THE EFFECTS OF TURBIDITY ON THE
RATE OF BIOCHEMICAL OXIDATION

by

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B.E., Feng-Chia College of Engineering & Business, 1970

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Civil Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

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INTRODUCTION

Because of the developments in modern industrial technology, pollution has become a severe problem in the world. In the last fifty years, stream pollution has drawn a great amount of attention from scientists and engineers.

A stream may be polluted by the organic or inorganic materials which are carried in with urban and rural land run-off, wastewater treatment plant effluents and other sources. These pollutants may deteriorate the stream water quality either physically and/or biochemically.

When wastewaters are discharged into a stream, the bacteria will utilize the organic matter present and exert an oxygen demand. The rate of this demand is determined by the deoxygenation rate constant, $K_1$. In order to predict the effect of the wastewater discharge on the dissolved oxygen resources of the stream, one must first estimate a value for the rate constant, $K_1$.

There have been many investigations conducted on the factors affecting the Biochemical Oxygen Demand (BOD) rate. Some of these factors are temperature, stream turbulence or mixing, and demands from organisms attached to the stream bottom.

These investigations have resulted in more accurate predictions of deoxygenation rate constants for streams. This has then allowed engineers to make more accurate predictions of stream dissolved oxygen concentrations, and thereby determine necessary degrees of wastewater treatment in order to maintain acceptable dissolved oxygen levels.
An additional factor that may affect the rate of stream oxygen demand is the effect of inorganic suspended solids or turbidity. Many streams draining agricultural lands have high turbidities, particularly after extensive run-off arising as a result of precipitation and snow melt. Therefore, this research is directed toward evaluating the effect of turbidity on stream deoxygenation rates.
PURPOSE AND SCOPE

Studies have shown that $K_1$ values determined in the laboratory (from BOD bottles) may be considerably lower than values determined from stream studies. Differences between laboratory and stream $K_1$ values may be due to a variety of factors, such as mixing (turbulence), benthic demand and turbidity.

The effect of inorganic suspended solids (turbidity) on the rate of the BOD reaction is not known. Highly turbid streams may have higher or lower $K_1$ values. It is the purpose of this study to show the effects of turbidity on the deoxygenation rate constant.

This study was conducted in the laboratory with a Hach Manometric BOD Analyzer. Wastewater samples were settled domestic wastewater from the Manhattan Wastewater Treatment Plant. Samples were diluted with turbid and non-turbid dilution water in order to simulate the mixing of wastewater effluents with a natural stream or river. Comparisons were then made between turbid and non-turbid samples to determine the effect of turbidity on the rate of deoxygenation.
Natural Phenomena In Streams

The capacity of a stream to receive and oxidize wastewaters depends on its oxygen resources. The condition of a polluted stream at any time is the result of a balance between these sources and the demand made upon them by the polluting matter carried by the stream.

Oxygen Demand Upon a Stream

The major oxygen demands that result from the oxidation of organic and inorganic materials by organisms for energy and growth can be grouped into carbonaceous and nitrogenous BOD. Carbonaceous BOD is the result of oxidation of organic compounds (to CO₂ and H₂O) while nitrogenous BOD is the result of oxidation of ammonia to nitrates.

Streeter and Phelps (1) studied the pollution phenomenon in the Ohio River from 1914 to 1916. They came to a conclusion about the biochemical oxidation of organics. They stated that "the rate of biochemical oxidation of organic material is proportional to the remaining concentration of unoxidized substances, measured in forms of oxidizability." Mathematically, this statement can be expressed as follows:

\[- \frac{dL}{dt} = K_1 L\]  \hspace{1cm} (1a)

integrated, equation (1a) becomes,

\[\ln \frac{L}{L_a} = -K_1 t\]  \hspace{1cm} (1b)

or \[L = L_a e^{-K_1 t}\]  \hspace{1cm} (1c)
or \[ L = L_a 10^{-k_1 t} \] (1d)

then, the BOD exerted at any time, \( t \), will be

\[ Y = L_a (1 - 10^{-k_1 t}) \] (2)

where: \( L \) = ultimate BOD remaining at time \( t \)
\( L_a \) = ultimate BOD at time zero
\( Y \) = BOD exerted at time \( t \)
\( k_1 \) = deoxygenation rate constant, base e
\( k_1 \) = deoxygenation rate constant, base 10
\( K_1 = 2.303 k_1 \)

Streeter and Phelps' first order, or monomolecular, reaction formulation is generally accepted as representative of the reaction by the dispersed group of microorganisms in a stream.

The progressive exertion of BOD in polluted waters actually breaks down into two stages (Figure 1). In the first stage, primarily, the carbonaceous materials are oxidized. In the second stage, ammonia is oxidized by nitrifying bacteria.

Under some circumstances, these two oxidations can proceed simultaneously, and the resultant BOD curve will be a composite of the two reactions. Normally, however, the nitrification will not begin until the carbonaceous demand has been partially satisfied. This is because the nitrifying bacterium are not normally present in large number and there is a resultant lag period during which their numbers are building up sufficiently to activate nitrification. It has been reported (2) that 1 mg/l of ammonia nitrogen, if completely oxidized to nitrate, will exert an oxygen demand of 4.33 mg/l.
THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE. THIS IS AS RECEIVED FROM CUSTOMER.
The significance of $K_1$ values on the carbonaceous BOD reaction is that when ultimate BOD is evaluated, the higher the $K_1$ value, the faster the biochemical oxidation is exerted. For example, the BOD$_5$ will be higher if the $K_1$ value is higher. If the BOD$_5$ is fixed, then the higher the $K_1$ value, the lower will be the ultimate BOD.

If a domestic wastewater has an ultimate BOD of 200 mg/l and a deoxygenation rate of 0.1/day, its BOD$_5$ will be 120 mg/l. If its deoxygenation rate is 0.2/day, then the BOD$_5$ will be 180 mg/l. However, if the BOD$_5$ of the wastewater is fixed to be 120 mg/l, its ultimate BOD will be 180 mg/l if $k_1$ equals 0.1/day and will be 133 mg/l if $k_1$ equals 0.2/day.

Reoxygenation from the Atmosphere and Photosynthesis

In polluted streams the demand imposed upon the dissolved oxygen supply by the progressive satisfaction of the oxygen demand reduces the oxygen content below its saturation value. As soon as this depression occurs, adsorption of oxygen from the atmosphere follows.

In a quiescent, unsaturated body of water the surface film, in immediate contact with atmosphere, rapidly becomes saturated with oxygen and can dissolve no more air until air already dissolved at surface diffuses into the deeper unsaturated strata.

In a turbulent, rapidly flowing stream, the water surface at the air-liquid interface is being continuously replaced by the turbulence of the stream movement. Mixing brings layers of saturated water from the surface into intimate contact with other less oxygenated layers from below, and thus the oxygen can diffuse into the unsaturated strata.
The rate of reaeration from the atmosphere is at all times proportional to the saturation deficit in the stream,

\[- \frac{dD}{dt} = K_2D\]  

(3a)

integrated, equation 3a becomes

\[D_t = (D_a) e^{-K_2t}\]  

(3b)

or \[D_t = (D_a) 10^{-k_2t}\]  

(3c)

where: \(D\) = variable DO deficit  
\(D_a\) = deficit at time zero  
\(D_t\) = deficit at time \(t\)  
\(K_2\) = reaeration rate constant, base e  
\(k_2\) = reaeration rate constant, base 10

The solubility of oxygen in water is inversely proportional to the temperature. In other words, the higher the temperature, the lower the solubility of oxygen in the water.

The quantity of oxygen transferred into the water by plant photosynthesis is variable under various conditions. The degree of photosynthesis is sun-light dependent. In general, it reaches a maximum point in the late afternoon. Algae and other plants will consume a certain amount of dissolved oxygen day and night as a result of respiration. The total result of photosynthesis, respiration and reaeration process on stream dissolved oxygen content results in a diurnal variation in a 24-hour period. On a rainy day or under a cloudy sky, the photosynthesis process is rather poor. As to seasonal variations, in the summer algae flourish and will produce more oxygen than in any other season. Also, penetration of sun light into the water is an important
factor. Highly turbid water may block light penetration and greatly reduce or eliminate photosynthetic activity.

All of these factors make the effect of photosynthesis on a stream dissolved oxygen resources extremely difficult to predict. Therefore, this factor is usually not included in mathematical models for prediction of stream dissolved oxygen.

**Mathematical Formulation of Oxygen-Sag Equation**

From the primary laws of oxidation of carbonaceous matter and of reaeration in the stream, the resultant general equation of stream conditions may be derived, expressed in terms of dissolved oxygen. The net change in oxygen content is the result of both deoxygenation and reaeration reactions. It can be expressed as:

\[
\frac{dD}{dt} = K_1L - K_2D
\]

(4a)

integrated, equation 4a becomes,

\[
D = \frac{K_1L_a}{K_2 - K_1} (e^{-K_1t} - e^{-K_2t}) + D_a e^{-K_2t}
\]

(4b)

or

\[
D = \frac{K_1L_a}{K_2 - K_1} (10^{-k_1t} - 10^{-k_2t}) + D_a \cdot 10^{-k_2t}
\]

(4c)

where:  
L_a = BOD at time zero  
D_a = DO deficit at time zero  
D = DO deficit at time t  
K_1 = deoxygenation rate, base e  
k_1 = deoxygenation rate, base 10  
K_2 = reaeration rate, base e  
k_2 = reaeration rate, base 10
The relationship between deoxygenation and reaeration is shown in Figure 2. This typical DO-Sag is the result of a wastewater discharge. Initially, the deoxygenation exceeds the rate of reaeration and DO begins to decrease. As the wastewater travels downstream, the organic matter in the wastewater is oxidized. Then the rate of reaeration exceeds the rate of deoxygenation and the DO begins to increase until it eventually reaches saturation once again. In order to predict the effect of wastewaters on the DO of streams, the reaction rate constants, \( K_1 \) and \( K_2 \), must be known.

Factors Affecting Deoxygenation Rates

Factors already known to have a definite effect on the deoxygenation rate are temperature, benthal demand, stream turbulence and plant respiration.

Temperature

The deoxygenation rate constant, \( K_1 \), has been found to be a function of temperature. Streeter and Phelps (1) found empirically that it can be expressed as:

\[
\frac{K_1'}{K_1} = \theta (T' - T)
\]

(5)

where: \( T', T \) = two different temperatures
\( K_1', K_1 \) = corresponding values of the deoxygenation rate
\( \theta \) = thermal coefficient, a constant determined experimentally

Phelps and Streeter studied the \( \theta \) value in the Cincinnati, Boston and Washington, D. C., areas and found it to average 1.047.
Figure 2 - The Relationship Between Deoxygenation and Reaeration in a Stream
The variation in the value of $K_1$ at different temperatures, as defined by a value of $\theta$ equal to 1.047, is illustrated in Figure 3.

**Benthal Demand**

According to McKinney (3), there are two forms of microorganisms that utilize organic material in the stream. They are: (1) the dispersed growths, and (2) the attached growths. The dispersed growths flow with the stream and act in the same manner as the microorganisms in a BOD bottle. The attached growth microorganisms include those growing on fixed objects such as stones or twigs and those deposited in the bottom muds and silts.

The rate of metabolism of the attached microorganisms is constant since the concentration of organic matter passing around them is relatively uniform and the space for attachment is limited. The attached growths can fluctuate somewhat with stream flow in those areas where all the surfaces for attachment are not full. This normally occurs in the latter ends of the recovery zone.

The demand upon the oxygen resources in the stream flow through the reach of active biological extraction depends not only upon the rate of extraction, but also upon the level of BOD accumulation of excess biological floc in deposit zones or attached growths.

The rate of biological extraction is dependent upon contact opportunity between the biological mass and the water mass. The biological growth and river channel characteristics are the
Figure 3 - The Relationship Between $K_1$ and Temperature
(After Streeter & Phelps)
factors influencing the contact opportunity. In an attached type, surface contact area is increased by undulating streamers; if of the dispersed type, by turbulent distribution in the channel cross-section. In general, the dispersed microorganisms predominate in most stream pollution problems.

Mixing and Turbulence in Stream

A shallow, rapidly moving, turbulent stream will have a high degree of mixing. When wastewater or run-off are discharged into the stream, there also exists an overturning phenomenon. The effect from temperature on the water density will also cause overturning.

Both turbulent mixing and overturning in the stream will distribute the suspended organic matter and microorganisms uniformly. In addition, they may resuspend the organic matter and attached microorganisms.

When microorganisms and organic materials are under continuous mixing conditions, microorganisms will have more chance to utilize the food (organic matter) and will increase the stream deoxygenation rate.

Turbidity

Most streams in the Midwest exhibit wide variations in stream inorganic suspended solids. Turbidity is an indirect measure of suspended solids. It is a measure of the light reflection and adsorbance through a sample. Usually the higher the suspended solids, the higher the turbidity. Turbidity in streams draining agricultural lands can reach values over 2,000
units during runoff conditions. Most of the turbidity is due to inorganic suspended solids such as clay and silt particles, but considerable organic suspended solids may also be washed from land.

In many Midwest streams, water quality in terms of BOD and DO is the poorest during high flow periods after runoff. This is the result of the organic material washed in from the land. Gray (4) reports that "water quality in Kansas rivers is poorest during periods of rainfall runoff as it relates to the turbidities, dissolved oxygen, phosphate, nitrogen and bacterial concentrations."

Wallace (5) indicated that the only cause of DO's below 5 mg/l in the Iowa River was land runoff.

The question of how turbidities affect the deoxygenation rates is not known. Do highly turbid streams have greater or lesser deoxygenation rates than non-turbid streams? The inorganic suspended solids could increase deoxygenation rates by providing a source of attachment for the microorganisms and thereby increasing their growth rate in some way. On the other hand, the inorganic suspended solids might inhibit deoxygenation by interfering in some fashion with the microorganism's ability to come in contact with and process organic matter.

**Measurement of Deoxygenation Rates**

The deoxygenation rate, $K_1$, can be measured after the ultimate BOD has been estimated. There are three different ways to estimate the ultimate BOD.
Conventional Lab Analysis

Conventional lab analysis is carried on by first taking a sample from the stream right after the wastewater is discharged. Then a set of BOD bottles is prepared for measuring the BOD at one or two day intervals for a period ranging from ten to 15 days. The dilution technique and the procedure for the BOD determinations are outlined in Standard Methods (6).

The resulting BOD curve is commonly described as the "first-order" or "Monomolecular" expression. Once the curve is determined, the constant $K_1$ and $L$ can be estimated by one of a number of mathematical or graphical methods available.

Stream Field Survey

The stream field survey method of measuring the river deoxygenation rate is determined from five-day BOD samples taken at river sampling stations. The method consists generally of plotting on semi-log paper the stream BOD values determined by incubation in the laboratory against time-of-travel representation of sampling points along the stream. The slope of the $BOD_5$ reduction is the stream deoxygenation rate.

Gannon (7) conducted a 48-hour, around-the-clock, intensive survey on the Clinton River below the City of Pontiac Wastewater Treatment Plant and the Tittabawassee River below Dow Chemical Company at Midland, Michigan. Velz (8) suggested that for fresh water streams, a minimum of six to eight samples taken through the day at all stations for two or three days will provide a representative measurement.
Manometric Apparatus Analysis

Warburg, Hach, etc., are manometric methods developed for measuring the BOD progression. They are designed to simulate the real stream situations. The BOD bottle with a magnetic stirrer will keep the water under continuous mixing. The air above the water surface will supply the required oxygen for reaeration and the KOH will absorb CO₂ produced from the oxidation of carbonaceous organics.

By diluting the sample under a predetermined dilution factor, the BOD exerted can be read from the manometric scale. A 15-day long term continuous recording will give a best figure of the ultimate BOD. This only gives the BOD progression. The rate constant, K₁, still has to be evaluated.

The deoxygenation rate constant can be measured in several ways:

Reed-Theriault Method - This method was developed by Reed and Theriault in 1931 (9). This method follows the conventional pattern of linearizing a transcendental equation such as equation (2) by assuming a trial value of K and using the first term of a Taylor's expansion in a least squares treatment. Such methods undoubtedly give the most consistent and accurate results. Unfortunately, the calculations involved are somewhat long and cumbersome. Moreover, the computation may have to be repeated because of the selection of a trial value of K₁ which was not sufficiently near the true value.

Log-Difference Method - The Log-Difference Method was developed by Fair (10) in 1936. This method is based on the
assumption that the $K_1$ value is proportional to the logarithm of BOD reduction against time, and $K_1$ may be found by least squares procedures. Fair derived two normal equations to solve $K_1$ and $L$. This method is limited in application to observations made at equal time intervals.

**Slope Method** - The Slope Method was developed by Thomas (11) in 1937. This method is based entirely upon a least squares treatment of the differential equation:

$$\frac{dy}{dt} = K (L-y) \quad (6)$$

where: $y$ = BOD exerted in time $t$
$L$ = ultimate BOD of first stage
$K$ = reaction velocity constant
$rac{dy}{dt}$ = rate of increase of BOD

This approach deals with the rate of change of $y$, which is the slope of equation (2).

By solving the normal equations derived from the least squares treatment, $K_1$ and $L$ can be evaluated.

**Moment Method** - The Moment Method is a graphical method and was developed by Moore, Thomas and Snow (12) in 1950. This method is based on the taking of moments of the determined values about the vertical coordinate axis of the best-fit curve of BOD against time.

The sum of a given series of observed BOD values, $Ey$, divided by the sum of the products of the observations and their times, $Ety$, is a numerical quantity that depends only on the $K_1$ values of the wastewater observed. Therefore, the value
of this ratio can be determined in advance for a range of $K_1$ values and plotted as a curve of $\Sigma y/\Sigma ty$ vs. $K_1$. Different curves apply to different time sequence of observations.

Marske and Polkowski (13) analyzed the accuracy of these methods. They concluded that the Reed-Teriault Method is the best method if a digital computer is available, while the Moment Method is the best if the digital computer is not available. They also found that the Thomas Slope Method consistently underestimated the $K_1$ value and overestimated the ultimate BOD and the Log-Difference Method gave the least accurate estimates of $K_1$. 
LITERATURE REVIEW

In 1930, Streeter (14) studied the difference in field and laboratory determined deoxygenation rates for the Illinois River. The value for the field determination was 0.51* and the laboratory value was 0.165. The possible reasons for the difference are: first, the existence of an immediate oxygen demand in the river; second, the combined sedimentation and adsorption of oxidizable material by attached microorganisms; and third, the different temperature between the natural stream and the laboratory.

In 1944, Phelps (15) pointed out in his book, Stream Sanitation, that in natural streams quiescent conditions are seldom attained. Therefore, the conventional BOD bottles don't approximate the real conditions in the stream.

In 1947, Kittrell and Kocztitzky (16) studied the natural purification characteristics of shallow, turbulent streams in Tennessee. They found the stream deoxygenation rates ranged from 0.039 to 5.243 and were, in general, many times greater than the laboratory rates which ranged from 0.176 to 0.789. In addition, the rate of reduction in BOD was much more rapid in the shallow, turbulent stream than in the usual deep, sluggish stream.

They also gave possible reasons for the wide variations of $k_1$ values in the stream when water progresses downstream. They are: (1) sedimentation of some of the oxidizable matter; (2)

*Note: All deoxygenation coefficients referred to herein are in units of day$^{-1}$ and to the base $e$. 
oxidation of dissolved and colloidal matter by slimes attached to the bed of the stream; (3) anaerobic digestion (oxidation) of organic matter within sludge beds; and (4) more rapid utilization of organic food by bacteria when concentration of food is high.

In 1948, Thomas (17) analyzed the pollution load capacity of streams. He pointed out that in natural streams the reaeration from the atmosphere is continuous and the BOD through a reach is generally reduced by biochemical oxidation and sedimentation and increased by channel scouring or anaerobic flotation of the bottom deposits.

As to the deoxygenation rate, Thomas further stated that "another factor that affects the magnitude of $K_1$ is the degree of longitudinal hydraulic mixing." The greater the mixing, the smaller will be the value of $K_1$ as calculated from BOD measurements made at two adjacent sampling points.

In 1963, Velz and Gannon (18) reported the results from their studies on the Jackson and James Rivers in Virginia. They concluded that the normal river BOD removal should include a biological extraction and accumulation factor. They said that the high BOD removal is not solely a high rate of satisfaction, $K_1$, but rather is ascribed to the phenomena of biological extraction and accumulation. In the Jackson River, the overall BOD removal rate is 0.835 while the normal rate of BOD satisfaction is 0.232.

In 1964, Lordi and Heukelkian (19) conducted a series of laboratory studies on the deoxygenation rate of wastewater
filtered through glass wool. They found that rates of deoxygenation obtained in the open cylinders at various rates of mixing are higher than those obtained in an unstirred closed jug system, and the higher the mixing rate, the greater the increase in the BOD rate constant, $K_1^c$. The results are shown in Table 1.

In 1966, Gannon (7) made a survey on the Clinton and Tittabawassee Rivers, and concluded that the higher river deoxygenation rate of 2.552/day (base e) as compared to the laboratory determined rate of 0.139/day, might be the result of a combination of biological extraction and accumulation, and certain other natural conditions such as turbulence.

Gannon also used the Clinton River water as the sample in conventional BOD tests under both quiescent and turbulent conditions. He confirmed mixing as a factor in increasing the deoxygenation rate.

In 1967, Zanoni (20), using the same wastewater sample, ran the BOD test at different temperatures. He found that the ($\theta$) value in deriving the deoxygenation rate can be separated into three types. They are as follows:

$$K_t/K_{20} = (0.796) (1.126)^{(t-15)} \quad \text{range 2 to 15°C}$$

$$K_t/K_{20} = (1.047)^{(t-20)} \quad \text{range 15 to 32°C}$$

$$K_t/K_{20} = (1.728) (0.985)^{(t-32)} \quad \text{range 32 to 40°C}$$

Figure 4 shows the summary of the averaged calculated first order reaction curve on different temperatures.

Figure 5 shows the relationship between first order reaction velocity constant and temperature.
Table 1 - Comparison of Deoxygenation in Open and Closed Systems With and Without Stirring (after Lordi and Heukelekian)

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<th>Run 3</th>
<th>Run 4</th>
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<tr>
<td></td>
<td>Quiescent</td>
<td>Open</td>
<td>Closed</td>
<td>0.46 cpm</td>
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<tr>
<td>7-day BOD mg/l</td>
<td>17.3</td>
<td>17.2</td>
<td>15.2</td>
<td>13.4</td>
</tr>
<tr>
<td>K (base e)</td>
<td>0.302</td>
<td>0.297</td>
<td>0.483</td>
<td>0.485</td>
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<tr>
<td>BOD₅ mg/l</td>
<td>19.1</td>
<td>19.4</td>
<td>15.5</td>
<td>13.6</td>
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</table>
Figure 4 - Summary of First Order Reaction Curves for Different Temperatures (After Zanoni)
Figure 5 - The Relationship Between the First Order Reaction Rate Constant and Temperature (After Zanoni)
In 1971, Martin and Bella (21) studied the effects of mixing on the oxygen uptake rate of estuarine bottom deposits. He found the oxygen uptake rate increased with mixing, although the experimental mixing was not related to the actual mixing in the river.

They further explained that the oxygen uptake rate in the experiment was a result primarily of the release of biodegradable substance from the bottom material into the overlying water.

In 1972, Ali and Bewtra (22) used raw, settled, and biologically treated wastewater to determine the influence of mixing on bio-oxidation rates. They found that there is an average increase of 17 percent in 5-day BOD values when test samples were stirred at different speeds. The optimum speed was 680 rpm rather than the higher speed, 1,180 rpm, or the lower speed of 120 rpm. They formulated the effects of mixing on the deoxygenation rates as follows:

\[ K_{\text{stirred}} = K_{\text{quiescent}} \times 0.000033 \times \text{speed} \]

where \( K \) is base 10 and speed in rpm.

In 1972, Stack (23) summarized the basic difference between lab and stream BOD studies. He said, "the BOD as measured by standard methods is a meaningful measurement within itself, but its usefulness as a parameter has been impaired by misinterpretation, misuse and misunderstanding." The misinterpretation and misunderstanding begins when the closed system in the BOD bottle is prepared. The assumption is made that the closed system is parametrically related to the system from which the sample was taken. Stack further said, "the basic difference
between the BOD bottle and a stream is that the BOD bottle is a static system which is controlled to provide aerobic conditions, while the stream is a dynamic system which may include anaerobic areas."
EXPERIMENTAL PROCEDURE

The laboratory BOD tests used in this study can be grouped into two different methods. In the beginning of the study, two conventional BOD bottles with magnetic stirrers were used to investigate the effects of turbidity on the five-day BOD. In these tests, silty-clay was used to make up the turbid dilution water. After several test runs of this method, the Hach Manometric BOD Analyzer was used in order to better simulate stream conditions.

In the Hach Manometric apparatus simulations, primary effluent from the Manhattan Wastewater Treatment Plant was used as the wastewater discharging into the stream. A mixture of wastewater and dilution water was made in order to get a five-day BOD in the range of 20 to 30 mg/l which, as shown in Figure 6, will create an oxygen sag in most streams.

Wastewater samples were collected at the Manhattan Municipal Wastewater Treatment Plant, Manhattan, Kansas. It is a primary treatment plant treating domestic wastewater.

Non-turbid dilution water was prepared by adding 2 ml of wastewater (optional) and 1 ml. each of Phosphate Buffer, Calcium Chloride, Magnesium Sulfate, and Ferric Chloride solution to 1 liter of distilled water.

Turbid dilution water was prepared by using an electric blender to mix the soil (silty-clay or bentonite) with the distilled water. After a sedimentation period, the supernatant was poured into a beaker and diluted to a desired turbidity. To each liter of turbid distilled water, 2 ml. of wastewater
Figure 6 - A Typical Relationship Between Stream BOD and Dissolved Oxygen
(optional) and 1 ml. of each, Phosphate Buffer, Calcium Chloride, Magnesium Sulfate, and Ferric Chloride solution was added to make up the turbid dilution water.

The turbidity of the sample and turbid dilution water was measured by using a Hach Turbidimeter--Model 1860. When the turbidity was over 100 JTU, a dilution technique was employed.

The dissolved oxygen content of the dilution water and wastewater after aeration and incubation were measured according to the Standard Methods (6). The Sodium Azide modification of the Winkler Method was used.

The BOD bottles and Hach Manometer after set up were incubated at 20 ± 1° C temperature in a jumbo incubator in the Sanitary Engineering Research Laboratory.

Oxygen uptakes were measured according to the process adopted. In the first several test runs, the conventional laboratory BOD bottles with magnetic stirrer were used. The rest of the test runs were done using Hach Manometric BOD Analyzer--Model 2173.

The Hach Manometric BOD Analyzer consisted of a manometer with a reading scale, a glass bottle connected by a vinyl tube to the manometer, a magnetic stirrer and a seal cup containing two drops of 45% KOH to absorb Carbon Dioxide. The BOD progression was read directly from manometric scale.

A more complete description of the Hach Manometric apparatus can be found in the Hach Chemical Company Laboratory Manual.
The following explanation of test procedure applies to each of the manometric tests conducted.

Collected wastewater was stored under 2 to 5° C temperature conditions until the test run was set up.

The first step was the preparation of the turbid and non-turbid dilution water. The turbidity of the turbid dilution water should be controlled by the weight of soil added. However, this was true only for bentonite because of its colloidal character. In general, 8.35 gm. of bentonite, when completely dissolved in 1,000 ml. distilled water, would produce turbidity of around 1,000 JTU.

After the dilution waters were prepared, they were aerated for 30 to 40 minutes with compressed air through porous air diffusers.

After the dilution water was aerated, wastewater and dilution water were poured into the bottle to the total amount of 428 ml. at the ratio so that the five-day BOD reading was in the range of 20 to 30 mg/l. The ratio used in these tests was 75 ml. sample and 353 ml. dilution water.

Two initial dissolved oxygens and blanks were run on each dilution water using the same technique as mentioned in the last section. This was done to determine if there was any significant BOD associated with the material (bentonite or silty-clay) used to create the turbidity.

While using the Hach Manometric BOD Apparatus, the author found a lot of trouble, such as the manometer scale staying at zero or staying at low reading after one or two days. These
problems often made the tests fail. It is the author's opinion that the main reason is the possible leakage from the seal cup and the bottle cap. The other possible reason is that the carbon dioxide produced was not adsorbed by the Potassium Hydroxide.
RESULTS AND DISCUSSION

Table 2 shows the effects of silty-clay turbidity on the five-day BOD of two samples. The five-day BOD of turbid samples was more than 11% higher than those of zero-turbid samples. These results appear to show that turbidity increases the rate of biochemical oxidation and thus led to further testing on the effects of turbidity on oxidation rates.

Table 3 shows the effects of silty-clay turbidity on the rate of exertion of BOD. Calculation of the ultimate Biochemical Oxygen Demand and deoxygenation rate, $K_1$, of each sample was done on the University's IBM 360/50 computer by the Reed-Theriault Method. The computer program used is listed in the Appendix.

The turbidities shown in Table 3 are for the wastewater sample (S) and the dilution water (D.W.). Later in the study turbidities were run on the wastewater and dilution water mixture. It can be seen that dilution water turbidities ranged from 110 to 1,000 JTU. From the Table, it appears that silty-clay turbidity in most cases depresses the biological oxidation of organic materials contained in the wastewater. Generally, the deoxygenation rates for turbid samples are somewhat lower than those with zero turbidity. The March 15 sample shows a large decrease in $K_1$ values for the turbid samples, while others exhibit a rather minor decrease, such as March 21. There is only one case with an increase in $K_1$ for turbid samples. This is on April 3. The average of all $K_1$'s of samples with zero turbidity is 0.613, while the turbid samples have an average $K_1$ of 0.546, a decrease of 10.9%. If the sample of March 15
### Table 2 - Effects of Silty-Clay Turbidity on 5-day BOD

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</thead>
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<td>Zero</td>
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Table 3 - Effects of Silty-Clay Turbidity on the Rate of Exertion of BOD

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<th>$BOD_L$</th>
<th>$K_1$</th>
<th>Average $K_1$</th>
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is excluded (its turbidity of 1,000 units is much higher than all the others), the average $K_1$ of the turbid samples is 0.590, which is about 3.75% less than that of non-turbid samples.

Theoretically, the five-day and ultimate BOD of each set of samples should be the same, but the BOD test is not a precise one. Wastewater is usually not a homogenous mixture. Even though equal volumes of wastewater sample are measured out for the test, one volume could very well contain slightly more or less organics than another. Since the BOD test is a bioassay procedure, identical samples can result in different BOD's because of the nature of microorganism growth and reproduction. Therefore, the accuracy of BOD test is usually thought to be about ±5%. That is, if the BOD is 30 mg/l, the range for the same samples may be from 28.5 to 31.5 mg/l. In general, most of the observed results in Tables 3 and 4 fall within this range.

Table 4 shows the effects of bentonite turbidity on the rate of exertion of BOD. It can be seen that turbidities of the wastewater-dilution water mixture range from 84 to 880 units. The bentonite turbidity has the same effect as silty-clay; that is, it depresses the $K_1$ value in most of the cases. An example from April 28 showed the sample with zero turbidity has higher $K_1$ over turbid sample. The example from April 15 showed a rather consistent $K_1$ value in both samples, while an example from April 21 and May 3 showed that turbid samples can sometimes have higher $K_1$ values than zero-turbid samples. The average of all $K_1$'s of zero-turbid samples is 0.656 while the turbid samples have a value 23% less, or 0.504.
<table>
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<th>Date</th>
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<th>BOD$_5$</th>
<th>BOD$_L$</th>
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It is apparent that bentonite has greater effect on $K_\perp$ than silty-clay. A possible explanation for the difference is that bentonite has finer particulate size of 1 to 100 μm and is colloidal in nature. The colloidal particulate may bind up with bacteria and inhibit the biochemical oxidation processes.

Table 5 shows the effects of a range of bentonite turbidities on the rate of exertion of BOD. The increase in turbidity didn't show a definite trend of an increase or decrease of $K_\perp$ values. In one case there appears to be an increase. In the others, some decrease.

The $K_\perp$ values derived through all of the study are higher than the commonly used $K_\perp$ value for domestic wastewater of 0.23. For example, the April 21 sample of zero turbidity has a $K_\perp$ value of 0.706 and the April 22 sample of 380 JTU has a $K_\perp$ value of 0.429. The reason for this increase might be due to the continuous mixing by a magnetic stirrer during the five-day incubation.

Figures 7 through 10 show a series of first-order BOD progression curves for selected samples, which is derived from the equation $Y = L_{ult} \left(1 - e^{-k_1t}\right)$, with the calculated ultimate BOD and $K_\perp$. The manometric scale readings are also plotted and these show a very good consistency with the first-order curves. This indicates that the assumption of first order kinetics for the Biochemical Oxygen Demand rate is correct and that there is no nitrogenous oxygen demand during the five days of incubation.
Table 5 - Effects of a Range of Bentonite Turbidities on the Rate of Exertion of BOD

<table>
<thead>
<tr>
<th>Date</th>
<th>Turbidity</th>
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<th>$\text{BOD}_L$</th>
<th>$K_1$</th>
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</tr>
<tr>
<td></td>
<td>200</td>
<td>28.5</td>
<td>30.5</td>
<td>0.490</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>23.8</td>
<td>23.9</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>22.9</td>
<td>23.2</td>
<td>0.573</td>
</tr>
</tbody>
</table>
Figure 7 - A Comparison of the Derived First Order Reaction Curve and the Manometric Scale Readings for the April 27 Sample

\[ y = L \left( 1 - e^{-0.547t} \right) \]
Figure 8 - A comparison of the derived first order reaction curve and the manometric scale readings for the April 21 sample.
Figure 9 - A Comparison of the Derived First Order Reaction Curve and the Manometric Scale Readings for the April 27 Sample

\[ Y = L(1 - e^{-0.769t}) \]
Figure 10 - A Comparison of the Derived First Order Reaction Curve and the Manometric Scale Readings for the April 21 Sample
Figures 11 and 12 show the difference in BOD progression between selected non-turbid and turbid samples.

The Moment Method was also used in deriving the ultimate BOD and $K_1$ values. Table 6 shows some of the results obtained from both the Moment Method and the Reed-Theriault Method. It is apparent that they are very close to each other.
Figure 12 - A Comparison of Turbid and Non-Turbid Samples for May 8

Y = L(1 - e^{-0.542t})

Y = L(1 - e^{-0.382t})
Table 6 - A Comparison of Results Obtained From the Moment and Reed-Theriault Methods

<table>
<thead>
<tr>
<th>Date</th>
<th>Moment Method</th>
<th>Reed-Theriault Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$</td>
<td>$BOD_L$</td>
</tr>
<tr>
<td>3/15/73</td>
<td>0.51</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>21.4</td>
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<tr>
<td></td>
<td>0.44</td>
<td>23.2</td>
</tr>
<tr>
<td>4/22/73</td>
<td>0.49</td>
<td>34.4</td>
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<tr>
<td></td>
<td>0.68</td>
<td>29.4</td>
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<tr>
<td></td>
<td>0.48</td>
<td>24.1</td>
</tr>
<tr>
<td>4/27/73</td>
<td>0.75</td>
<td>32.5</td>
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<tr>
<td></td>
<td>0.74</td>
<td>32.5</td>
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<td>30.8</td>
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<tr>
<td></td>
<td>0.56</td>
<td>31.6</td>
</tr>
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</table>
CONCLUSIONS

Turbidity due to inorganic suspended solids appears to interfere with the rate of biochemical oxidation. In the majority of the samples tested, the deoxygenation rates of the turbid samples were less than those for non-turbid samples.

The smaller the size of the inorganic suspended solids, the greater the decrease in deoxygenation rates. The decrease in deoxygenation rates from turbidity due to bentonite (which created a fairly stable colloidal suspension) was considerably greater than the decrease from turbidity due to silty-clay (which had little colloidal character).

All of the biochemical oxidation progressions in the study closely followed first order kinetics. Both the Reed-Theriault and Moment Method of determining deoxygenation rates are satisfactory. The Reed-Theriault Method is easily programmed on the computer and appears to be the best method to use if computer facilities are available.
ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Dr. Douglas A. Wallace, my major professor, for his advice and guidance during this study, and also for his friendly encouragement during my study at K-State. I am grateful to Dr. Lawrence A. Schmid for his help in the past two years. I am also grateful to Dr. Robert R. Snell, Head of the Civil Engineering Department, and to Dr. Harry Manges, Professor of Agricultural Engineering, for serving on the Review Committee. Thanks should also go to my family, for without their support and encouragement, my study abroad would not have been possible.
REFERENCES


APPENDIX
THE FOLLOWING PAGE IS CUT OFF

THIS IS AS RECEIVED FROM THE CUSTOMER
CALCULATION OF KC VALUE (THE DEOXYGENATION COEFFICIENT) AND THE
ULTIMATE FIRST STAGE DEMAND

Y = BOD SATISFIED AT TIME T IN MG PER LITER
T = TIME OF OBSERVATION IN DAYS
EK = ESTIMATED VALUE OF KC SUPPLIED BY THE USER

F3 = EXP(-KC*T)
DIMENSION Y(50), T(50)
NN = 1

12 READ (5,1) N, EK
1 FORMAT (I10, F10.4)
READ (5,2) (T(J), J = 1, N)
READ (5,2) (Y(J), J = 1, N)
2 FORMAT (8F10.3)
I = 1

SUMF1Y = SUM OF THE TERMS F1*Y
SUMF2Y = SUM OF THE TERMS F2*Y
SF1F1 = SUM OF THE TERMS F1+F1
SF1F2 = SUM OF THE TERMS F1+F2
SF2F2 = SUM OF THE TERMS F2+F2

SUMF1Y = 0.0
SF1F1 = 0.0
SF1F2 = 0.0
SF2F2 = 0.0

DO 3 J = 1, N
F3 = EXP(-EK*T(J))
F1 = 1.0 - F3
F2 = T(J)*F3
SUMF1Y = SUMF1Y + F1*Y(J)
SUMF2Y = SUMF2Y + F2*Y(J)
SF1F1 = SF1F1 + F1+F1
SF1F2 = SF1F2 + F1+F2
SF2F2 = SF2F2 + F2+F2

3 SF2F2 = SF2F2 + F2+F2
DENOM = SF1F1*SF2F2 - SF1F2*SF1F2
AL = (SF2F2*SUMF1Y - SF1F2*SUMF2Y)/DENOM
B = (SF1F1*SUMF2Y - SF1F2*SUMF1Y)/DENOM
F = B/AL

IF (ABS(F) - 0.005) LTE 4, 5, 5
5 IF (I-10) LTE 6, 4, 4
6 EK = EK + F
I = I + 1
GO TO 7
4 WRITE (6, 8)
8 FORMAT (1HG, 15X, 13H TIME IN DAYS, 6X, 14H BOD SATISFIED)
DO 9 J = 1, N
9 WRITE (6, 10) T(J), Y(J)
10 FORMAT (15X, F10.3, 10X, F10.3)
WRITE (6, 11) EK, AL, F, I
11 FORMAT (5H K1 =, F6.3, 3X, 15H ULTIMATE BOD =, E15.5, 3X, 4H F =, F7.3, 3X, I20H NC. OF ITERATIONS =, I2)

IF (NN - 5) LTE 80, 77, 80
80 NN = NN + 1
GO TO 12
77 STOP
END
THE EFFECTS OF TURBIDITY ON THE
RATE OF BIOCHEMICAL OXIDATION

by

JIAAN-HWA CHUEH
B.E., Feng-Chia College of Engineering & Business, 1970

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Civil Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973
ABSTRACT

The purpose of the study was to determine the effects of turbidity due to inorganic suspended solids on the rate of biochemical oxidation. Settled wastewater from the Manhattan Wastewater Treatment Plant was mixed with turbid and non-turbid dilution water to obtain a specific BOD. The BOD progression was measured with a Hach Manometric BOD Analyzer and deoxygenation rates and ultimate BOD's were determined by the Reed-Theriault Method using the computer.

It was concluded that turbidity appears to suppress the rate of biochemical oxidation. In addition, it appeared that the smaller the inorganic suspended solids, the greater the decrease in deoxygenation rates.