rate a considerably higher decay rate coefficient than 0.2 per day was
indicated.

Further BOD experiments tended to support the theory that the
major portion of DO uptake was due to the diffusion of BOD exerting
materials out of the bottom deposits.

BOD Measurement

The removal of organic material by bio-degradation is common-
ly expressed as a first order reaction which assumes that the rate
change of the concentration of degradable material is proportional
to the concentration of the degradable material present (equation [5]).

$$\frac{dL}{dt} = -K_1 L \tag{5}$$

Where t is time, L is the concentration of bio-degradable material
at time t, and K_1 (base e) is the reaction coefficient.

The BOD of a sample is usually measured by the standard BOD
test (1). Several methods have been described to determine the
reaction rate, some of which Fair et al. and Tsivoglov (22) do not
require the ultimate BOD. The BOD exerted over several time
intervals is required in all the methods and normally the investigator

would measure 1, 2, 3, 4, and 5 day BOD. Typical values of the
reaction coefficients were measured by Camp (3) and were in the
range of 0.14 to 0.21 per day (base e).

The unoxidized material in a natural system is a mixture of
an undetermined number of substances all of which may have differ-
ent reaction coefficients. A first order reaction for any of these
substances would be an over simplification. The reaction rate occur-
ring in the natural system would be the reaction rate at time zero in
the standard BOD test if the effect of the bottles, absence of mixing
and other unnatural conditions had little effect on the results.

The influence of some rapidly degradable materials in the natur-
al situation might be undetected when following a standard procedure.
As an example, consider a column of water over a unit area of bot-
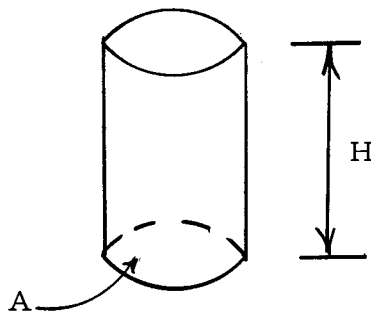tom deposit shown in Figure 11.

Figure 11. Water column.

Where H is the height of the water column, A is the area of
the bottom deposit exposed to the water and V is the volume of the
water column. Assume that the BOD measured in the water is ex-
erted by two materials originating in the bottom deposit. One

material has a slow reaction coefficient, K_1, and BOD remaining of

L and the other material has a rapid reaction coefficient, K_1' and

BOD remaining of L'. The transfer rate of the rapidly reacting

material from the bottom into the overlying waters is La' in mass

transferred per unit time per unit area and La is the corresponding

rate for the slowly reacting materials. The superscript applies to

the materials with high decay rates. A mass balance of the slow

reacting material is written in equation 6.

$$\frac{dVL}{dt} = LaA - K_1VL \qquad (6)$$

Dividing equation 3 by V gives

$$\frac{dL}{dt} = \frac{La}{H} - K_1L \qquad (7)$$

Assuming a steady state where $dL/dt = 0$ and rearranging equation

(7) leads to

$$L = \frac{La}{K_1H} \qquad (8)$$

A similar mass balance can be written for the rapidly decaying

materials.

$$L' = \frac{La'}{K_1'H} \qquad (9)$$

Consider a situation where $K_1' = 10\,K_1$ and La' = 2 La. Substituting

the above relationships into (8) leads to

$$L = \frac{(La')(10)}{(2)(K_1')(H)} \qquad (10)$$

or

$$L = \frac{5\,La'}{K'H} \qquad (11)$$

Combining (9) and (11) gives

$$L = 5\,L' \qquad (12)$$

Equation (12) shows that the slower reacting material has a concentration five times greater than the faster reacting material even though the faster reacting material is being transferred into the overlying waters at twice the rate. Similarly, the rate of DO uptake by the faster reacting material, $K_1 L'$, is twice the DO uptake rate of the slower reacting material, $K_1 L$. Despite the fact that the faster reacting material has twice the DO uptake rate, the slower reacting material would dominate a long term BOD test as shown by equation (12).

As an example, consider Figure 12 which shows plotted results of a BOD test in which a fast and slow reacting material are present. A lag time for the slowly reacting material is assumed. The BOD test in the example is dominated by the slowly reacting material. The BOD results would indicate a DO demand rate of

$$K_m L_m = 0.276(6) = 1.656 \text{ mg/L-day of DO exerted} \qquad (10)$$

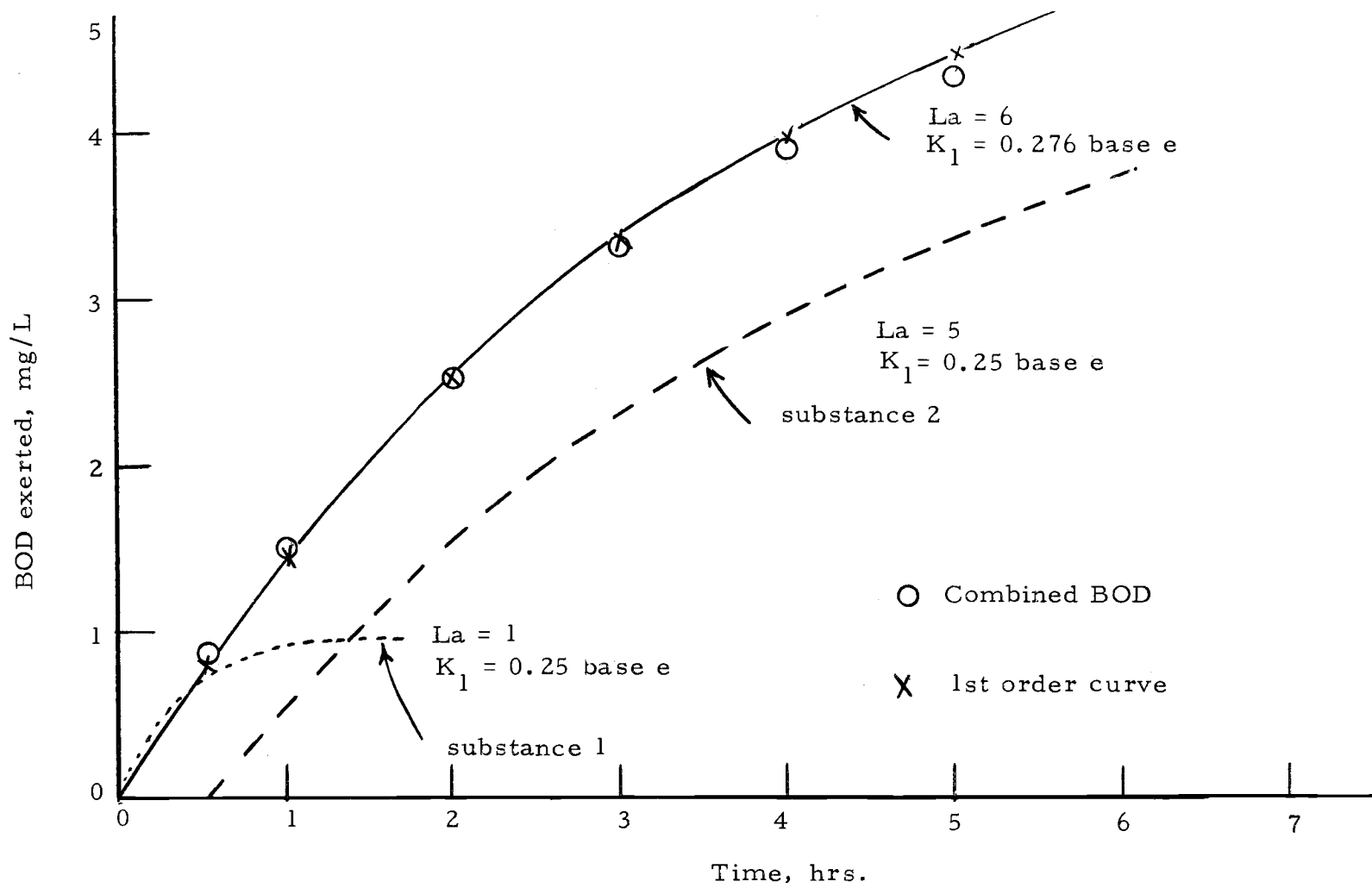where the subscript m indicates measured or observed from Figure 12.

Figure 12. Influence of high decay rate on BOD.

If these two substances were actually being oxidized in the water at the rates shown, the DO removal rate would be the same as the rates of the two materials which is given by

$$K_1L + K_1L' = 0.25(5) + 2.5(1) = 3.75 \text{ mg/l-day of DO exerted} \tag{11}$$

Thus the measured results would tend to underestimate the DO uptake rate by more than a factor of two.

Experiments 30 and 32 were performed in an attempt to increase the amount of possible fast reacting materials so that measurements indicating their presence could be made. Experiment 30 was mixed in an anaerobic state for 48 hours to concentrate the products of anaerobic decomposition from the bottom deposit in the overlying water. Experiment 32 was maintained in an aerobic state by reaeration. A time series of BOD tests were conducted on a mixture of 50% anaerobic supernatent and 50% aerobic supernatent. Figures 13 and 14 show the BOD curve for the mixture.

Experiments 30 and 32, although far from conclusive, suggest the possibility of a substance with a high decay rate coefficient. The decay rate was estimated at approximately ten times as great as the long term reaction rate. The possible high initial decay rate in the experiments would account for the high oxygen uptake rate measured compared to the very low ultimate BOD. However, the differences were very small and do not enable one to make positive conclusions.
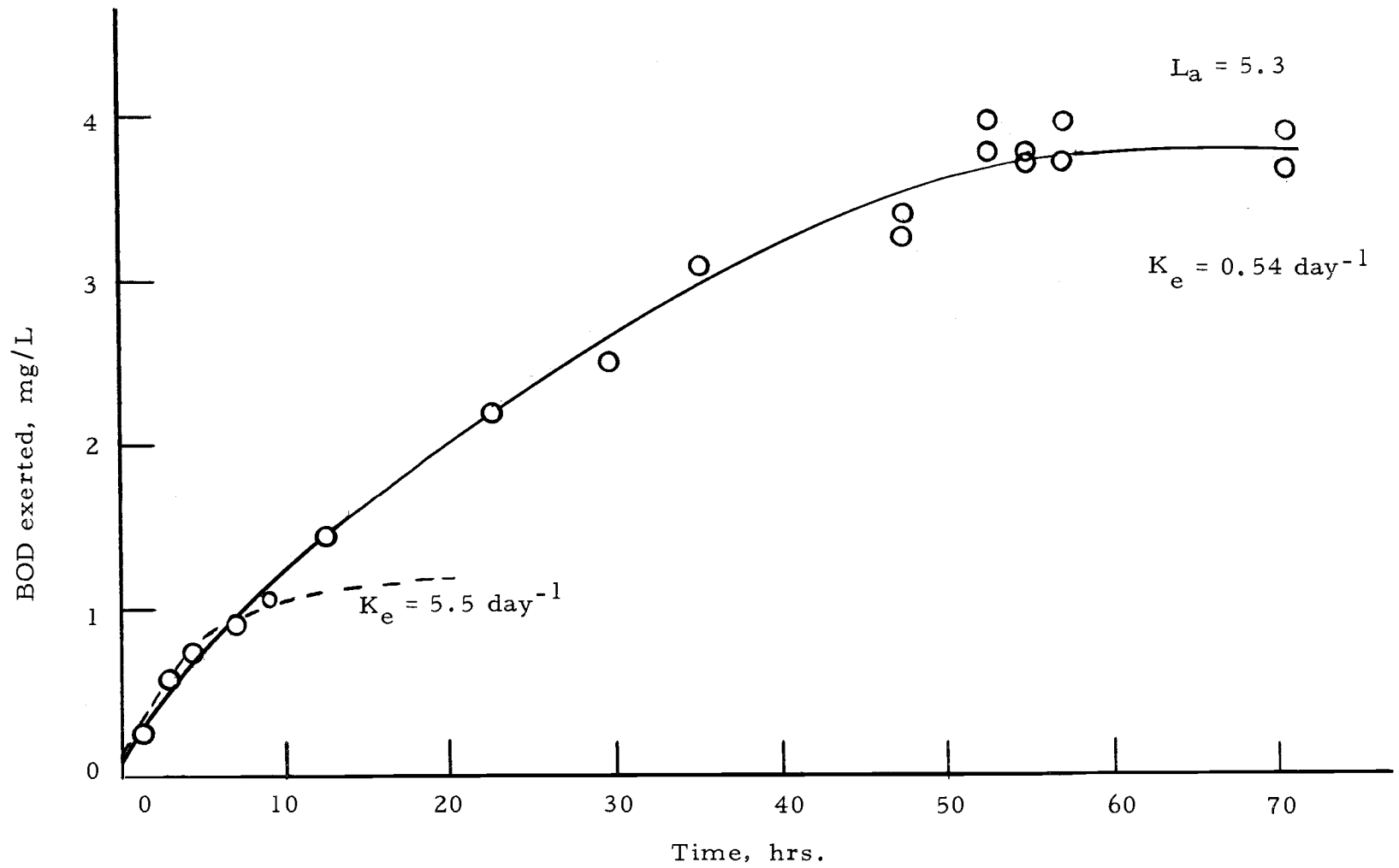
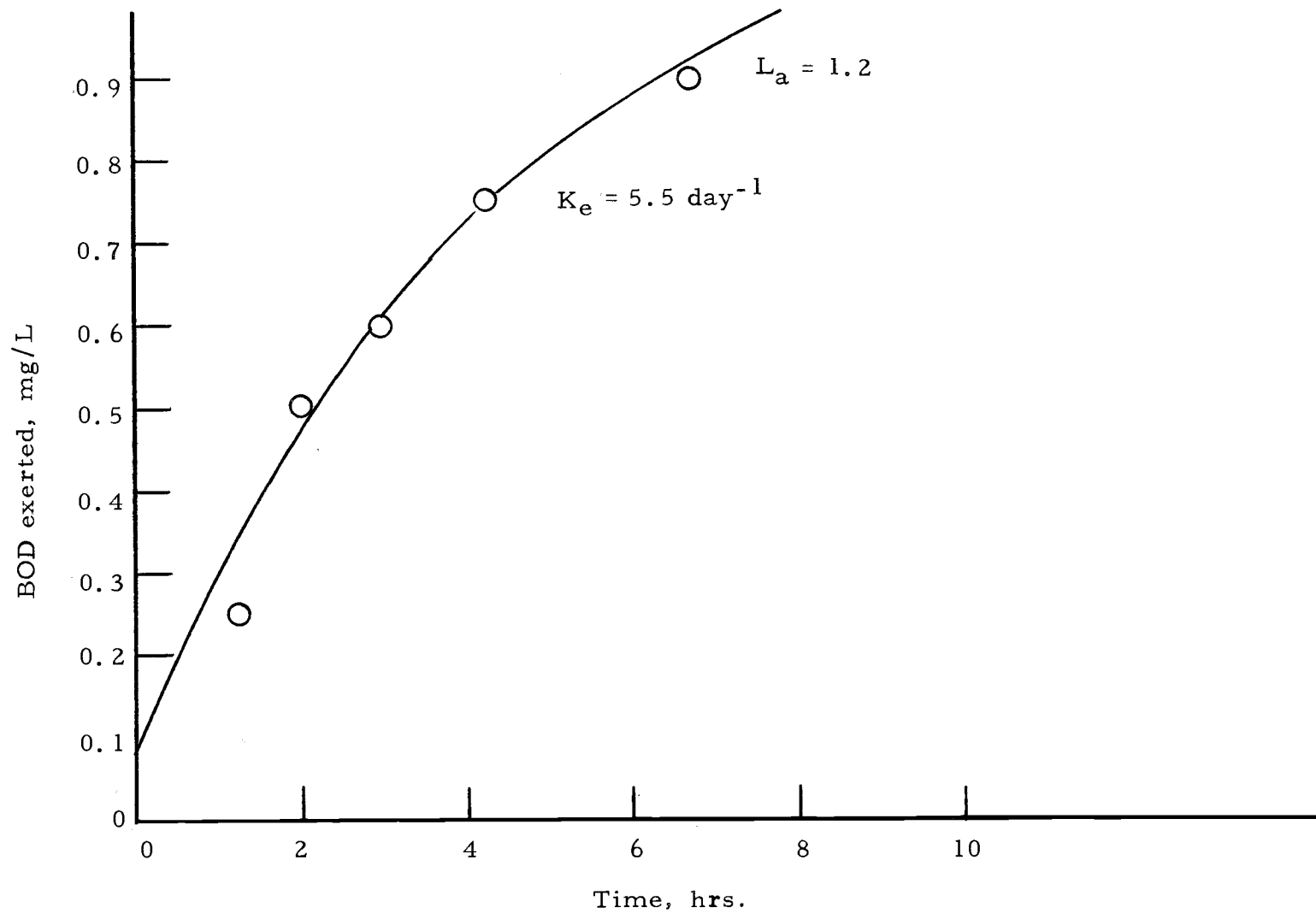Figure 13.   BOD exerted by aerobic-anaerobic mixture.

Figure 14. Initial BOD exerted by aerobic-anaerobic mixture.

Future studies of the oxygen demand of waters overlying bottom deposits should include a time series of BOD tests through the first 12 hours of incubation instead of the more standard five day time series measured daily.

Effect of Depth

The oxygen uptake rate of the bottom deposits did not vary in any predictable manner with the depth of deposit. Experiments 17, 18 and 19 show the same uptake rate for varying depths of bottom deposit.

The results indicate that the small interfacial area between the mud and the water may be of particular importance. The mechanisms of oxygen transfer and BOD transfer across that boundary justifies further study.

Effect of the Concentration of Suspended Matter

The change in concentration of suspended matter was not measured throughout the experiments. The highest rate of oxygen uptake was measured during experiment 21 which was observed to have no apparent suspended matter. All of the remaining mixed experiments showed some significant increase in the concentration of suspended matter in the order of 100 milligrams per liter.

CONCLUSIONS

1. Mixing has a pronounced effect on the oxygen uptake rate. Failure to consider mixing can result in underestimates of the oxygen uptake rate of estuarine bottom deposits.

2. The results tend to confirm that the oxygen uptake rate is due to the release of bio-degradable substances from the bottom into the overlying water.

3. The oxygen demand of benthic gases appears to be very small compared to the total oxygen uptake rate of the bottom deposits.

4. The depth of deposit has no effect on oxygen uptake between the depths of two and 12 inches.

5. The possibility of a material having a high decay rate coefficient being released from the bottom deposit warrants further investigation.

6. The change in concentration of matter suspended from the surface of deposits in the order of 100 mg per liter appears to have no apparent effect on the oxygen uptake rate of water overlying the deposits.

BIBLIOGRAPHY

1. American Public Health Association. Standard methods for the examination of water and waste water. 12th ed. New York, 1965. 769 p.

2. Baity, H. G. Studies of sewage sludge. Sewage Works Journal 10:539-568. 1938.

3. Camp, Thomas R. Water and its impurities. New York, Reinhold, 1963. 355 p.

4. Carey, Andrew G., Jr. Energetics of the benthos of Long Island Sound. I. Oxygen utilization of sediment. In: Aspects of the oceanography of Long Island Sound. New Haven, Connecticut, 1967. p. 136-144. (Yale University. Peabody Museum of Natural History. Bingham Oceanographic Foundation. Bulletin of the Bingham Oceanographic Collection. Vol. 19, article 2)

5. Edwards, R. W. and H. L. J. Rolley. Oxygen consumption of river muds. Journal of Ecology 53:1-19. 1965.

6. Fair, G. M., E. W. Moore and H. A. Thomas, Jr. Sewage Works Journal 13:270-307. 1941.

7. Haines, Bruce N. and Robert L. Irving. Oxygen uptake rates of benthal systems by a new technique. In: Proceedings of the 21st Industrial Waste Conference, Lafayette, Indiana, 1966. Lafayette, 1966. p. 468-479. (Purdue University Engineering Bulletin, vol. 50, no. 2. Engineering Extension Series no. 121)

8. Hayes, F. R. and M. A. MacAulay. Lake water and sediment. V. Oxygen consumed in water over sediment cores. Limnology and Oceanography 4:291-298. 1959.

9. Jansa, Victor and Gunnar Akerlindh. A method for computing the oxygen curve in a polluted stream with special reference to the oxygen consumption by sludge deposits. Sewage Works Journal 13:551-556. 1941.

10. Knowles, G., R. W. Edwards and R. Briggs. Polarographic measurement of the rate of respiration of natural sediments. Limnology and Oceanography 7:481-484. 1962.

11. Lardieri, Nicholas J. The aerobic and benthal oxygen demand of paper mill waste products. Tappi 37:105-708. 1954.

12. McKeown, J. J., A. H. Benedict and G. M. Locke. Studies on the behavior of benthal deposits of wood origin. Water Pollution Control Federation, Journal 40:R-333-R-353. 1968.

13. Mohlmann, F. W., T. L. Herrick and H. G. Swope. Technique of stream pollution investigations. Industrial Engineering Chemistry 23:209-213. 1931.

14. Mortimer, C. H. The exchange of dissolved substances between mud and water in lakes. Journal of Ecology 30:147-201. 1942.

15. Rudolfs, Willem. Stabilization of sewage sludge banks. Industrial and Engineering Chemistry 30:337-340. 1938.

16. Stein, J. E. and J. G. Dennison. In situ benthal oxygen demand of cellulose fibers. In: Advances in water pollution research: Proceedings of the Third International Conference on Water Pollution Research, Munich, Germany, 1966. Vol. 3. Washington, D. C., Water Pollution Control Federation, 1967. p. 181-197.

17. Streeter, H. W. Effects of sewage discharge on streams. Sewage Works Journal 3:713-723. 1931.

18. Streeter, H. W. Measures of natural oxidation in polluted streams. I. The oxygen demand factor. Sewage Works Journal 7:251-279. 1935.

19. Streeter, H. W. Disposal of sewage in inland waterways. In: Modern sewage disposal. Lancaster, Pennsylvania, 1938. 371 p.

20. Streeter, H. W. and Earle B. Phelps. Factors concerned in the phenomena of oxidation and reaeration. In: A study of the pollution and natural purification of the Ohio River. Washington, D.C., 1925. 75 p. (U. S. Public Health Service. Public Health Bulletin no. 146)

21. Theriault, Emery J. and Paul D. McNamee. Experimental studies of natural purification in polluted waters. VI. Rate of disappearance of oxygen in sludge. Public Health Reports 46:1301-1319. 1931.

22. Tsivoglou, R. V. 1965. Information given in a series of lectures to a summer school class at Oregon State University. Corvallis.

23. Velz, C. J. Sognificance of organic sludge deposits. In: Oxygen relationships in streams. Proceedings of a seminar sponsored by the Water Supply and Water Pollution Program of the Sanitary Engineering Center, Cincinnati 1957. Cincinnati, 1958. p. 47-61. (U. S. Robert A. Taft Sanitary Engineering Center. Technical Report no. W 58-2)

24. Wyckoff, Bruce M. Rapid solids determination using glass fiber filters. Water and Sewage Works 111:R-349-R-352. 1964.

APPENDIX

APPENDIX I

METHOD FOR DETERMINING DISSOLVED OXYGEN CONCENTRATION IN A SMALL VOLUME OF WATER

General Discussion

The Azide Modification of the Iodometric Method described in

Standard Methods (1) was modified to determine the dissolved oxygen

concentration in a 20 ml sample. The reagents specified in the stand-

ard method were diluted in convenient proportion to the reduction in

volume of the sample in the micro-method. Twenty ml samples

were collected in a syringe and the solutions added through the acid

step were mixed in the syringe. The solution was titrated in a sepa-

rate flask.

Apparatus

1. Thirty ml syringe with 1 ml graduations.

2. Reagent Bottles with serum caps for convenient storage

of $M_n SO_4$, Alkai-Iodide-Azide, and H_2SO_4 solutions. Vacuum flasks

mounted upside down with a serum cap placed over the tubing connec-

tors were convenient. A short length of glass tube through the flask

stopper to above the surface of the liquid was required.

3. Medium sized, three prong grip, clamp to keep the plunger

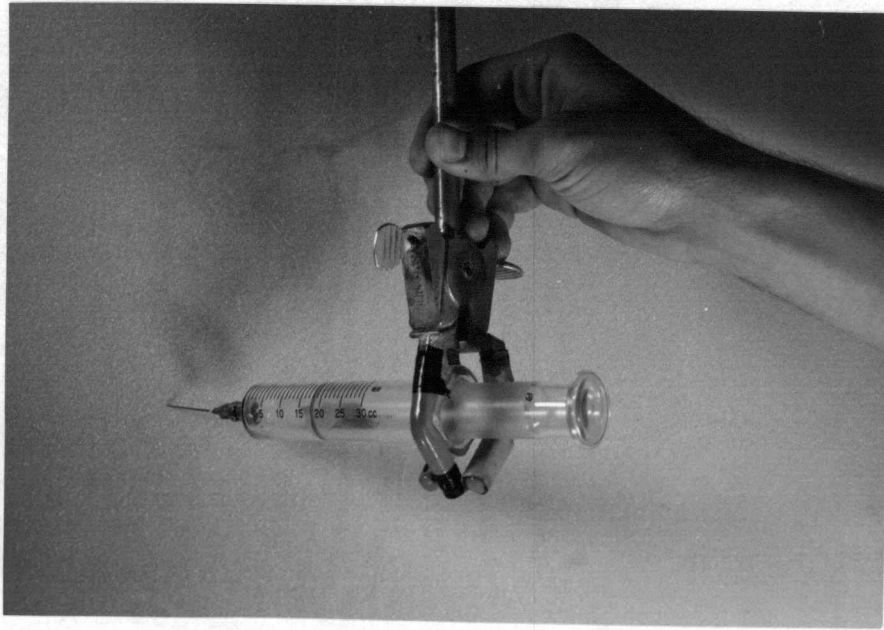from slipping and letting air into the syringe (Figure 15).

Figure 15. Micro-Winkler apparatus.

4. Buret and necessary glassware for titration.

Reagents

MnSO$_4$, Alkai-Iodide-Azide and H$_2$SO$_4$

Prepare and store according to Standard Methods (1) and dilute 20 ml to 100 ml with distilled water for use.

Starch Solution

Prepare as described in Standard Methods (1).

Sodium thiosulfate titrant, 0.0025N

Prepare as described in Standard Methods except that 0.6205 g Na$_2$S$_2$O$_3$ · 5H$_2$O is dissolved in freshly boiled and cooled distilled water.

Potassium dichromate solution, 0.0025N

Prepare as described in Standard Methods except that 0.1226 g should be dissolved in distilled water.

Standardization of sodium thiosulfate

Standardize according to Standard Methods except KI should be dissolved in 20 ml distilled water and not diluted further.

Procedure

Withdraw 2 or 3 ml of the sample in the syringe and after point-ing the needle upwards, eject all but about 1 ml of the sample. Allow some of the sample to drip out of the needle while inserting the needle into the sample for the second time. No bubbles should be visible in the syringe. Withdraw 20 ml of the sample and tighten the clamp around the syringe to prevent movement of the plunger.

Pull 1 ml of the alkali-iodide-azide reagent into the syringe followed by 1 ml of $MnSO_4$ solution. The order is reversed from Standard Methods to avoid a reaction of alkali with acid in the needle.

After mixing by gently overturning the syringe several times, let the floc settle and re-mix as directed by Standard Methods (1) according to the type of water sample.

Pull 1 ml of H_2SO_4 solution into the syringe and gently mix until dissolution is complete.

Expel the contents of the syringe into a flask and titrate with sodium thiosulfate using starch as an indicator as directed by Stand-ard Methods (1).

Calculation

Apparently the relatively large volumes of $MnSO_4$ and Alkali-iodide-azide reagents add some dissolved oxygen to the sample.

Therefore a calibration curve is necessary. Compute the micro-DO concentration by adjusting for the actual normality of the micro-titrant for several samples of varying concentrations of DO. Plot the micro-DO vs. the DO measured by the standard test for the same samples. The data should plot as a straight line with no points deviating more than 0.05 mg/l DO. To avoid further errors due to the DO in the reagents it is recommended that the reagents be used at the same temperature at which the calibration curve was prepared.