A STUDY ON REAERATION AND THE KINETICS OF DEOXYGENATION IN OPEN AND CLOSED SYSTEMS

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CHAPTER I

INTRODUCTION

A. Nature and Importance of the Problem

Today, public opinion and with it public demand for pollution abatement has evolved to the point that the gross misuse of our water resources can no longer be tolerated. The magnitude of the concern is manifested in the number of state and federal laws which have been enacted in recent years to control water pollution. While there have been a number of regulations enacted at the various levels of government, the most important piece of legislation is the Water Quality Act of 1965 (P. L. 234, 89th Congress). The stated objective of this act is "to enhance the quality and value of water resources and to establish a national policy for the prevention, control, and abatement of water pollution." This act represents a major change in the scope of water pollution abatement from that of protecting the public health to that of maintaining our water resources suitable for many other beneficial uses, such as protection of aquatic life and recreation.

Some segments of our society are dissatisfied with the progress which has been made in pollution abatement, and advocate the establishment of standards providing for the return of our streams to their natural purity. While it is not possible or even desirable to require that the streams be returned to the pristine purity existing when the

Indians roamed the land, the failure of the bioenvironmental engineer to develop and put into use sound scientific practices for the control of pollution will, in the opinion of the writer, lead to the enactment of excessive pollution abatement legislation.

Fortunately, streams have the facility to dilute and assimilate limited quantities of organic material. Thus, with the use of sound methods of analysis, a balance can be achieved, permitting a maximum utilization of a stream without creating any deleterious effects. In fact the addition of organic material to a stream can enhance the stream productivity and contribute to its overall utility.

Generally the biological, chemical, and physical manifestations associated with pollution are the result of exceeding the oxygen assets of the stream. Thus the undesirable features which are associated with a polluted stream, such as the disappearance of the clean water flora and fauna, discolorations, floating solids, gas bubbles, etc., are brought about by failure to maintain a satisfactory level of dissolved oxygen in the water. Hence the oxygen balance is usually the critical or limiting stream characteristic with regard to the degree of degradation, and when the oxygen liabilities exceed the assets, the stream is said to be polluted.

The classical approach to the analysis of the oxygen balance in a stream is that reported by Streeter and Phelps in 1925 (1). This work is predicated on the occurrence of two natural phenomena, deaeration and reaeration. The rate of oxygen utilization (deaeration) results from the addition of organic matter to a body of water. Based on studies of Ohio River water and sewage, it was found that the rate of oxygen uptake very closely followed, and could be defined by the monomolecular law,

which is given by

$$-\frac{dL}{dt} = K_1 L \qquad (1)$$

where L is the amount (in mg/l) of organic material remaining, t is time, and K_1 is the deoxygenation rate constant. The integration of this equation gives

$$\ln\left(\frac{L_t}{L}\right) = -K_1 t \qquad \text{(base e)} \quad (2)$$

or $$\log (L_t/L) = -0.4343K_1 t = -k_1 t \qquad \text{(base 10)} \quad (3)$$

where k_1 is the rate constant for use with logarithms to the base 10.

The rate of replenishment of the oxygen supply (reaeration) was found to be defined by Henry's Law, which in effect states that the rate is proportional to the driving force. For reaeration, the driving force is the oxygen deficit (O_2 solubility - O_2 content). Thus the rate of reaeration is given by

$$-\frac{dD}{dt} = K_2 D \qquad (4)$$

where D is the oxygen deficit, t is time, and K_2 is the reaeration rate constant. Upon integration, the following equation is obtained:

$$\ln\left(\frac{D_t}{D}\right) = -K_2 t \qquad (5)$$

or $$\log (D_t/D) = -04343K_2 t = -k_2 t \qquad (6)$$

Upon the addition of organic matter to a stream the two reactions, deoxygenation and reaeration, tend to counterbalance each other, and the rate of change in the oxygen balance is determined by the sum of the two reactions.

$$\frac{dD}{dt} = K_1 L - K_2 D \qquad (7)$$

The integration of Equation 7 was shown by Streeter and Phelps (1) to give

$$D = \frac{K_1 L_a}{K_2 - K_1}\left(e^{-K_1 t} - e^{-K_2 t}\right) + D_a e^{-K_2 t} \qquad (8)$$

which is the well-known oxygen sag equation, where

D = oxygen deficit in mg/l at time t

K_1 = deoxygenation rate constant, time^{-1} (base e)

K_2 = reaeration rate constant, time^{-1} (base e)

t = time

L_a = initial carbonaceous oxygen demand of the water, mg/l

D_a = initial oxygen deficit of the water, mg/l.

While it is recognized that the sag equation does not include several factors which may influence the oxygen balance, such as sedimentation, scour, runoff, benthal demand, absorption by attached growths and photosynthesis, it seems reasonable to assume that the principal forces are deoxygenation by the organotrophic organisms and reaeration due to physical transfer of oxygen from the atmosphere. Furthermore, if one accepts the concept that the monomolecular equation defines deoxygenation, then the oxygen sag equation would seem to be a rational approach toward defining the oxygen balance. However, it is emphasized that the biological degradation of organic wastes is a complex phenomenon; the oxygen utilized is affected by many environmental factors and may or may not be defined by a kinetic formulation. Also, it should be emphasized that in order to apply the sag equation, five parameters must be defined. Two of these, the initial deficit and time, may be ascertained directly. The other three are K_1, K_2, and L_a. Since it is impossible to separate the effects of reaeration and deoxygenation in

natural streams it is not possible to measure the latter three directly.

The deoxygenation rate constant, K_1, and the carbonaceous oxygen demand, L_a, are commonly determined in the laboratory by the bottle technique, which is described in the Materials and Methods section of this thesis. Using the K_1 and L_a values found in the laboratory, the reaeration rate is usually found by trial and error. While analog and digital computers can be used to facilitate the estimation of K_2, the estimate is still based on the laboratory data for K_1 and L_a.

This procedure casts a doubt on the validity of all three parameters, i.e., k_1, K_2, and L_a, because the method is based on the assumption that biological degradation occurs at the same rate and to the same degree in the closed bottle as it does in the flowing stream.

While the oxygen sag equation has commonly been used to predict stream assimilating capacity, engineers have, in general, found the equation unreliable and inadequate.

The development of a unique stream simulating apparatus by Isaacs and Gaudy (2) at the Oklahoma State University bioenvironmental engineering laboratories made it possible to study reaeration across the surface of a flowing body of water, and to determine K_2 in the absence of any biological activity. After accurate determination of K_2 (at a particular velocity and depth of flow) in the simulated channel, biological degradation could be assessed from the observed oxygen sag produced by a known volume of waste water. Thus, it has now become possible to determine if the course of degradation in a flowing stream is the same as that observed in the BOD bottle.

B. Objectives of This Investigation

The prime object of this investigation was to determine if there

was a difference in the mode of biological degradation of a waste in a flowing stream and in the BOD bottle, and if differences existed, to determine the reason for these differences. The following four systems were selected for study in each experiment: (1) a simulated channel, (2) a stirred tank, (3) standard 300 milliliter BOD bottle, and (4) both mixed and quiescent 2.4 liter bottles. This arrangement permitted the measurement of the effects of both dilution and mixing in each experiment.

In order to accomplish the prime objective, it was necessary to determine the reaeration rate for both the stirred tank and the channel simulator. An important phase of this part of the investigation was determining the solubility of oxygen in tap and distilled water. Determination of K_2 values permitted the calculation of the oxygen uptake rates in the open systems. The experimental design provided a means of comparing biological degradation of the waste in bottle systems and in open mixed systems. Experiments were conducted using three different substrates with sewage, and sewage acclimated to the substrate being used as seed.

CHAPTER II

LITERATURE REVIEW

A. Oxygen Solubility

As noted in the introduction, this research included, of necessity, a study of the total oxygen balance of each biological system employed in the investigation. In open systems the oxygen assets are related to the oxygen solubility in the water; Isaacs and Gaudy (2) have shown that the use of incorrect oxygen solubility data leads to significant errors in the reaeration rate constant, K_2. Their study also indicated that natural water may not have the same oxygen solubility as distilled water, therefore it was necessary that the solubility of oxygen be determined for the water used in this investigation.

Data from early experiments indicated that the solubility of oxygen in cold tap water being used in this laboratory was not in agreement with published solubility data. Also, there are significant differences in published values for the solubility of oxygen in distilled water (3)(4)(5). Therefore, this investigation was extended to include oxygen solubility experiments, using both distilled water and tap water.

There have been many studies reported in the literature on reaeration where the rate of oxygen transfer was related directly to the oxygen deficit. However, the bioenvironmental engineer has neglected

the establishment of reliable oxygen solubility data. This deficiency is evidenced by the fact that the twelfth edition of Standard Methods (3) contains solubility data which are very obviously incorrect, as shown by the results reported from recent studies (4)(5).

In 1909, Fox (6) published data on the solubility of oxygen in pure water. These data were obtained by measuring the reduction in volume of pure oxygen when it was exposed to the surface of pure water which had recently been deaerated, until equilibrium was obtained. The solubility of atmospheric oxygen was then calculated by assuming that air contains 20.90 per cent oxygen.

In 1911, Whipple and Whipple (7) applied corrections to the data reported by Fox for a saturated atmosphere, and converted the data from cubic centimeters of oxygen per liter of water to milligrams per liter. These data are reported in the twelfth edition of Standard Methods as being the solubility of atmospheric oxygen in pure water at 760 mm pressure.

In 1955, Truesdale, et al (4) reported the results of an extensive laboratory study on the solubility of oxygen in water. In this study samples of water were deaerated using nitrogen gas and then allowed to come to saturation by passing CO_2 free air across the surface. The oxygen content of the water was determined by the Winkler Method. Twenty milliliter aliquots were analyzed, with the endpoint being determined amperometrically by back titration, using bin-iodate. The following equation was reported for the solubility of oxygen in distilled water when the water surface was exposed to air at a pressure of 760 mm of mercury:

$$C_s = 14.161 - 0.03943T + 0.007714T^2 - 0.0000646T^3 \qquad (9)$$

where C_s is the saturation concentration in milligrams per liter at a pressure of one atmosphere for the respective temperature T in degrees centigrade.

Equation 9 is the same type as first proposed by Fox and later adopted by Whipple and Whipple. Gameson and Robertson (8) have shown that the following simpler mathematical formulation can be used to define the relationship of oxygen solubility and temperature as reported by Truesdale, without any sacrifice of accuracy.

$$C_s = \frac{475}{33.5 + T} \tag{10}$$

The solubility data reported by Truesdale and his associates differ significantly from the values reported in Standard Methods. The data reported by the former are lower, varying from about 2.83 per cent lower at 0^oC to 1.33 per cent lower at 30^oC.

A committee of the Sanitary Engineering Division of ASCE has accepted the data from the Tennessee Valley Authority as being the most representative of the correct solubility of oxygen in distilled water. These data were published in 1960 as the Twenty-ninth Progress Report of the Committee on Sanitary Engineering Research (5). Laboratory procedures adopted for this study are essentially the same as those developed by Truesdale and his associates. The oxygen concentration was determined by the Winkler method by back titration using an amperometric endpoint. The water was deaerated with nitrogen gas and allowed to come to equilibrium. The water was stirred gently and 250 cc air/min was withdrawn from near the water surface during the aeration period to assure a constant oxygen pressure at the water surface. Also, at each temperature, a second experiment was conducted by supersaturating the water with oxygen and allowing the water to come to equilibrium with the

atmosphere under the same conditions as were maintained for the deaerated water. It was concluded that carbon dioxide in the air had no measureable effect on oxygen solubility, so the CO_2 was not removed.

The following equation was proposed for the solubility of oxygen in water exposed to the atmosphere at a pressure of 760 mm:

$$DO = 14.652 - 0.41022T + 0.00799107T^2 - 0.000077774T^3 \qquad (11)$$

where DO is the dissolved oxygen concentration in mg/l, and T is the temperature in ^oC.

While essentially the same procedure was employed by Truesdale and his associates as was employed by the TVA group, the results differ significantly, particularly at low temperatures. The oxygen solubility as given in the ASCE Progress Report is higher at low temperatures than that proposed by Truesdale, et al. The Progress Report data are essentially in agreement with the solubilities reported in Standard Methods at low temperatures, and lower than the data of Truesdale, et al. at 30^oC.

B. Reaeration

The basic concern of the present research involves the kinetics and mechanisms of the two principal forces determining the dissolved oxygen level in a receiving stream. These are reaeration and exertion of the biochemical oxygen demand.

Any treatise relating to the oxygen balance of streams must refer to the extraordinary contributions of Streeter and Phelps (1) to this subject. As noted previously, it was they who first applied the basic relationship for gas absorption as proposed by Adeney and Becker (9) to stream reaeration (Equation 1), and formulated the "sag equation" (Equation 8) for the oxygen balance in streams.

A serious deficiency in the application of the sag equation has been the lack of suitable means of evaluating the reaeration coefficient. Phelps (10) suggested the construction of several sag curves using selected values of k_2 to aid in the interpretation of the constant corresponding to the deficit existing in a stream. However, this procedure requires the acceptance of bottle data for calculating the deoxygenation constant, K_1, and the carbonaceous or "first stage" demand, L_a.

Recognizing the need for a mathematical expression for K_2, Streeter and Phelps (1) proposed the following equation:

$$k_2 = \frac{CV^n}{H^2} \tag{12}$$

where C is a constant for a specific river stretch, and is influenced by the physical conditions which affect turbulence for a given flow. The constant n is related to the river stage, V is the velocity in ft/sec, and H is the mean depth in feet for the stretch of river in question. This prediction equation was developed from a survey of the Ohio River, and the constants were found to vary over a wide range. For the Ohio River between Pittsburgh, Pennsylvania, and Louisville, Kentucky, C varied between 0.23 and 131, and n ranged from 0.57 to 5.40 for selected reaches.

Following the publication of Public Health Bulletin #146 (1), many equations have been proposed for calculating K_2. Some of these equations are prediction equations where K_2 was correlated to certain hydraulic parameters, giving the same form as Equation 12. Many of the equations which have been proposed are based partly on theory and partly on assumptions, to give the desired relationship. However, all of the proposed equations relate reaeration to the degree of agitation or

turbulence. Phelps (10) proposed that agitation or turbulence not only increases the extent of mixing, but that it also increases the actual exposed surface.

Osborne Reynolds demonstrated in 1883 that there are two distinctly different types of fluid flow (11). The first type is known as laminar, streamline, or viscous flow. These are descriptive terms for the flow, since the fluid appears to move by the sliding of laminations of infinitesimal thickness relative to adjacent layers. A dye injected into a viscous flow will appear to move in definite paths or streamlines. Viscous flow is not found in water systems except in the infinitesimally thin layer of water adjacent to the channel boundary.

The second type is known as turbulent flow, which is characterized by fluctuating pressures and particle velocities. There is a random formation and decay of many small eddies throughout the flow stream, and the resulting intermixing causes additional shear stresses. This viscous interaction is of a much larger scale than the molecular interaction associated with laminar flow, giving rise to much larger energy losses.

Large eddies and swirls and irregular movements of large bodies of water as observed in flowing streams do not constitute turbulence per se. This large scale mixing or agitation is caused by boundary conditions (channel irregularities) and represents additional energy losses through shear stresses. Thus, in stream flow, the channel boundaries generate the large eddies and transfer energy to or from them which, in turn, transfer their energy to smaller and smaller eddies.

There are presently two distinct approaches for defining turbulence. First, the older approach is the Prandtl mixing-length theory (12). The

mixing-length in a liquid is analogous to the mean-free path theory in gases. The mixing length represents the average distance travelled by particles of fluid before their excess momentum is absorbed by their new environment. If a particle moves from a position of greater momentum to a position of lower momentum, the excess momentum will be absorbed by the fluid in the new region, and when the particle moves to a position of higher momentum, the reverse is true. The greater the mixing length, the higher the degree of turbulence and the more uniform the velocity distribution. A conceptual defect in this theory is that the momentum of a fluid particle is gradually changed throughout its path, and not changed abruptly, as assumed.

The second and more rigorous treatment of turbulent flow is a statistical approach. This approach is based on a concept of a primary steady velocity on which is superimposed a secondary velocity fluctuation. While this approach has attracted the interest of many capable theorists, workable relationships for use in engineering applications have not been developed (12). For the bioenvironmental engineer, the greatest need is for a workable model for defining turbulence or agitation and for defining the rate of surface renewal.

O'Connor and Dobbins (13) have proposed the following equations, which are developed partly from turbulent theory for reaeration:

$$k_2 = \frac{480\, D_M^{\frac{1}{2}}\, S^{\frac{1}{4}}}{H^{\frac{3}{4}}} \qquad \text{(nonisotropic flow)(13)}$$

and

$$k_2 = \frac{127\, D_M U^{\frac{1}{2}}}{H^{\frac{3}{2}}} \qquad \text{(isotropic flow)(14)}$$

where D_M is the coefficient of molecular diffusion for the assumed liquid film in ft^2/hr, S is the channel slope, and H is the mean depth

of flow in feet. An isotropic flow is one where the velocity fluctuations are independent of the axis of reference and the position in the fluid. The authors have assumed that nonisotropic flow occurs at Chezy coefficients less than about 17, and that isotropic flows occur at greater values of the Chezy coefficient. The equations are related to the concepts of mass transfer as proposed by Higbie (14), and Danckwerts (15). These concepts are discussed in Chapter III of this thesis. Several authors have pointed out the questionable assumptions made in the development of these equations (16)(17).

Dobbins (18) has proposed the following expression for the reaeration rate constant:

$$K_2 = \frac{C_A}{H}\sqrt{D_m}\quad \operatorname{Coth}\sqrt{\frac{rx^2}{D_m}} \tag{15}$$

where r is the rate of liquid surface renewal, x is the film thickness, D_m is the diffusivity, C_A is the ratio of the true surface area to the horizontal projected area, and H is the depth in feet. The questionable assumptions made by the author are thoroughly discussed in the literature (19)(20).

The most extensive study on reaeration of natural streams is that reported by Churchill, et al. (16). Data were obtained from reaches of streams below large impoundments. Thus, nearly ideal conditions existed for observing reaeration since the water released from the lower depths of the impoundments was low in dissolved oxygen, relatively free of any oxygen demand, and the stream beds were clean and exhibited practically no benthal demand. Furthermore, the flow could be accurately regulated during the study periods.

Using multiple regression techniques, the authors concluded that it

is possible to define the reaeration rate in terms of velocity, U, and the depth, H, by the following equation:

$$k_2 = \frac{5U}{H^{5/3}} \tag{16}$$

Their study indicated that inclusion of other hydraulic variables in a prediction equation did not offer a significant increase in the accuracy of the predicted reaeration rate.

Krenkel and Orlob (21) proposed a model for the reaeration rate based upon a concept of diffusion as measured by the spread of a tracer in a turbulent field. The overall mixing characteristics are reflected in a "longitudinal mixing coefficient," D_L. At constant temperature and pressure, the following equation was proposed:

$$k_2 = C\, D_L\, H^{-2} \tag{17}$$

where H is the depth, and C is a constant.

Thackston and Krenkel (22), using a recirculating flume similar to that utilized by Krenkel and Orlob (21), defined reaeration in terms of measurable physical parameters. Their study was also based on measurements of longitudinal mixing, but the parameters were related to flow and channel characteristics, giving the following equation:

$$k_2 = 0.000125 \left[1 + \frac{U^2}{gH}\right]\left[\frac{Sg}{H}\right]^{1/2} \tag{18}$$

where U is the stream velocity, H is the mean depth, S is the channel slope, and g is the gravitational constant. The group $\left[1 + U^2/gH\right]$ represents the changes in surface area with flow conditions.

Owens, Edwards, and Gibbs (23) have proposed an empirical equation for reaeration which has the same form as that proposed by Streeter and Phelps (1). Using their own data, those of Gameson, et al. (24), and

those of Churchill, et al. (16), the authors showed a high correlation with the following equation:

$$k_{2\text{-}20^o} = \frac{9.4\ U^{0.67}}{H^{1.85}} \tag{19}$$

However, as shown by Isaacs (25), the groups of data do not belong to the same statistical population, and the regression coefficient of 9.4 is biased by the larger group of observations. The authors report the best regression equation for their data to be:

$$k_{2\text{-}20^o} = 10.09\ \frac{U^{0.75}}{H^{1.75}} \tag{20}$$

whereas Isaacs (25) reported the regression equation for the Churchill data as being

$$k_{2\text{-}20^o} = 6.070\ \frac{U^{0.9075}}{H^{1.761}} \tag{21}$$

Equations 19, 20, and 21 are examples of the variations in the regression coefficient and the exponent on the velocity as observed by Streeter and Phelps (1) for the Ohio River data, where it was found that wide variations existed in these terms for various reaches and stages of a stream.

Isaacs and Gaudy (2), from dimensional analyses of data obtained on a unique simulated channel, proposed the following equation for reaeration in streams:

$$k_{2\text{-}20^o} = \frac{CU}{H^{\frac{3}{2}}} \tag{22}$$

where U is the velocity, H is the liquid depth, and C is a constant and was found to be 3.053 for the authors' laboratory data. However, the constant C was found to vary slightly when fitted to stream data, and

they suggested that the difference was due to channel geometry. Isaacs and Maag (26) have proposed that the variation in the constant was indeed caused by the channel geometry and surface velocity, and have shown that nondimensional functions can be used to improve the correlation. Thus, the following equation has been proposed:

$$k_{2\text{-}20^{\circ}} = C\, \phi_S\, \phi_V\, \frac{U}{H^{3/2}} \tag{23}$$

where C is a proportionality constant, ϕ_S is the nondimensional variable for the effect of channel geometry, ϕ_V is the nondimensional variable for the effect of surface velocity, U is the velocity, and H is the depth of flow.

The prediction equation proposed by Isaacs and Gaudy (2) gave excellent correlation coefficients for their data, also for the data of Krenkel and Orlob (21), and that of Churchill, et al. (16).

Tsivoglou, et al., noting the shortcomings of direct measurement of the oxygen resources of a stream, have proposed a method of measuring the reaeration rate that is independent of the effects of all other oxygen resources and demands. In part one (27) of the report, a relationship between the transfer capability of specific inert gases and oxygen was established. It was found that the ratio of krypton-85 transfer from and oxygen transfer into water was 0.83, and it was suggested that the ratio of the exchange coefficient for any two gases is equal to the inverse ratio of the molecular diameter of the gases. The exchange ratios were not affected significantly by temperature (within the range investigated), by the degree of turbulence, or by the presence or absence of broken water surface. The temperature coefficient, θ, of 1.0241 as reported by the Committee on Sanitary Engineering Research of

ASCE (28) was in good agreement with the results obtained in the study.

In part II (29) of the study, results using the gas tracer technique on a natural stream were reported. The reaeration coefficients observed in the study varied from 0.96 to 4.70 times the values predicted by the Churchill model, and from 0.57 to 2.95 times the values predicted by the O'Connor-Dobbins model.

It seems evident from the extensive studies reported in the last decade on reaeration of natural streams, that all of the proposed models for reaeration are limited in their application. That is, they are limited in that the engineer has no rational approach to evaluating the constants. As noted by Isaacs and Gaudy (2), the equation for the reaeration coefficient proposed by Streeter and Phelps (1) in 1925 has not been widely adopted because of the lack of means for determining these constants. However, the model proposed by Isaacs and Gaudy (2) has been shown to give good correlation with data from various sources. The refinements to the equation as proposed by Isaacs and Maag (26) would appear to give the equation even greater applicability.

C. Deoxygenation Studies

The BOD test has been the subject of a tremendous quantity of research. O'Brien and Clark (30) have published an extensive literature review on the BOD test, and the interested reader is also referred to the reports by Streeter and Phelps (1), and Theriault (31) as sources of interesting and pertinent reports on the early development of the test.

Three principal and perplexing facets of the standard BOD test are: (1) that the oxygen uptake is approximately defined by decreasing rate monomolecular kinetics, (2) the 5-day oxygen uptake is a meaningful measure of the oxygen demand of a waste, and (3) the oxygen uptake as

measured in a dilute bottle system expresses the kinetics of deoxygenation in a more concentrated turbulent stream.

A mathematical model describing the deoxygenation curve as proceeding according to the well-known monomolecular reaction kinetics was first proposed by Phelps in 1909 (32). Theriault later reported data that indicated good agreement with the monomolecular formulation (31). Theriault also developed the first-order concept into the mathematical form in use today, and proposed the rate constant of 0.1 (k_1 = 0.1 day^{-1}) from statistical analyses of BOD data on Ohio River water. This rate constant was later widely accepted as being applicable to all wastes. It is emphasized that the research results reported by Adeney, Streeter and Phelps, and Theriault were based on studies of polluted river water, and the authors never suggested that the findings were applicable to all types of pollution. In fact, Phelps has noted that there is no logical reason for the BOD reaction to have a decreasing monomolecular rate (10).

The origin of the 5-day BOD standard is found in excerpts from Adeney's reports to the London Royal Commission on Sewage Disposal during the last decade of the nineteenth century as given by Theriault (31). In the Eighth Report, Adeney noted that a 5-day period of incubation was selected as the error of experiment is minimized by giving sufficient time for the oxidation of a reasonable portion of the matter present. It was recognized by Adeney and others that long-term experiments were not practical, and that the results of short-term experiments were too erratic to be significant, and the author was of the opinion that by the end of five days' incubation the variability inherent in the first few days of incubation had, to a large extent, been equalized.

The literature on BOD research indicates that the results of many

of the early studies clearly indicated that the BOD reaction was not a decreasing function, but a diphasic one related to biological growth. In 1911, Muller (31) reported a correlation between bacterial growth and oxygen uptake. It was also observed that the point of maximum oxygen depletion coincided with the time of maximum bacterial count. Theriault noted from the findings of Muller that when the bacteria were in a state of multiplication, the rate of oxygen uptake was much greater than when the bacterial count remained fairly stationary (31).

Purdy and Butterfield (33) in 1918 concluded from BOD bottle studies employing a synthetic waste inoculated with pure cultures isolated from sewage that oxygen uptake occurred only during the period when the bacteria were multiplying, and that oxygen uptake was very low after bacterial multiplication ceased.

Butterfield (34), using a dextrose and peptone substrate with a pure culture inoculum, reported a rapid oxygen uptake during the period of bacterial cell multiplication. The oxygen consumption showed no significant increase once a steady bacterial population was attained.

Hoover, Jasewicz, and Porges, working with milk wastes inoculated with an acclimated pure culture, proposed that the BOD test consists of two biochemical reactions (35). First there was a rapid growth of cells with assimilation of available nutrients into the cells, followed by the subsequent slow endogenous respiration of these cells. The rapid growth phase was complete in a maximum of twenty-four hours, and it was reported that it was often completed before the sample was introduced into the BOD bottle. Bacterial counts reached about 5×10^6 during the first day, and slowly decreased to approximately 200,000 in twenty days. The authors noted that the commonly-employed velocity constant of 0.1 could

be associated only with the endogenous phase of the oxygen uptake. They also suggested that to imply that the rate of oxidation in the BOD test is related to monomolecular kinetics is at variance with all existing knowledge of the bacterial growth process. It should be noted that the conditions employed in the research were not the same as normally found in natural streams and the BOD bottle. In order to achieve the rapid uptake of substrate as reported, an actively-growing inoculum with a high ratio of biological solids to substrate was required. In the normal BOD test and in the receiving stream the bacterial population is low, and the substrate is removed during the growth phase.

Orford and Ingram (36) reported that the constants k and L in the BOD forumulation do not remain constant over the entire BOD curve. It was found that as the observation period increases, k values decrease and L values increase. They concluded that there was no fundamental reason why oxidation should take place according to decreasing monomolecular kinetics, and that the parameters k and L have very little physical or biological significance.

In 1952, Garrett and Sawyer reported on the kinetics of substrate removal in continuous flow studies (37). They proposed that the rate of growth was directly proportional to the BOD concentration. They also reported a growth rate constant of 0.21, giving a bacterial generation time of 3½ hours. The proposed linear relationship between growth and substrate concentration imposes no limits on the growth rate.

In 1958, Busch reported on the BOD progression in soluble substrates where the carbonaceous BOD curve was found to consist of a two-phase oxygen uptake with the phases separated by a plateau (38). The first phase of oxygen uptake was attributed to the conversion of

substrate into cell material which included new cell synthesis and storage products. The second phase was attributed to endogenous respiration of the bacteria and protozoa activity. The plateau in the oxygen uptake curve was found to occur in from twelve to forty-eight hours, depending on the lag, and was reported to have a characteristic value for a given substrate. He proposed that as the ratio of predators to substrate-consuming population increases, the separation of the two phases begins to blur. A single strain of organisms or a predominance of substrate-consuming organisms gave the most distinct plateau. Busch, et al. have reported that the plateau affords a much more valid point for determining the ultimate oxygen demand than the conventional 5-day BOD (39). It was proposed that the 24-hour oxygen uptake for a glucose-glutamic acid mixture represented 39 per cent of the theoretical demand. However, other reports have shown lag periods much greater than twenty-four hours (40), and it is shown by Busch (38) that the plateau occurs between twelve and forty-eight hours. Hoover also reports that the rate of oxidation for the first one or two days is difficult to interpret because of lag in growth of organisms (35).

Pipes, et al. reported on experiments employing various substrates and settled sewage as seed (41). It was reported that growth commenced with some substrates within a few hours, and the maximum bacterial population was attained in one or two days. On other substrates an extended lag period occurred, or growth proceeded slowly, and the maximum bacterial cell count was not attained for several days. A 35^{o}C incubation temperature was used, which may have inhibited some sewage organisms and the protozoa.

Wilson and Harrison, using a pure bacterial culture and phthalic

acid substrate, reported a 2-phase oxygen uptake with the exogenous and endogenous phases separated by a plateau (42). Initial cell concentration had no effect on the oxygen demand for the exogenous phase, but the oxygen uptake during the endogenous phase was related to the number of cells present.

McWhorter and Heukelekian (40) reported that substrate removal was complete at 30 per cent of the theoretical uptake when using sewage seed and glucose substrate. A residual COD amounting to 5 to 15 per cent of the original COD was found to remain in the supernatant. Seed concentration produced no significant variation in the cell yield. The oxygen uptake rate was reported to be near maximum at the point of substrate depletion, and the cell mass also reached a maximum at this time. The plateau duration was reported to decrease with an increase in substrate concentration, and the plateau did not exist at 1000 mg/l of glucose substrate. The average lag period when using a one per cent seed was 44 ± 10 hours.

Butterfield, et al. had reported in 1931 that the addition of the protozoan Colipidium to a pure culture of Bacterium aerogenes resulted in an oxygen uptake beyond the peak observed in the control containing only bacteria (43). Also, there was a rapid decline in the bacterial count after one day in the system containing the protozoa followed by an increase in protozoa count which reached a peak after four days. There was no corresponding decrease in bacterial count in the control containing no protozoa. They proposed that the role of protozoa was to reduce the bacterial population, thus providing suitable conditions for continuous bacterial growth.

Extensive studies were conducted at the bioenvironmental engineering

laboratories at Oklahoma State University to elucidate the nature and cause or causes of the plateau in the oxygen uptake curve. Gaudy, Bhatla, Follett, and Abu-Niaaj (44) observed the occurrence of a plateau in forty-three out of fifty-one experiments. The plateau was found to occur for a fairly wide range of simple and complex substrates with various types and concentrations of seeding materials. The seed included both heterogeneous populations and pure cultures of Escherichia coli. The plateau occurred within the first two days of incubation, and usually 30 to 40 per cent of the theoretical oxygen demand of the substrate had been exerted at the plateau. They reported that while the plateau was found to occur in most of the experiments, the geometry of the BOD curves which exhibit a plateau cannot be defined with sufficient precision to warrant the use of the plateau for predicting the course of BOD removal.

Bhatla and Gaudy (45) reported on their tests of the applicability of four theories for the instituting of the plateau. Briefly, the four theories were: (1) changes in predominance of species in a heterogeneous population where the secondary predominating cells may be either bacteria or predators such as protozoa, (2) part of the cells which have grown up during the first phase of the oxygen uptake may lyse and release products which produce a secondary growth, (3) an acclimation period may be needed for synthesizing new enzyme systems required for endogenous metabolism of various cell materials after removal of the exogenous substrate, and (4) cellular intermediates or metabolic byproducts may be released to the medium during the period of substrate utilization, and an acclimation period may be required before these compounds can be metabolized.

In addition to the preceding four theories, Gaudy, Komolrit, and Bhatla (46) have shown that a diphasic oxygen uptake curve can be

produced in high energy systems because of the sequential use of exogenous substrates in multicomponent media. Bhatla (47) has shown that sequential use of exogenous substrates can also cause a diphasic oxygen uptake in dilute systems.

Bhatla and Gaudy (45) concluded that the plateau actually represents the endogenous respiration phase of bacterial metabolism, and that the secondary phase in oxygen uptake was usually caused by the predator population. The length of the plateau was considered to be proportional to the relative time lag between the peaks in bacterial and protozoan populations.

Gates, Mancy, Shafie, and Pohland reported the results of a series of experiments which were conducted in an open tank reactor (48). Oxygen sag curves were presented using sewage and Ohio River water, glucose, and lactose as substrates. The same type of curves was observed using sewage or pure cultures of Escherichia coli as seed. Oxygen uptake and glucose utilization occurred concurrently. While no attempt was made to separate the effects of deoxygenation and reaeration, the authors did observe in their interpretation of the sag curves, that the sag was not described by decreasing kinetics but actually consisted of lag period followed by a period of increasing oxygen uptake during the time of substrate utilization.

Isaacs and Gaudy reported the results of a series of experiments conducted in the simulated channel used in the present research (49). In these experiments it was observed that one of the primary differences in the oxygen uptake in the open turbulent system and the BOD bottle was the existence of a much longer lag period in the bottle system than in the turbulent system. Three distinct phases were observed in the oxygen

uptake curves. The first phase was associated with substrate utilization and an increase in biological solids. The second phase of the oxygen uptake was a period during which the rate of oxygen uptake was very low, producing a plateau in the uptake curve. The oxygen uptake at the plateau for the four experiments where a glucose-glutamic acid substrate was used, varied between 25 and 45 per cent of the theoretical oxygen demand. The plateau was followed by a second phase of oxygen uptake which was associated with protozoan activity. The authors were able to reproduce the observed oxygen sag curve by the use of a separate equation for each of the three phases. However, the theoretical oxygen sag curve computed from the Streeter-Phelps equation (Equation 8) did not adequately define the observed data.

CHAPTER III

EXPERIMENTAL AND COMPUTATIONAL RATIONALE

A. Theoretical Concepts

1. General Comments

As may be noted from Chapter II of this thesis, reaeration equations have been proposed along two general lines. These are the prediction equation, which is developed from stream data, and the equation developed from a theoretical concept. Since reaeration is a mass transfer process, it is deemed desirable to review briefly the present state of mass transfer theory as it relates to turbulent flow. A new equation based on turbulence in terms of streamflow parameters for the reaeration rate constant is also presented. Also, since, the overall approach utilized in this research to analyze the data is somewhat unique, a section on computational methods is presented to provide examples of the procedures used.

2. Gas-Liquid Transfer Theories

There are two universally accepted theories for the transfer of a gas to a liquid when the two are placed in contact. These are the "film theory" and the "penetration theory." The following discussion of the two concepts is admittedly brief, and the reader is referred to the references given for a more complete presentation. The older concept

is that proposed in 1924 by Lewis and Whitman (50). They presented a model for gas absorption which has been widely accepted and is designated in the literature as the "film theory." According to the model, all of the driving force acts across a stagnant film which, it is assumed, exists in both the gas and liquid phases at the interface. The assumption is also made that there is no concentration gradient in the bulk of either the gas or the liquid. This may be shown as follows:

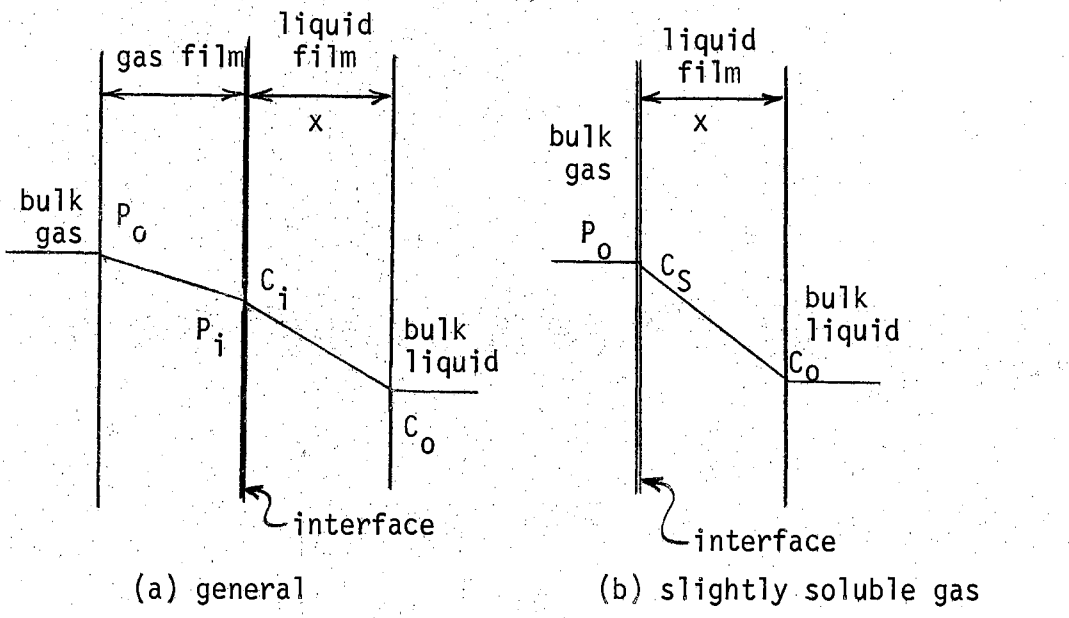


Figure 1 - Concentration gradient for gas at gas-liquid interface as proposed by film theory.

where P_o and P_i are the partial pressure of the diffusing gas in the bulk of the gas and at the interface, respectively, and C_i and C_o are the concentration of the absorbed gas at the interface and in the bulk liquid, respectively. The concentration difference across either of

these films represents the driving force for molecular diffusion across that film. For a slightly soluble gas (e.g., oxygen in water), there is no loss assumed for the gas film, and the partial pressure of the gas at the interface is taken as being the same as found in the bulk gas. An increase in turbulence is assumed to decrease the "liquid film" thickness, and to give an increase in the oxygen transfer rate.

Since the rate of transfer is considered to be controlled by the liquid film, the rate may be expressed as

$$\frac{1}{A}\frac{dM}{dt} = k_L(C_i - C_o) = k_L(C_S - C_o) \qquad (24)$$

where A is the area, M is the mass of gas transferred in pound moles, t is time, and k_L is the transfer coefficient for the liquid film. Since the surface is considered to be saturated for a slightly soluble gas, C_i is taken as the saturation concentration, C_S in mg/l.

The transfer coefficient can be replaced by the diffusivity coefficient, giving

$$R = \frac{D_M}{x}(C_S - C_o) = k_L(C_S - C_o) \qquad (25)$$

where R is the flux or transfer rate in the pound moles/hr/ft^2, D_M is the diffusivity through the liquid film in sq ft/hr, and x is the thickness of the liquid film in feet. The thickness of the fictitious liquid film cannot be determined; however, Equation 25 provides a working mathematical formulation which gives an increase in transfer rate with a decrease in film thickness.

As noted by the authors, the "film theory" has no physical basis, and no film has been observed, but the theory has been widely used in the correlation and interpretation of mass transfer data. The widespread use of the theory has led to studies seeking some physical

evidence of a liquid film, but there have been no reports of any physical evidence to indicate the existence of a film at the interface.

Fage and Townend (51) studied the behavior of dust particles in turbulent waters. Particles were observed within 1/40,000 inch from the surface, and there was no indication of the existence of a laminar film. To anyone who has sat on a riverbank and watched the water, it would certainly seem that the water surface of the flowing stream is not homogeneous but is continuously being replaced as water from beneath the surface is exposed. By carefully adding orthotolidine to the surface of flowing water containing a chlorine residual in the simulated channel used in this research, the writer was able to observe the rapid dispersion of the colored complex throughout the liquid by what certainly seemed to be eddy diffusion. Thus the existence of a liquid film does not seem reasonable, nor can its existence be demonstrated by any known methodology.

Tsivoglou and his associates (27) have also concluded from their studies on gas transfer that the apparent liquid film is purely a hydrodynamic phenomenon that is not related to the ability of the oxygen molecule to enter the liquid surface. Furthermore, if the film theory did define reaeration, then the mass of oxygen crossing the film would not vary with depth of flow. Thus, for a given rate of mass transfer, the rate of concentration change in the liquid would vary linearly with volume. This would give a linear relationship with k_2 and depth of flow. However, Isaacs and Gaudy (2) have shown that the rate constant varies with depth to the 3/2 power.

Higbie (14) studied the absorption of a pure gas into a still liquid during very short periods of exposure. The author reports that

several investigators had shown in the last century that a gas diffuses through a liquid according to Fick's law, which may be given as

$$\frac{dC}{dt} = D_M \frac{d^2C}{dx^2} \tag{26}$$

where C is the concentration at depth x, t is exposure time, and D_M is the diffusivity of the gas through the liquid. From Fick's law it can be shown that the absorption rate at the liquid interface is not constant, but that it varies inversely as the square root of the exposure time according to the following equation:

$$k_L = 2\sqrt{\frac{D_M}{\pi t}} \tag{27}$$

where k_L is the liquid film coefficient. Thus, the rate of absorption of the gas at an exposed liquid surface would become very great as the exposure time approaches zero. The rate of gas absorption is

$$R = 2\sqrt{\frac{D_M}{\pi t}} \quad (C_s - C_o) \tag{28}$$

where C_s is the saturation concentration for the gas, and C_o is the concentration of the gas in the liquid. This relationship is called the "penetration theory." While the theory had been verified for periods of exposure from ten seconds to one hundred and fifty hours, the work reported by Higbie covered periods of exposure from 0.01 to 0.1 second.

The penetration theory as given by Equation 28 indicates that the absorption rate is related to the period of exposure, t. If the liquid at the interface is exposed for a very short period of time, the transfer rate will be great, but the actual quantity of gas transferred will be small because of the short exposure period. If the exposure period is long, the transfer rate is small and approaches a constant rate as

time increases. For long exposure periods, the penetration theory is in agreement with the film theory. The penetration theory assumes no limitation on the reaeration rate. The more rapidly the surface is replaced by turbulent action, the greater the reaeration rate. However, Higbie (14) found that the transfer rate was not without limit as indicated by the penetration theory, but as the exposure time was decreased, the amount of gas absorbed was consistently below the theoretical value. As the time of exposure was increased, the amount of gas absorbed approached the theoretical quantity asymptotically and the two values were in good agreement at exposure times of about ten seconds, and above.

Elgin (52) suggests that the deficiency in transfer rate reported by Higbie is in agreement with the kinetic theory of gases. The upper limit of absorption would represent the actual rate of absorption at the initial instant of contact if every gas molecule striking the surface actually penetrated it. Since only a fraction of the molecules striking the surface actually penetrate it, the upper limit observed was somewhat less. As the exposure time is increased, the fraction penetrating the surface would follow the monomolecular law as observed by Higbie. Thus, it is quite evident that on the basis of the penetration theory the rate of oxygen absorption into water is related to the exposure period or rate of surface renewal. When water is in turbulent motion it is a mass of eddies which are continuously changing their conformation and position. These eddies are continually exposing fresh surface to the atmosphere while remixing into the bulk of the liquid parts of the exposed surface which have been in contact with the air for varying lengths of time. During the exposure period, the reaeration rate is given by Equation 28. Thus, under the penetration theory for reaeration, the rate of oxygen transfer is related to surface renewal.

The penetration theory was applied to turbulent flow by Danckwerts (15). He postulated that for a given state of turbulence the mean rate of production of fresh surface will be constant and equal to r, and the chance of an element of surface being replaced within a given time will be independent of its age. Here r is the fractional rate of surface renewal. The absorption rate was shown to be

$$R = \sqrt{D_M r}\ (C_s - C_o) \tag{29}$$

where R is the absorption rate per unit area, D_M is the diffusitivity of the absorbed gas, and $(C_s - C_o)$ is the oxygen deficit. It is seen that $\sqrt{D_M r}$ replaces k_L in Equation 25; however, the significance of the term is quite different from that associated with the film theory.

If a surface resistance does exist to decrease the rate of absorption, the rate of absorption is shown by Danckwerts (15) to be

$$R = \frac{1}{\frac{1}{\sqrt{D_M r}} + \frac{1}{k_A}}\ (C_s - C_o) \tag{30}$$

where the total transfer is given by

$$\sqrt{D_M r}\ (C_s - C_i) = k_A(C_i - C_o) = k_L(C_s - C_o) \tag{31}$$

where k_A represents the surface resistance, $C_i - C_o$ is the deficit across the surface, $\sqrt{D_M r}\ (C_s - C_i)$ is the transfer across the interface, and $k_L(C_s - C_o)$ is the overall transfer rate. At equilibrium conditions the three terms in Equation 31 are equal. Thus the rate of oxygen transfer in accordance with the penetration theory is given by

$$R = k_L(C_s - C_o) \tag{32}$$

where k_L is the overall transfer coefficient, and $C_s - C_o$ is the oxygen deficit.

The surface resistance, k_A, may be caused by detergents, oils, or any other conditions which would affect the surface density or surface tension. However, for any given condition it would be a constant, and the rate of transfer would still be related directly to the rate of surface renewal.

Following the transfer of oxygen across the air-water interface, it must then be distributed throughout the bulk of the liquid. Here again there is a difference in the film theory and the penetration theory. In the former case the oxygen is assumed to be distributed by molecular diffusion, whereas according to the penetration theory the oxygen is carried throughout the bulk of the liquid by eddy diffusion with molecular diffusion occurring primarily on an intra-eddy scale.

Convection by molecular diffusion alone is slow and difficult to achieve except for very viscous fluids. Even in the so-called quiescent vessel of water in the laboratory, convection by eddies is not eliminated, since slight convection currents are invariably present. These are due to slight temperature gradients, to density currents resulting from the more densely saturated surface layer, or to undamped mechanical motion. Stratification in natural lakes is factual evidence that molecular diffusion is most probably insignificant in stream reaeration. Here the thermal density barrier is sufficient to prevent mixing by eddy diffusion and convection currents, but it offers no resistance to molecular diffusion. In fact, the colder water at the lower depths actually promotes a net flux to the lower depths by molecular diffusion, yet it is well established that very little transfer occurs across the thermal density barrier.

O'Connor and Dobbins (13) attempted to relate reaeration to the

rate of surface renewal through the age distribution theory proposed by Danckwerts (15), however, their basic assumption that the rate of surface renewal is equal to the velocity gradient is without foundation and contrary to the Prandtl universal logarithmic velocity distribution law which was demonstrated by Vanoni (53) to apply to open channel flow. The integrated form of the equation for the velocity distribution may be written

$$u = U + \frac{1}{z}\sqrt{gDS}\ \ (1 + \ln \frac{y}{D}) \tag{33}$$

where u is the velocity at distance y from the channel bed, D is the depth, U is the mean velocity, z is the von Karman constant, having a value of about 0.4 for water, g is the gravitational constant, and S is the energy gradient. Differentiation of Equation 33 with respect to y yields a more useful equation for the velocity gradient

$$\frac{du}{dy} = \frac{2.5}{y}\sqrt{gDS} \tag{34}$$

where $\frac{du}{dy}$ is the velocity gradient at distance y from the channel bed. Since the energy gradient, S, is a function of several hydraulic parameters, it is desirable to replace this term in the equation. The Darcy-Weisbach equation can be rearranged to give the following form:

$$\sqrt{gDS} = \sqrt{\frac{f}{8}U^2} \tag{35}$$

Thus the vertical velocity distribution is given by

$$\frac{du}{dy} = \frac{2.5}{y}\sqrt{\frac{f}{8}U^2} \tag{36}$$

where f is the dimensionless friction factor. As noted by Churchill, et al. (16), the vertical velocity distribution is related to both the velocity and the square root of the friction factor. Also, the Darcy-

Weisbach equation in terms of the energy slope gives

$$S = \frac{f}{8} \frac{U^2}{Dg} \tag{37}$$

From an examination of Equations 36 and 37 it is seen that the energy gradient does not define flow for a turbulent system. The energy gradient, S, is the volumetric rate of energy dissipation in ft-lb/lb per unit length of flow, and as shown by Equations 36 and 37, this rate of energy dissipation in turbulent systems is related to f and U, and both of these variables are related to depth. At constant depth, both the energy gradient and the vertical velocity distribution are defined by f and U. Any combination of f and U yielding the same constant will give the same vertical velocity distribution and the same energy gradient at constant depth.

In summary, the penetration theory is considered by the author to be the more proper approach to mass transport in turbulent flow even though the theory is not completely developed at this time because of the lack of a suitable expression for the surface renewal rate. However, surface renewal would seem to be related to the intensity and scale of turbulence, and any relationship for expressing surface renewal rates must include the parameters f, U, and D, since these are required to define the rate of energy dissipation.

3. Velocity Gradient in Flowing and Stirred Systems

A logical approach to stream reaeration is that proposed by Camp and Stein (54) for defining turbulence in flocculation basins. Since in a turbulent flow all of the energy input to the system must be dissipated as heat through kinematic and eddy viscous forces, these authors have shown that turbulence is related to the volumetric rate of

energy loss through the root mean square velocity gradient. For turbulent flow in streams, the velocity gradient, G, is shown to be given by the square root of the volumetric rate of energy dissipation divided by the water viscosity. Therefore

$$G = \sqrt{\frac{W}{\mu}} \tag{38}$$

where μ is the dynamic viscosity in lbs/ft-sec, and W is the energy dissipation rate per unit volume of water, which is given by

$$W = \frac{AU\rho g h_f}{AL} = \frac{AU\rho g}{AL} \cdot f \frac{L}{4D} \frac{U^2}{2g} = \frac{f\rho U^2}{8D} \tag{39}$$

and

$$G = \sqrt{\frac{f}{8} \frac{U^3}{\nu D}} \tag{40}$$

where G is the velocity gradient in seconds $^{-1}$, ν is the kinematic viscosity in feet^2/sec, f is the dimensionless friction factor, U is the mean velocity in ft/sec, and D is the mean depth in feet.

For a mechanically-stirred vessel, the velocity gradient is given by

$$G = \sqrt{\frac{Pg_c}{V\mu}} \tag{41}$$

where P is the power input in ft-lbs per second, g_c is the force-mass conversion factor (32.2 ft-lb mass/ft-lb-force sec^2), V is the volume in ft^3, and μ is the water viscosity in lbs/ft-sec.

4. Power Input in Stirred Tanks

Mechanical stirring is generally used in pilot plant studies to provide agitation and reaeration of the contents of small vessels. Also, mechanical mixing is often used in activated sludge and extended aeration waste treatment plants. However, in the latter, reaeration is

accomplished by high speed turbines, and the rate of oxygen transfer is greatly enhanced by surface agitation.

One would suspect that reaeration in stirred vessels is affected by the same principles as those for flowing streams; that is, mass transfer rates are related to the nature of the turbulence maintained in the vessel. The nature of the turbulence in a stirred vessel is related to the power number, N_p, which is defined by the following dimensionless ratios (55):

$$N_p = K(N_{Re})^a(N_{Fr})^b(\frac{T}{D})^c(\frac{z}{D})^d(\frac{C}{D})^e(\frac{p}{D})^f(\frac{W}{D})^g(\frac{l}{D})^h(\frac{n_1}{n_2})^i \qquad (42)$$

where

N_p = power number

N_{Re} = Reynolds number

N_{Fr} = Froude number

D = impeller diameter

T = tank diameter

z = liquid depth

C = distance impeller off tank bottom

p = impeller blade pitch

W = impeller blade width

l = impeller length

n = number of blades

K = constant for the system

The parameters have the dimension of length. In the English system of measurement, the length would usually be expressed in feet.

For geometrically similar systems, the power number equation reduces to:

$$N_p = K(N_{Re})^a (N_{Fr})^b \tag{43}$$

and in baffled tanks having no vortex, the exponent b is zero. Thus

$$N_p = K(N_{Re})^a \tag{44}$$

and since the power number is independent of the Reynolds number in turbulent flow (which will almost always exist in stirred water systems), the power number is given by

$$N_p = \text{constant}, \; K^1 = \frac{Pg_c}{\rho N^3 D^5} \tag{45}$$

or

$$P = \frac{K^1 \rho N^3 D^5}{g_c} \tag{46}$$

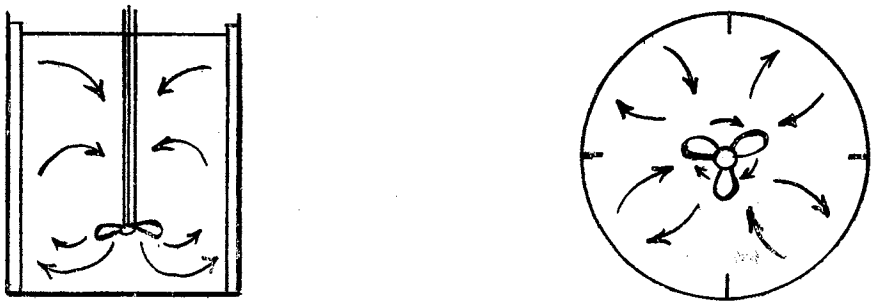
Therefore, the power imparted to the liquid is proportional to the third power of the impeller speed and the impeller diameter to the fifth power. For water, the relationship for an impeller becomes

$$P = CN^3 \tag{47}$$

Thus, a log-log plot of power versus speed has a slope of 3 and an intercept of log C.

While it is possible to have any combination of geometric ratios in a mixing operation, the manufacturing procedures have become somewhat standardized. It is conventional to use four baffles, equally spaced around the tank, with the baffle extending radially into the water approximately 0.1 of the tank diameter. This is sufficient to prevent swirling and the creation of a vortex. A 3-blade square pitch marine impeller is generally used with water. A square pitch is a pitch of one, and indicates that the impeller would move forward one diameter per revolution if free. This gives an axial flow toward the bottom of the

tank with a flow pattern as shown in Figure 2.



(a) elevation view (b) bottom view

Figure 2 - Flow pattern in baffled tanks.

Data presented by Rushton (56) indicate that for impeller heights from the tank bottom of between 0.7D and 1.6D there appears to be no effect on the power. $\frac{T}{D}$ ratios have been shown to have little effect on power input.

5. Summary

There is considerable theoretical justification for expecting Equation 40 to define the reaeration rate in streams. It has been shown by Rickard and Gaudy (57) that the reaeration rate in a stirred reactor can be defined by the velocity gradient. The equation contains f, U, and D, which were shown by Equations 36 and 37 to be required to define the vertical velocity distribution and the energy gradient. Thus, Equation 40 is also completely compatible with current hydraulic theory for relating turbulence to the physical parameters of the streams. The dimensionless friction factor, f, can be evaluated from nomograms and equations which are found in all texts on hydraulics.

A regression analysis of the reaeration data reported by Isaacs and Gaudy (2), using Equation 40, gave a correlation coefficient of 0.987 which is essentially the same as that found by the authors using a prediction equation developed by dimensional analysis.

The reaeration data of the present research was also correlated with the velocity gradient. Equations are presented for the reaeration rate constant in terms of the velocity gradient for both the channel simulator and the stirred reactor.

B. Oxygen Utilization Systems

The experiments in the biological degradation portion of this research were designed to compare biological stabilization processes and O_2 utilization as measured in the usual bottle system with the corresponding responses in a flowing or stirred system. Such comparison and development of possible relationships needs to be accomplished, because present engineering practice requires that BOD bottle data be used as the principal measure of the pollutional strength of wastes in natural streams and because the bottle data must of necessity usually be used to estimate the reaeration rate for the receiving stream.

Four systems selected to be run concurrently were (1) the standard BOD bottle and a 2.4 liter bottle under quiescent conditions, (2) a 2.4 liter bottle under stirred conditions, (3) a flowing system, and (4) a stirred reactor. All four systems were seeded with identical biological populations in each experiment. The 300 ml BOD bottle systems were used because they are a standard in professional practice. The 2.4 liter quiescent and mixed systems were selected to provide sufficient volume for the selected analyses, and since the effects of mixing were to be evaluated it was necessary that a quiescent system be run as a

standard along with the mixed bottle system. The flowing system experiments were conducted in a simulated stream in order to measure the degradation process under stream conditions. If the bottle data were found to be insufficient for defining the effects of a waste on a receiving stream, then it would be desirable to have other laboratory procedures for measuring the degradation process. Hence, the open stirred reactor was selected, since the reaeration rate found in the stream could be replicated by varying the mixing rate and because the system was easily adapted to laboratory use.

It was reasoned that by conducting concurrent experiments in the four systems it would be possible to evaluate any relationship which exists between degradation in the BOD bottle and the turbulent stream. Basically, the differences to be evaluated were the effects of dilution and mixing on biological growth and substrate stabilization. Also, the data from the selected systems would permit evaluation of the validity or the engineering usefulness of the assumption that degradation occurs as a first-order decreasing function.

Since the object of this research was to compare laboratory bottle data and stream data, the simulated channel and the stirred tank were operated at speeds which gave reaeration rates approximating those occurring in natural streams. The simulated channel was operated at a velocity of 0.49 fps, and the stirred tank was mixed at an impeller speed of 184 rpm.

C. Methods Used in Data Analysis

1. Calculation of Reaeration Rate Constant

The differential equation for reaeration is

$$-\frac{dD}{dt} = K_2 D \tag{48}$$

which, upon integration and rearranging, gives

$$K_2 = \frac{\ln(D_o/D_t)}{\Delta t} \quad \text{(log base e)} \tag{49}$$

or

$$k_2 = \frac{\log (D_o/D_t)}{\Delta t} \quad \text{(log base 10)} \tag{50}$$

where D_o is the initial deficit, D_t is the deficit (i.e., $C_s - C_t$) at time t, and k_2 is the rate constant or the slope of the deficit line as shown in the example given in Figure 3 for the data in Table I, where the deficit was plotted on a logarithmic scale, and time on an arithmetic scale.

The reaeration rate, k_2, can be obtained by drawing a line through the deficit points and determining the slope of the line as given by Equation 50. In Figure 3 the deficit is 7.0 at t = 0, and 1.35 at t = 20, thus

$$k_2 = \frac{\log (7.0/1.35)}{20 - 0} = \frac{0.714}{20} = 0.0357 \text{ hr}^{-1}$$

or

$$k_2 = 24\ (0.035) = 0.857 \text{ day}^{-1}$$

It is essential that the deficit data plot as a straight line, since a curved line is not in agreement with the first-order rate equation, and in the absence of chemical and biological interference, reaeration follows first order kinetics.

2. Calculation of Oxygen Uptake from Dissolved Oxygen Data

In an open system for which the oxygen absorption or reaeration rate constant has been defined, it is possible to compute the biological

TABLE I

DATA USED IN EXAMPLE COMPUTATION OF REAERATION RATE CONSTANT

Rim Speed: Inside rim = 6 rpm
Outside rim = 4 rpm

Velocity = 0.622 fps

Temperature = 23°C

Water Depth = 18 inches

Barometric Pressure = 29.1 inches

$C'_s = [8.50 - 0.1] [29.1/29.92] = 8.2$ mg/l

Note: 8.5 is from ASCE Progress Report data, and 0.1 is correction for water using starch endpoint

Deficit = $C'_s - C_t = 8.2 - D.O$

Aeration Time Hours	Dissolved Oxygen mg/l	Deficit mg/l
0	1.1	7.1
1	1.6	6.6
2	2.3	5.9
3	2.8	5.4
4	3.3	4.9
5	3.7	4.5
7	4.3	3.9
8	4.6	3.6
10	5.2	3.0
12	5.6	2.6
14	6.0	2.2
16	6.4	1.8
18	6.6	1.6

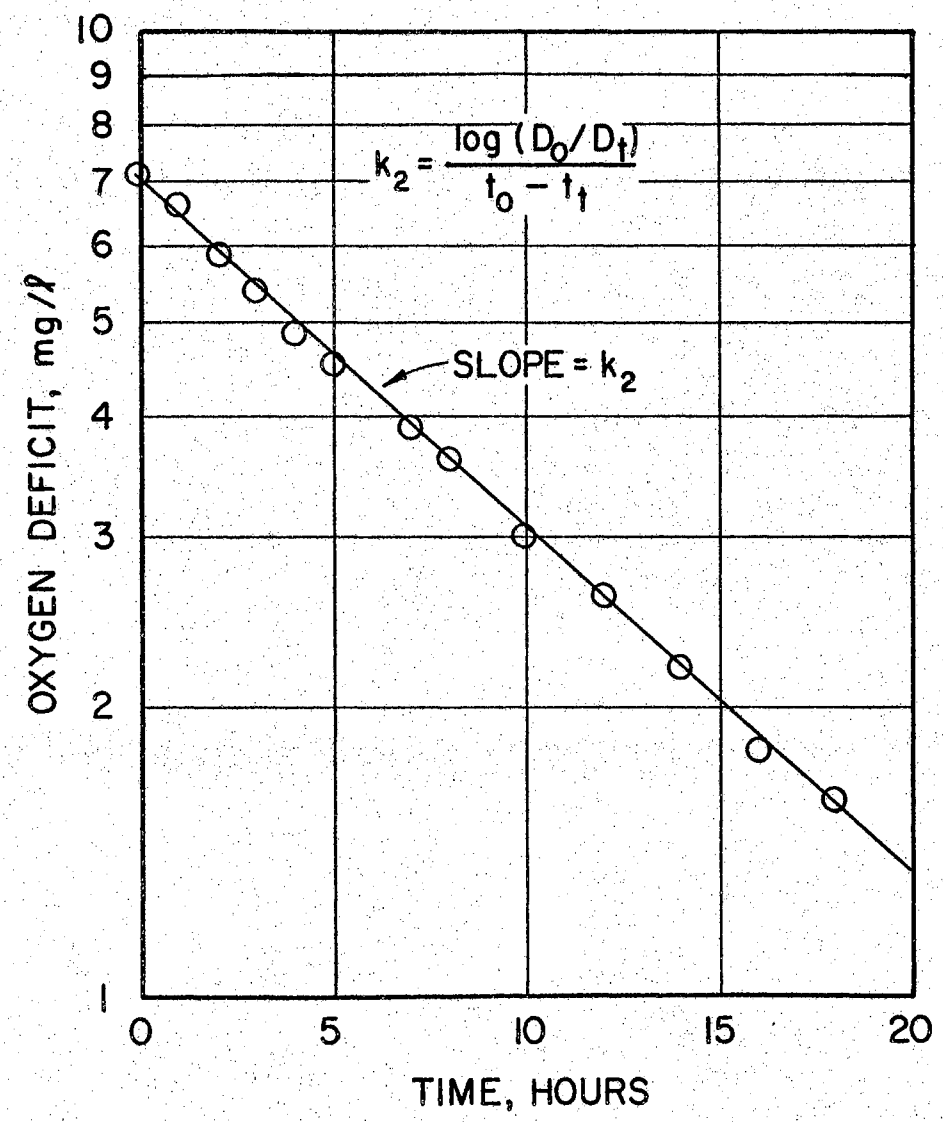


Figure 3 - Typical oxygen deficit data used in determining reaeration rate constant (plotted from data in Table I).

oxygen uptake during any period of time from observed dissolved oxygen data. The computational procedure by which O_2 uptake curves were computed in this study is essentially the same as that used by Isaacs and Gaudy (2). The following sample calculations are presented as an illustration of the procedure. In the top portion of Figure 4 the dissolved oxygen concentration in both the simulated receiving stream and the stirred reactor are plotted against time after introduction of a known amount of substrate, i.e., the observed dissolved oxygen sag curves are plotted. The lower portion of the figure shows the course of oxygen uptake in both reactors calculated from the sag curve and the reaeration data.

Tables II and III give the dissolved oxygen data together with the calculations required for producing the oxygen uptake curve. Columns 1-3 show the date, hour of day, and hours from the beginning of the experiment. Column 4 shows the dissolved oxygen concentration for the respective time, and in columns 5 and 6 the temperature and pressure are listed. Column 7 shows the dissolved oxygen saturation concentration at the respective temperature and a pressure of 29.92 inches mercury. The DO saturation concentration, adjusted for barometric pressure, is given as C_s' in column 8. C_s' minus DO given in column 4 is the deficit, D, which is given in column 9.

The rate of O_2 input to the system by reaeration, given in column 10, is calculated by the following equation:

$$\frac{\Delta D_r}{\Delta t} = K_2 D \qquad 51$$

and the total oxygen input in time period Δt, given in column 12, is calculated as

$$\Delta D_r = K_2 D \left[\Delta t\right] \qquad 52$$

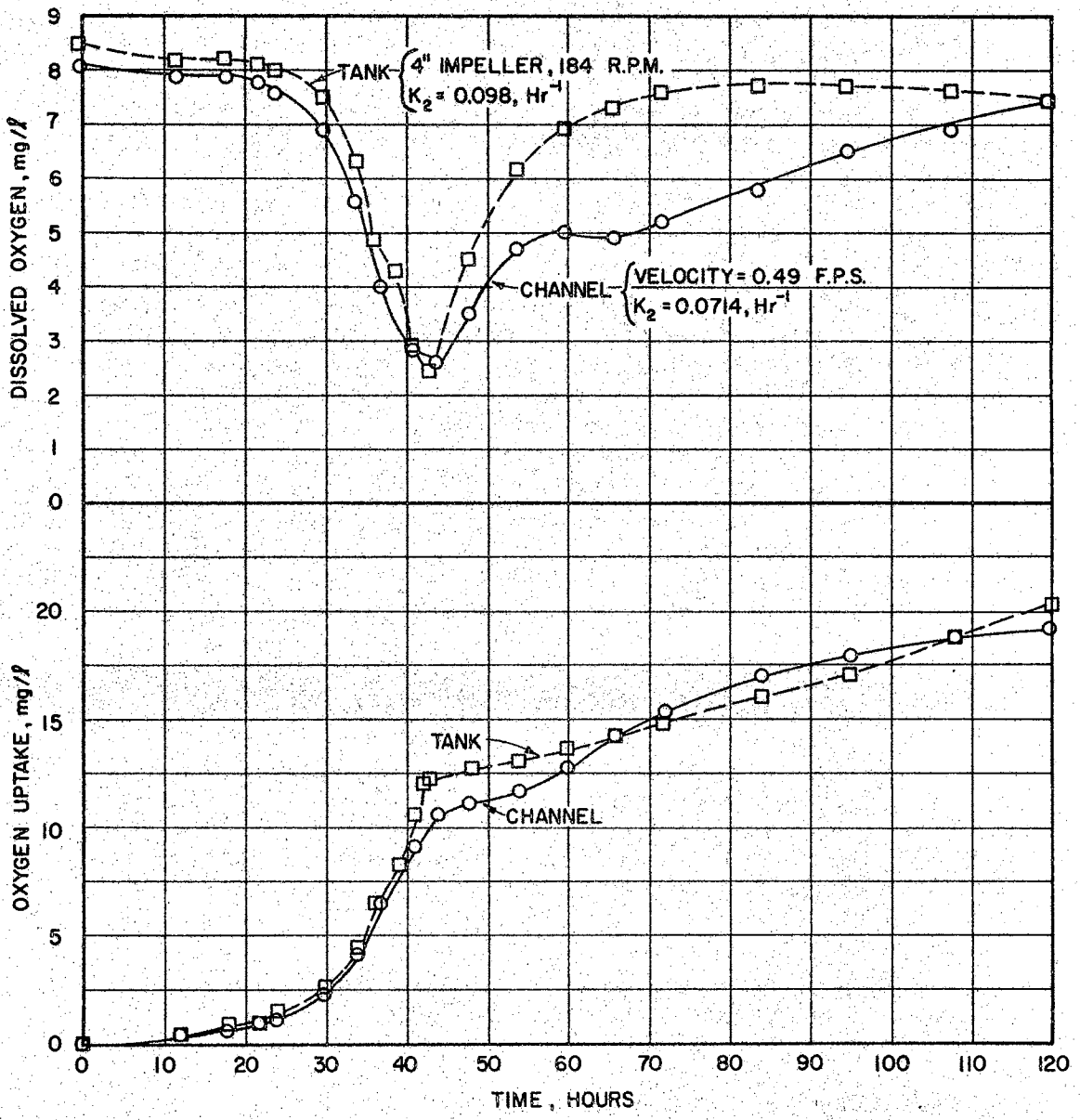


Figure 4 - Relationship between oxygen content and oxygen uptake.

TABLE II

CALCULATION OF OXYGEN UPTAKE FROM DISSOLVED OXYGEN DATA FOR EXPERIMENT IN SIMULATED CHANNEL

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Date	Time	Hours	DO mg/l	Temp °C	Pressure in.Hg	C_s mg/l	C_s' mg/l	D mg/l	K_2D mg/l-hr	Δt hr	$K_2D(\Delta t)$ mg/l	ΔDO mg/l	12-13 mg/l	Σ mg/l
4- 5	2100	0	8.1	22.7	29.20	8.55	8.35	0.25	0.0178					0
4- 6	0900	12	7.9	22.6	29.10	8.56	8.25	0.35	0.0250	12	0.26	-0.2	0.46	0.46
	1500	18	7.9	22.6	28.90	8.56	8.25	0.35	0.0250	6	0.15	0	0.15	0.61
	1900	22	7.8	22.7	28.80	8.55	8.20	0.40	0.0286	4	0.21	-0.1	0.31	0.92
	2100	24	7.6	22.8	28.80	8.53	8.20	0.60	0.0428	2	0.07	-0.2	0.27	1.19
4- 7	0300	30	6.9	22.6	28.70	8.56	8.20	1.30	0.0928	6	0.41	-0.7	1.11	2.30
	0700	34	5.6	22.5	28.70	8.58	8.20	2.60	0.1856	4	0.56	-1.3	1.86	4.16
	1000	37	4.0	22.6	28.70	8.56	8.20	4.20	0.2998	3	0.73	-1.6	2.33	6.49
	1400	41	2.8	22.7	28.85	8.55	8.20	5.40	0.3855	4	1.37	-1.2	2.57	9.06
	1700	44	2.6	22.8	28.85	8.53	8.20	5.60	0.3998	3	1.18	-0.2	1.38	10.44
	2100	48	3.5	22.9	28.90	8.52	8.20	4.70	0.3355	4	1.47	+0.9	0.57	11.01
4- 8	0300	54	4.7	23.0	28.90	8.50	8.20	3.50	0.2499	6	1.76	+1.2	0.56	11.57
	0900	60	5.0	23.1	29.10	8.48	8.25	3.25	0.2320	6	1.45	+0.3	1.15	12.72
	1500	66	4.9	23.2	29.10	8.46	8.20	3.30	0.2356	6	1.40	-0.1	1.51	14.23
	2100	72	5.2	23.5	29.10	8.42	8.15	2.95	0.2106	6	1.34	+0.3	1.04	15.27
4- 9	0900	84	5.8	23.7	29.30	8.38	8.20	2.40	0.1713	12	2.29	+0.6	1.69	16.96
	2000	95	6.5	23.7	29.30	8.38	8.20	1.70	0.1214	11	1.61	+0.7	0.91	17.87
4-10	0900	108	6.9	23.7	29.30	8.38	8.20	1.30	0.0928	13	1.39	+0.4	0.99	18.86
	2100	120	7.4	23.7	29.20	8.38	8.15	0.75	0.0535	12	0.88	+0.5	0.38	19.24

Velocity = 0.49 fps

K_2 = 0.0714

TABLE III

CALCULATION OF OXYGEN UPTAKE FROM DISSOLVED OXYGEN DATA FOR EXPERIMENT IN STIRRED TANK

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Date	Time	Hours	DO mg/l	Temp °C	Pressure in.Hg	C_s mg/l	C_s' mg/l	D mg/l	K_2D mg/l-hr	Δt hr	K_2Dt mg/l	ΔDO mg/l	13-14 mg/l	Σ mg/l
4- 5	2100	0	8.50	20	29.2	9.02	8.80	0.30	0.029					0
	2300	2	8.40	20	29.2	9.02	8.80	0.40	0.039	2	0.07	-0.10	0.17	0.17
4- 6	0900	12	8.30	20	29.1	9.02	8.75	0.45	0.044	10	0.41	-0.10	0.51	0.68
	1500	18	8.30	20	28.9	9.02	8.70	0.40	0.039	6	0.25	0	0.25	0.93
	1900	22	8.10	20	28.8	9.02	8.65	0.55	0.054	4	0.19	-0.20	0.39	1.32
	2100	24	8.00	20	28.8	9.02	8.65	0.65	0.064	2	0.12	-0.10	0.22	1.54
4- 7	0300	30	7.50	20	28.7	9.02	8.60	1.10	0.108	6	0.52	-0.50	1.02	2.56
	0700	34	6.30	20	28.7	9.02	8.60	2.30	0.225	4	0.67	-1.20	1.87	4.43
	0900	36	4.85	20	28.7	9.02	8.60	3.75	0.368	2	0.59	-1.45	2.04	6.47
	1200	39	4.30	20	28.8	9.02	8.65	4.35	0.426	3	1.19	-0.55	1.74	8.21
	1400	41	2.90	20	28.85	9.02	8.65	5.75	0.563	2	0.99	-1.40	2.39	10.60
	1500	42	2.00	20	28.85	9.02	8.65	6.65	0.652	1	0.61	-0.90	1.51	12.11
	1600	43	2.45	20	28.85	9.02	8.65	6.20	0.608	1	0.63	+0.45	0.18	12.29
	2100	48	4.50	20	28.9	9.02	8.70	4.20	0.412	5	2.55	+2.05	0.50	12.79
4- 8	0300	54	6.15	20	29.0	9.02	8.70	2.55	0.250	6	1.99	+1.65	0.34	13.13
	0900	60	6.90	20	29.1	9.02	8.75	1.85	1.181	6	1.29	+0.75	0.54	13.67
	1500	66	7.30	20	29.1	9.02	8.75	1.45	0.142	6	0.97	+0.40	0.57	14.24
	2100	72	7.55	20	29.1	9.02	8.75	1.20	0.118	6	0.78	+0.25	0.53	14.77
4- 9	0900	84	7.70	20	29.3	9.02	8.80	1.10	0.108	12	1.36	+0.15	1.21	15.98
	2000	95	7.70	20	29.3	9.02	8.80	1.10	0.108	11	1.19	0	1.19	17.17
4-10	0900	108	7.60	20	29.3	9.02	8.80	1.20	0.118	13	1.47	-0.10	1.57	18.74
	2100	120	7.45	20	29.2	9.02	8.80	1.35	0.132	12	1.50	-0.15	1.65	20.39

Speed = 5 $\quad T = 20^{\circ}C \quad K_2 = 0.098\ hr^{-1}$

where K_2D is taken as the mean for the time interval Δt. For the first 12-hour time interval the oxygen input by reaeration is

$$\Delta D = \left[\frac{0.0178 + 0.0250}{2}\right]12 = 0.26 \text{ mg/l}$$

The oxygen utilization in the time interval Δt is equal to the oxygen added to the system by reaeration minus the change in dissolved oxygen concentration in the system. For the first time interval (twelve hours) the oxygen utilization is the sum of the absolute values in columns 12 and 13 (0.46 mg/l). Column 15 is the summation of column 14 and the quantities listed therein represent the accumulated oxygen uptake of the system for the time given in column 3. The data in column 15 were used to plot the oxygen uptake curve in Figure 4. The time intervals in column 11 should be selected so that the change in dissolved oxygen is small over the interval and the change in the oxygen concentration should be uniform over the period selected.

In closed systems the oxygen utilization curve was generated directly from the observed data.

3. Calculation of the Deoxygenation Rate Constant (First Order Decreasing)

Because of the difficulty of fitting deoxygenation data to a monomolecular rate equation, there have been many methods proposed for analyzing BOD data. Gaudy, et al. (58) recently published an evaluation of sixteen methods that have been reported in the literature for calculating the deoxygenation rate constant from BOD data. The two most appropriate methods, in the writer's opinion, are those proposed by Tsivoglou (59), and by Isaacs and Gaudy (60). Both methods require the plotting of sufficient points to determine if the data is too scattered

to be used.

The data shown in Figure 5 can be used to illustrate the calculation procedure when using the method proposed by Isaacs and Gaudy (60). An examination of the O_2 curve indicates that a decreasing rate is effective from sixty to one hundred-twenty hours. A first approximation of the first stage demand, L_a', is taken as 20.0 mg/l. Then, as shown by Isaacs and Gaudy, the true first stage demand, L_a, for the data if it is to obey first order kinetics is

$$L_a = L_a' - \alpha \tag{53}$$

where the adjustment, α, which needs to be applied to the assumed demand of L_a' is given by

$$\alpha = \frac{L_1' L_2' - (L_3')^2}{L_1' + L_2' - 2L_3'} \tag{54}$$

where the L' values are equal to the BOD remaining at the respective times, t, and t_3 is the average of t_1 and t_2. Thus, as shown on the figure:

$$t_1 = 60 \text{ hours}, \quad L_1' = 20\text{-}12.7 = 7.3$$

$$t_2 = 120 \text{ hours}, \quad L_2' = 20\text{-}19.2 = 0.8$$

$$t_3 = 90 \text{ hours}, \quad L_3' = 20\text{-}17.5 = 2.5$$

and

$$\alpha = \frac{(7.3)(0.8) - 2.5)^2}{7.3 + 0.8 - 2(2.5)} = -0.1$$

giving

$$L_a = 20.0 - (-0.1) = 20.1$$

Knowing L_a, the following table can be constructed from the BOD data where Y is the BOD exerted at time t (see Table II for Y values).

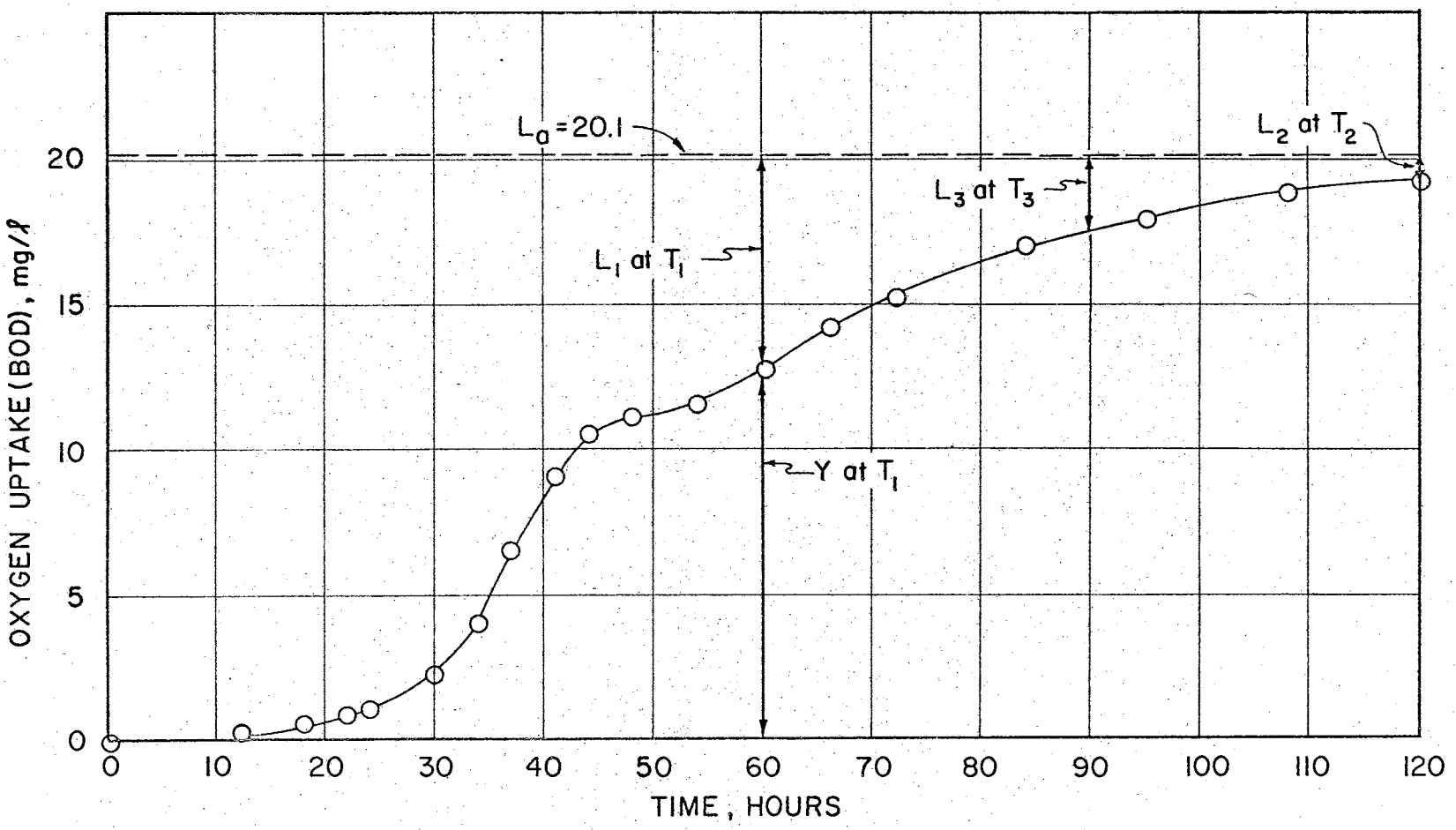


Figure 5 - Oxygen uptake curve used in example calculation of deoxygenation rate constant.

Time	Y	$L_a - Y = L_t$	t
60	12.7	7.4	0 hours
72	15.3	4.9	12 hours
84	17.0	3.1	24 hours
96	17.9	2.2	36 hours
108	18.9	1.2	48 hours
120	19.2	0.9	60 hours

A plot of log (L-Y) versus t gives a straight line which permits evaluating k_1 as follows from Equation 3:

$$k_1 = \frac{\log (L_1/L_2)}{t_2 - t_1} = \frac{\log (7.4/0.9)}{60/24 - 0} = 0.37 \text{ day}^{-1}$$

Thus the decreasing portion of the curve gives a first stage demand of 20.1 mg/l and deoxygenation constant of 0.37 day^{-1}. However, it is obvious from the figures that the entire course of O_2 uptake is not described by first order decreasing rate kinetics (see the first sixty hours), and therefore only the data for the last sixty hours were used.

4. Calculation of the Deoxygenation Rate Constant (First Order Increasing)

During the log growth phase the oxygen uptake can be expected to follow the biological growth curve and can therefore be defined by a first order increasing rate function. As shown by this research, the rate of oxygen uptake during this phase of the deoxygenation process is more significant in stream degradation than the decreasing rate. The increasing rate can be evaluated by plotting oxygen uptake versus time on semi-log paper. The slope of the straight line portion of the

curve is the increasing rate constant. Hence for the oxygen uptake curve shown in Figure 5 the increasing rate K_i is found by plotting the data from about twenty to thirty-eight hours, which is the increasing rate portion of the curve, and taking the slope of the line through the straight portion of the curve as follows (from Equation 4 or 5):

$$K_i = \frac{\ln(6.5/2.19)}{37 - 30} = 0.156 \text{ hr}^{-1}$$

or

$$k_i = \frac{\log (6.5/2.19)}{37 - 30} = 0.068 \text{ hr}^{-1} = 1.62 \text{ day}^{-1}$$

The increasing rate of oxygen uptake is 5.5 times greater than the decreasing rate for the same experiment. Hence it appears evident that this rate is more important in the deoxygenation of the receiving stream.

CHAPTER IV

LABORATORY EQUIPMENT, EXPERIMENTAL PROCEDURES, AND METHODS OF ANALYSIS

A. Laboratory Equipment

1. Oxygen Solubility Experiments

Two pyrex battery jars with inside diameters of eight inches and eighteen inches deep were used as aeration vessels. For experiments conducted above 15°C, a 30" x 15" x 15" water bath was used with a Precision Scientific Lo-temptrol temperature control unit. This unit contains both heating and refrigeration systems, and gave very sensitive temperature control.

Four 3/4" baffles were spaced equally distant along the wall of the aeration vessel. The water was stirred with a 2½" diameter stainless steel marine impeller. The impellers were driven by a Lightin Model V7 mixer. A Superior Electric Company Powerstat was used to control the motor speed.

A refrigerator was used for temperature control in the experiments conducted below 15°C. The shelving was removed from a household refrigerator, and the aeration vessels along with the stirring equipment were placed inside. Two thousand cc of air/min was added to the refrigerator to ensure a constant oxygen pressure.

A model RC 16 BC Conductivity Bridge manufactured by Industrial Instruments was used with a conductivity cell having a constant of 0.1

for measuring conductivity. pH was measured by a Beckman Zeromatic pH meter. The barometric pressure was obtained at the time of sampling from a recording barometer manufactured by the Taylor Instrument Company. The recording barometer was routinely checked against a standard mercury barometer in the meteorology department at Oklahoma State University.

2. Reaeration Experiments

The simulated channel used in this research was the apparatus developed by Isaacs and Gaudy (2) at the Oklahoma State University bioengineering laboratories. The apparatus is constructed of fiberglass and consists of a flat-bottomed cylinderical channel, as shown in Figures 6 and 7, having an inside diameter of forty-seven and five-eighths inches and an outside diameter of seventy-three and three-quarter inches. Rotating inner walls which extend nearly to the bottom of the channel provided a rectangular cross-section of flow having an inside diameter of forty-eight inches and an outside diameter of seventy-three inches. These rotating shell walls are independently belt-driven by 3-phase, 1740 rpm motors with Reeves Vari-speed pulleys. The drive for each wall also provides for interchange of pulley ratios at two positions, thus giving high flexibility in the selection of wall speeds. The apparatus provides a rectangular section of flow twelve and one-half inches wide with any depth up to eighteen inches.

The velocity of flow was determined in the simulated channel by use of an A. Ott small current meter (Model C1). The meter was supported by a template which was permanently attached to the frame of the apparatus. The template positioned the meter horizonatally, and the vertical position was achieved by adjusting the meter pole in the

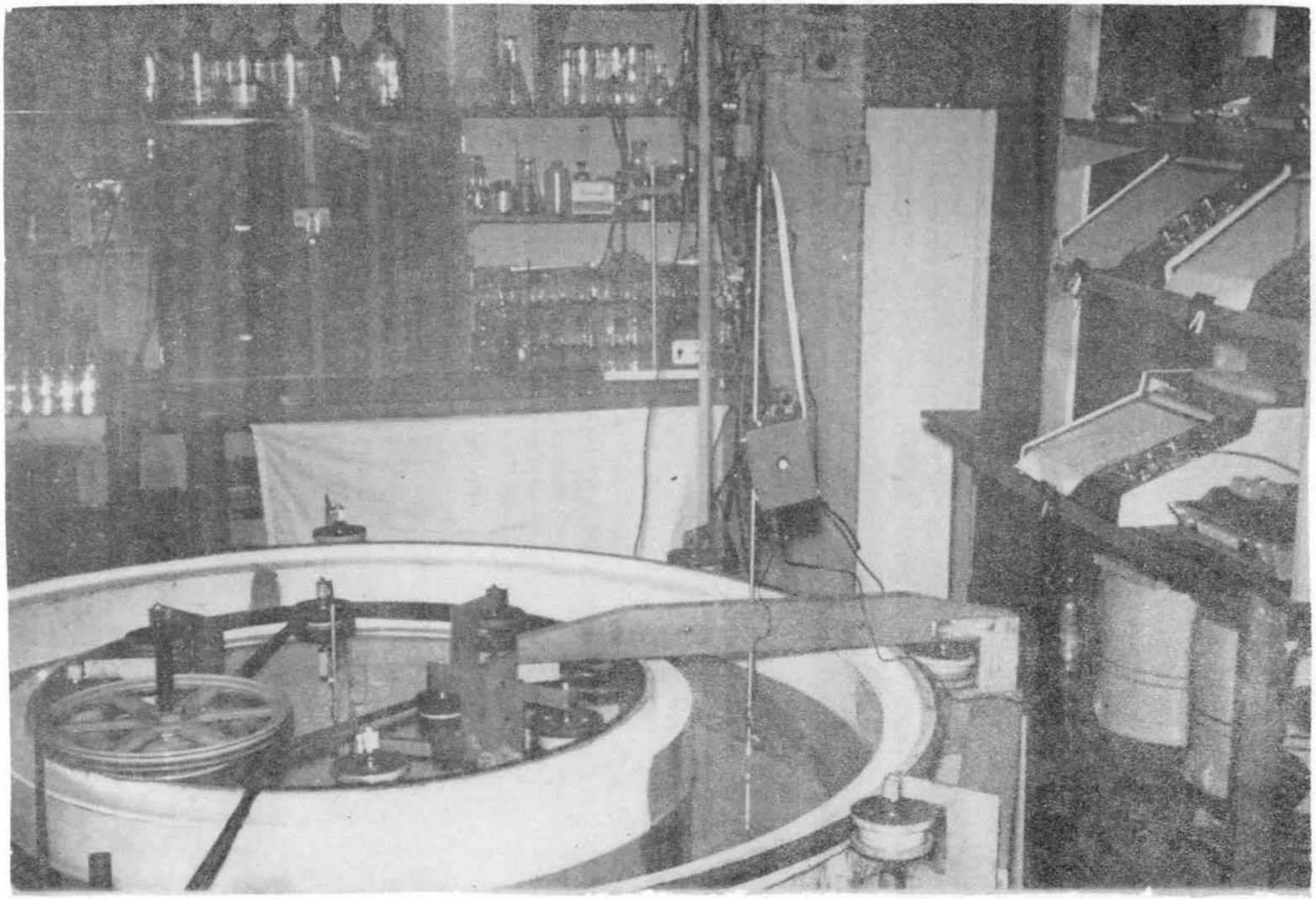
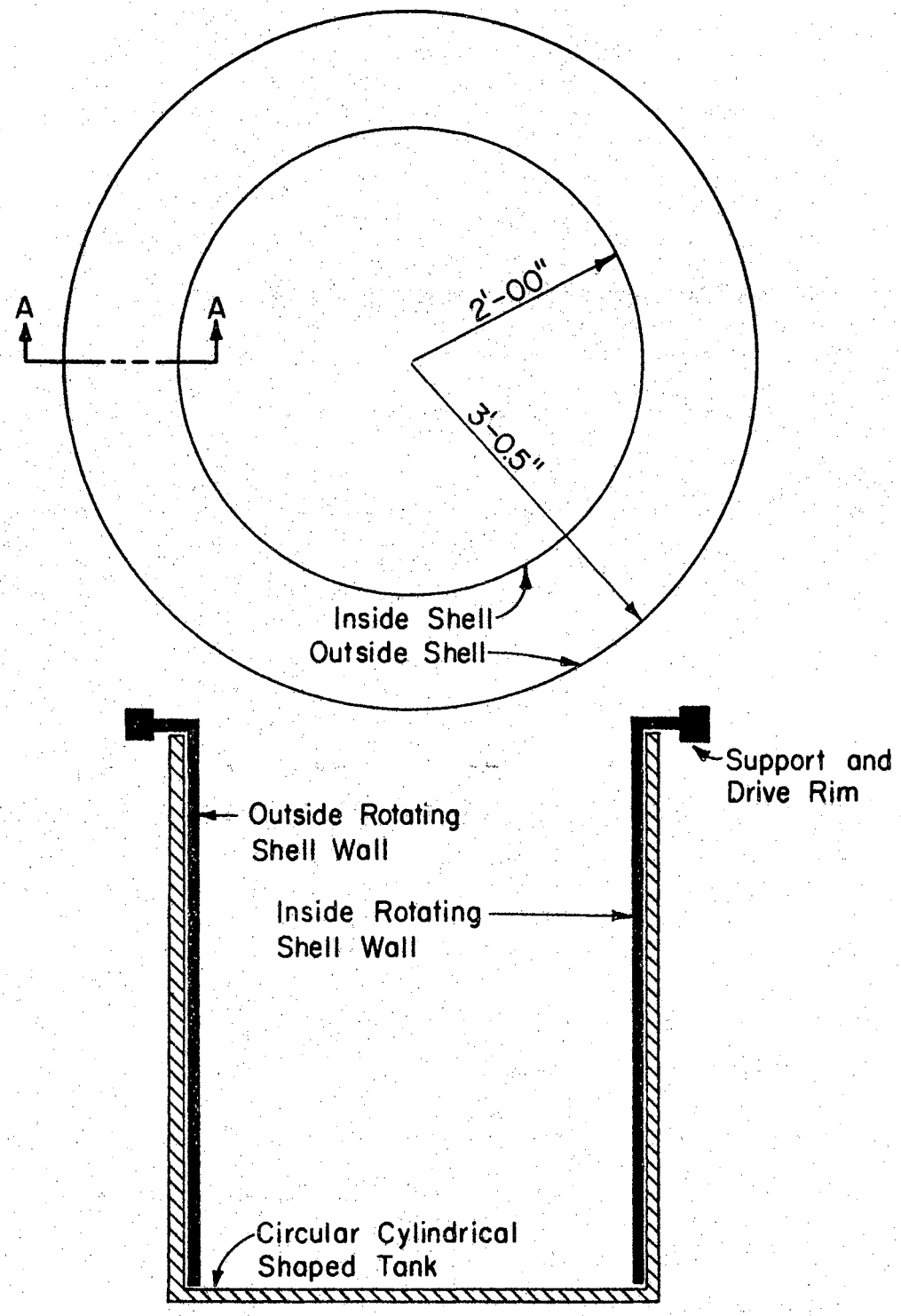


Figure 6 - Photograph of simulated channel apparatus.



SECTION A-A

Figure 7 - Plan and sectional view of simulated channel.

template.

The mechanically-agitated reactor was a flat-bottomed cylindrical pyrex vessel having a diameter of fifteen and one-quarter inches, and a depth of eighteen inches. Four stainless steel baffles which extended radially into the vessel one and one-fourth inches were equally spaced around the vessel. The mixing was provided by a four-inch square pitch marine impeller on a vertical shaft and positioned in the center of the reactor. The impeller was on the end of the shaft, and was positioned seven and one-half inches from the reactor bottom. Both impeller and shaft were stainless steel. The impeller was driven by a one-quarter horsepower motor together with a metallic traction-type compound planetary transmission having an output speed of 0 to 1100 rpm. Impeller speed was regulated by means of a micrometer control. The drive was calibrated in use by means of a Strobotac (type No. 631-BL, General Electric Company, Cambridge, Mass.). A photograph of the unit is shown in Figure 8.

Oxygen monitoring equipment consisted of the arrangement shown in Figure 9. Water was pumped from the bottom of the aeration chamber through a one-fourth inch rubber hose by means of a small centrifugal pump having a moulded rubber impeller and pump chamber. From the pump the water was passed through a one and one-half inch diameter by two and one-half inch high plexiglass chamber into which a Precision-Scientific lead-silver oxygen probe was inserted downward to within about one inch from the chamber bottom. A teflon-coated one and one-fourth inch magnet and a Sargent magnetic stirrer were used to ensure an adequate velocity across the face of the probe. The water entered near the bottom of the plexiglass chamber and was returned from the top

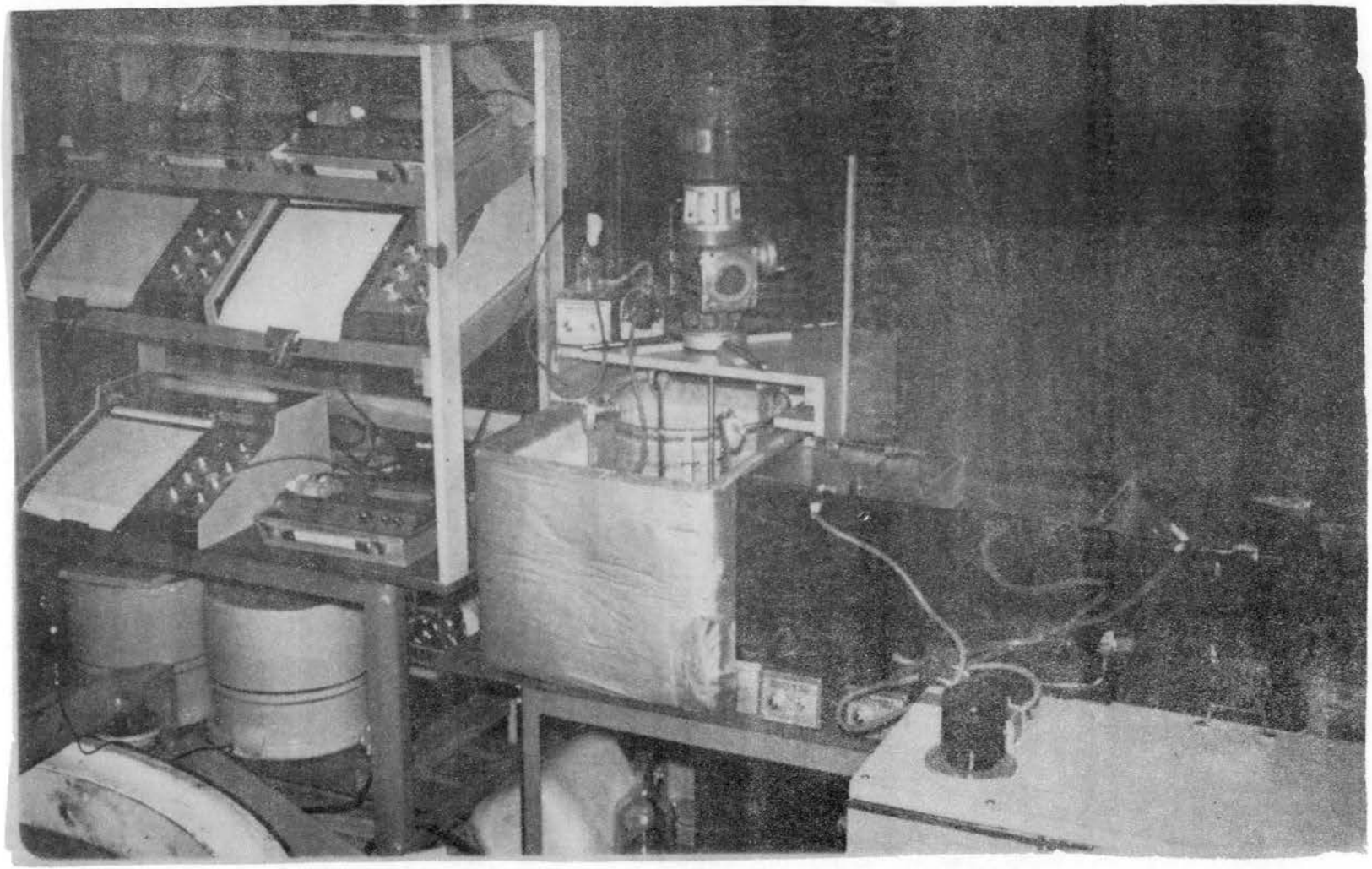


Figure 8 - Photograph of stirred tank apparatus, oxygen monitoring equipment, and water bath used in deoxygenation experiments.

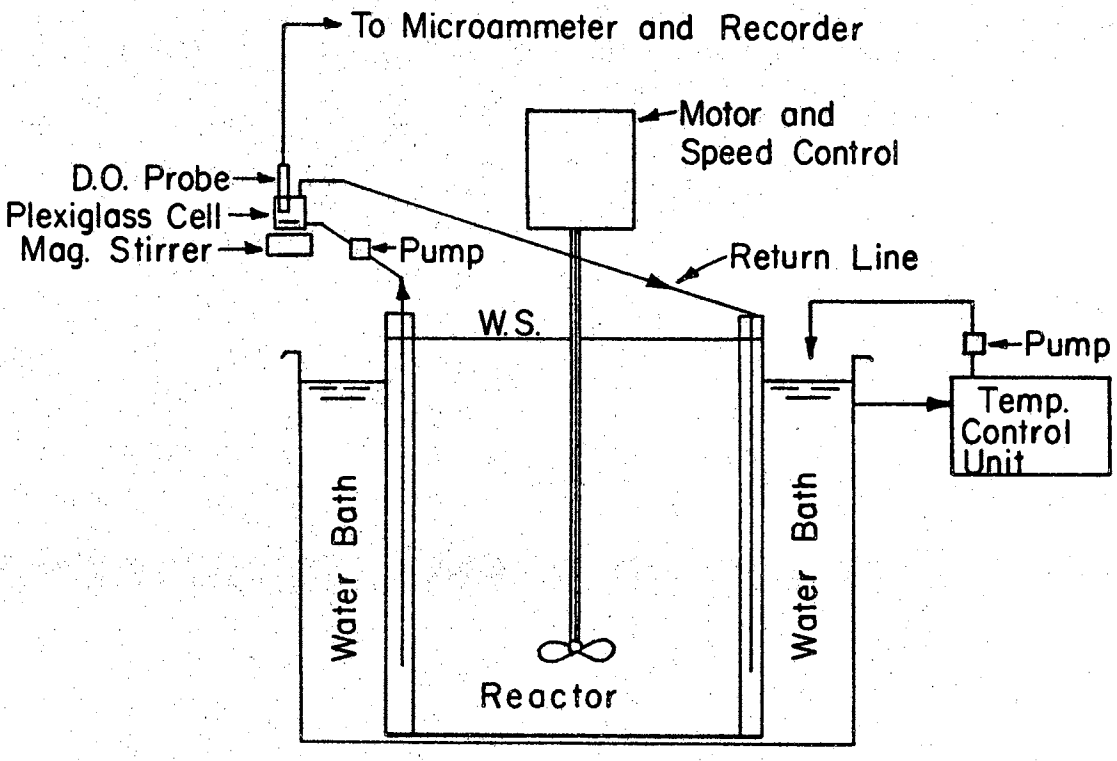


Figure 9 - Schematic diagram of stirred reactor and oxygen monitoring arrangement.

of the chamber to the bottom of the reactor. The hose used in the stirred tank was attached to a baffle to prevent any interference with the flow. Spacers were placed on the bottom of the plexiglass chamber to provide a one-fourth inch air space between the magnetic stirrer and the chamber to prevent heating the chamber. The following data are presented to give an indication of the amount of heating which can be realized from using a magnetic stirrer: A 250 ml beaker containing 100 ml water at a room temperature of 24°C was placed on a Sargent magnetic stirrer and the speed was adjusted to the midpoint of the scale. A one and one-fourth inch teflon magnet was used for mixing. After one hour the water temperature was 34°C, and after two hours the temperature was 36°C, which was 12° above the room temperature. Hence, without proper isolation, the magnetic stirrer can cause a considerable increase in the temperature of the contents of a stirred bottle.

The same procedures were used with the simulated channel to monitor O_2 concentration, except that nipples were placed in the channel bottom and the water was withdrawn and returned to the channel bottom. The monitoring system was completely closed, offering no opportunity for any reaeration to occur. The nipples in the channel were flush with the bottom to prevent any interference with the flow. Sargent Model SR stripchart recorders were used to monitor the dissolved oxygen concentration continuously.

A two and three-fourths inch diameter fan was used to pull air across the stirred reactor to ensure a constant oxygen pressure at the surface. The reactor vessel was placed in a water bath, and a Precision Lo-temptrol unit was used for temperature control.

3. Deoxygenation Experiments

The simulated channel and stirred tank reactor, together with the oxygen monitoring and recording arrangement and the temperature control unit used in these experiments, were the same as previously described for the reaeration experiments. A 12" x 36" x 13" deep covered water bath used for incubating the 2.4 liter bottles used in these experiments is shown in the right-hand portion of Figure 8. The water bath also provided a water seal for the bottles.

B. Experimental Procedures

1. Oxygen Solubility Studies

At the beginning of each experiment the two pyrex vessels were cleaned, rinsed with distilled water, and filled with twelve liters of water (14.6-inch depth). One vessel was filled with distilled water, and the other with water from the cold tap in the laboratory. Samples were taken at the beginning of the experiment for chemical analysis of the water, if analyses were to be made. The vessels were then either placed in the water bath or the refrigerator, depending on the temperature to be used.

The water was aerated for at least seventy-two hours before samples were taken for dissolved oxygen analysis. Samples were withdrawn by siphoning through a latex rubber hose directly into a standard BOD bottle. Three bottles were filled from each aeration vessel by allowing about 500 ml to overflow before adding 2 ml of manganous sulfate solution and 2 ml of alkali-iodide-azide reagent. After addition of these reagents, the bottle was immediately capped and vigorously mixed. The reagents were added with calibrated automatic pipets. The

precipitate was permitted to settle to approximately the midpoint of the bottles before they were shaken again and the precipitate allowed to re-settle. Two ml of concentrated sulfuric acid were then added to each bottle, and the contents mixed. A volumetric flask was used to transfer 203.0 ml to a 500 ml beaker for titration. A magnetic stirrer was used to provide agitation during the titration.

In all experiments samples were taken at 24-hour intervals until equilibrium conditions had been assured. Saturation conditions were assumed to prevail when the same saturation value was obtained on at least two successive days after the results had been corrected for barometric pressure. This procedure gave a minimum aeration period of five days for all experiments.

Several experiments were conducted by supersaturating the water using compressed oxygen at the beginning of the experiment. Sampling was not started for these experiments until after ninety-six hours following supersaturating. This was done because it was found that a longer period was required to reach equilibrium conditions from the supersaturated condition than from a condition of near saturation as found in the tap water.

2. Reaeration Experiments

The simulated channel and stirred tank were filled to the required depth with water from the cold tap in the laboratory. The rotating walls of the simulated channel were adjusted to the required speed by counting the revolutions for a 10-minute period. In all cases the walls were adjusted to give the same linear speed which gave an angular speed ratio for the two walls that was inversely proportional to the wall diameter. This gives an inside wall angular speed that is one and one-

half times greater than the outside wall speed.

Mean flow velocity in the simulated channel was then determined using an A. Ott small current meter (Model C1). Velocity measuring points, shown in Figure 12, were located so that all measurements represent equal areas of flow. The mean velocity was the average of 2-minute measurements taken at twenty-four positions for the 18-inch depth and at sixteen positions for the 12-inch depth. This is an extension of the procedure referred to in stream gauging as the "mid-section" method.

During periods when the tap water was below 20°C, hot water was mixed with the cold tap water to give a starting temperature of approximately 21°C, which was near an equilibrium condition with the laboratory temperature for the unit. The water was then aerated for twelve hours before adding 0.02 mg/l cobalt chloride catalyst, followed by the addition of sufficient sodium sulfite to remove 8.0 mg/l of oxygen.

The dissolved oxygen concentration was monitored continuously and recorded from before removing the oxygen until the end of the experiment. Samples were analyzed for oxygen content at sufficient intervals throughout the experiment to provide an accurate record of the sensitivity of the recording equipment. The simulated channel was emptied and cleaned before proceeding with another experiment.

The same procedure was used with reaeration experiments conducted in the stirred tank as was used with the simulated channel. However, most of these experiments were conducted at a controlled temperature by using a water bath and temperature control unit. The degree of agitation was controlled by adjusting the impeller speed.

3. Deoxygenation Studies

The mean velocity and channel wall speeds for the channel simulator

and the temperature control together with the degree of agitation for the stirred tank were established for these experiments in the same manner as given for the reaeration experiments.

Seed was collected on the evening prior to starting an experiment, and aerated over night in the laboratory by diffused air. The stirred reactor was also washed, filled with water, and reaerated overnight before starting an experiment. The simulated channel was washed, filled with water, and operated for about two hours with a strong solution of sodium hypochlorite to prevent biological solids carryover from one experiment to the next. The unit was then emptied, rinsed down with a hose prior to filling and aerating overnight before starting an experiment. Orthotolidine was used to check for any chlorine residual in the water before starting an experiment.

The following salts were also added to the reactor waters ten to twelve hours prior to starting an experiment:

(1) 1 ml/l phosphate buffer solution

(2) 1 ml/l magnesium sulfate solution

(3) 1 ml/l calcium chloride solution

(4) 1 ml/l ferric chloride solution

(5) 0.4 ml/l ammonium sulfate solution.

These solutions were prepared in accordance with Standard Methods (3) except for the ammonium sulfate solution, which contained 50 gr/l $(NH_4)_2SO_4$. Four-tenths ml/l of this solution was added to the open systems to provide additional nitrogen, since the substrate concentration in the reactors was higher than what is found in the BOD bottle. The BOD bottle dilution water was also aerated overnight by gently stirring with a marine impeller. Tap water was used and the required salts were

added in accordance with procedures given in Standard Methods. The water was mixed in a glazed ceramic vessel having a capacity of 30 liters.

At the start of the experiment in the open system, 5 ml/l of the the seed material were added followed by the addition of the substrates. The glucose was added from a standard solution containing 50 gm/l. Because of its low solubility, a suitable stock solution of the glutamic acid was not found feasible, and it was added directly to the reactor in the desired concentration. The contents of the reactors were mixed for about fifteen minutes before taking initial samples.

Samples were taken from a tee connection in the circulating system used in monitoring dissolved oxygen content (see Figure 9). DO was determined at each sampling period by the Winkler method to provide a frequent standardization of the probe and recorder. A sample was also obtained for the following analyses: COD, anthrone, viable count, optical density and, for some of the experiments, microscopic examination.

The stirred tank reactor was always operated at a speed of 184 rpm and depth of fifteen inches, giving a volume of 46 liters. The channel reactor was operated at a velocity of 0.49 fps and a depth of eighteen inches, giving a volume of 670 liters.

Five ml/l of seed and the substrate were added to the BOD dilution water at the same time as they were added to the open reactors. The contents were mixed, and ten 2.4 liter and fifteen 300 ml bottles were filled by siphoning through a rubber hose. Initial dissolved oxygen content was determined and a sample was taken for COD, anthrone carbohydrate, viable count and, for some experiments, microscopic examination. The ten 2.4 liter bottles were incubated in a water bath at 20°C. Five bottles were incubated under stirred conditions, and five were incubated

under quiescent conditions. The 300 ml BOD bottles were incubated in a BOD incubator at 20°C.

Samples were taken from the open systems for analyses at sufficient frequency to show the course of the biological and physical processes. During the lag period the frequency was twelve hours, and during the log growth and plateau phase the frequency was much greater in order to follow the rapid changes. After the plateau the frequency of sampling was again decreased to twelve hours.

In the 300 ml BOD bottles dissolved oxygen concentration was determined at 12-hour intervals. The contents of a mixed and a quiescent 2.4 liter bottle were analyzed every twenty-four hours for dissolved oxygen, COD, anthrone carbohydrate, viable count and, for some experiments, microscopic examination.

The seed used in experiments G, H, I, N, and O was grown up from an original sewage inoculum on the substrate to be used in a specific experiment. The culture was acclimated by repeated feeding of the substrate over a 7-day period. A three liter volume of seed was fed 50 mg/l of both glucose and glutamic acid daily for one week. Salts and buffer were also added daily, and the reactor was aerated and mixed with diffused air during the acclimation period. The same procedure was used to acclimate sewage seed to milk with 50 mg/l of non-fat dry milk solids being added daily. Experiments H and O were seeded with an acclimated seed containing a hay infusion. Jahn (61) has reported that the protozoa which feed mostly on bacteria may be helped by adding a little boiled hay infusion prepared by boiling a small quantity of hay in water. Therefore, a liter of the extract obtained from boiling hay was added to the seed used in these experiments at the beginning of the

acclimation period. The extract had the color of strong tea.

4. Oxygen Uptake in Experiments Conducted with High Initial Oxygen Tension

Dilution water was prepared in a 50 liter pyrex jar, using tap water and the buffer and salts as given in Standard Methods plus 0.4 ml $(NH_4)_2SO_4$ from a standard solution containing 50 gm/l of the salt. The water was oxygenated for about thirty minutes using compressed oxygen applied through three glass diffusers placed around the vessel at about one-third the radius from the vessel wall. Seed and sufficient substrate were added to give the required concentration for system A. After a brief mixing the bottles were filled for this system. After filling the bottles for system A, additional substrate was then added to the remaining liquid to give the required increase in substrate concentration for system B and the bottles for the second system were filled. This procedure was continued for the third and fourth systems.

Three 3/8 inch diameter latex hoses were used concurrently as siphons in filling the bottles which were filled and capped as rapidly as possible so as to give uniform conditions in all bottles within a system. Vigorous aeration was continued until all bottles were filled. A bottle from each system was analyzed for initial DO, and good agreement was found for the initial dissolved oxygen concentration in the four systems. It was possible to get about 35 mg/l of oxygen in solution using this procedure. The bottles were incubated at $20^{o}C$ in a standard BOD incubator.

C. Methods of Analysis

1. Chemical Oxygen Demand (COD)

The COD procedure employed in this research was the same as the alternate procedure given in paragraph 4.6, Section IV, of Standard Methods (3), except 10 ml of 0.04 N standard potassium dichromate was added to each flask, and 0.04 N ferrous ammonium sulfate was used in the back-titration. Mercuric sulfate and silver sulfate were used in all experiments. The dichromate solution and mercuric sulfate were added to the flask before adding the 20 ml sample. When sufficient samples were obtained for refluxing, sulfuric acid containing silver sulfate catalyst was added prior to refluxing.

2. Anthrone Carbohydrate

The concentration of carbohydrates was determined by the anthrone test as proposed by Gaudy (62). Nine ml of anthrone reagent plus a 3 ml sample were employed. Samples were filtered through a 0.45μ filter at the time of collection and immediately frozen until the termination of each experiment. The samples for the entire experiment were then thawed and analyzed. Glucose standards were run with each set of analysis. Optical density was read at 620 mμ.

3. Biochemical Oxygen Demand (BOD)

The procedures used in this research were in accordance with those outlined in Standard Methods (3). The Winkler method with the azide modification was used in all dissolved oxygen determinations.

4. Optical Density

Optical density measurements were obtained for samples from the open

systems using a Bausch and Lomb Spectronic 20 Spectrophotometer at 540 mμ and a 3/4 inch diameter sample tube.

5. Viable Counts

Samples were taken directly from the respective units, using sterile pipets for making serial dilutions for plating. Difco nutrient agar with 0.5 per cent Bacto agar added was used in all cases. The spot plate technique (63) was used in all experiments. Four 0.02 ml spots from each of three dilutions from one sample were applied per plate. The plates were incubated at $25^{o}C$ for forty-eight hours before counting, using a Quebec Colony Counter. All media, glassware, and equipment used in the viable count studies were sterilized in accordance with procedures given in Standard Methods (3).

6. Microscopic Counts of Protozoa

Protozoa counts were made with a light field microscope at 125 magnification using a Sedgwich-Rafter counting cell. The microscope used gave a field of view 1 mm x 1 mm at this magnification and the depth of the counting cell was 1 mm. Therefore each field represented a volume of 10^{-3} cc. The count was taken as the average of twenty fields from random positions of the cell times 1000.

7. Chemical Analyses of Tap Water

The routine chemical analyses consisting of free acidity, alkalinity, chlorides, and pH were made in accordance with procedures given in Standard Methods (3).

CHAPTER V

RESULTS

A. Oxygen Solubility

Seventy experiments were conducted on the solubility of oxygen in distilled and tap water. The data represent results obtained from triplicate samples taken after equilibrium conditions had been established. Figure 10 shows the algebraic difference in the observations of this research and the oxygen saturation concentration reported by Standard Methods (3), Truesdale and his associates (4), and the ASCE Progress Report (5).

The solubility of oxygen in water observed in this research lies between the values reported by Truesdale and his associates and those given in the ASCE Progress Report for temperatures less than 20°C. From twenty to 25°C the results of this study were essentially in agreement with those of the Truesdale study. At 30° the results of this study were in agreement with values reported in the ASCE Progress Report, and about 0.21 mg/l lower than values reported in Standard Methods. Figure 11 shows a plot of the O_2 solubility values found in this study and the reported solubilities from Standard Methods, the Truesdale group, and the ASCE Progress Report. The curve for Standard Methods was not plotted for temperatures below 12°C, since the values are essentially the same as those given by the ASCE Progress Report.

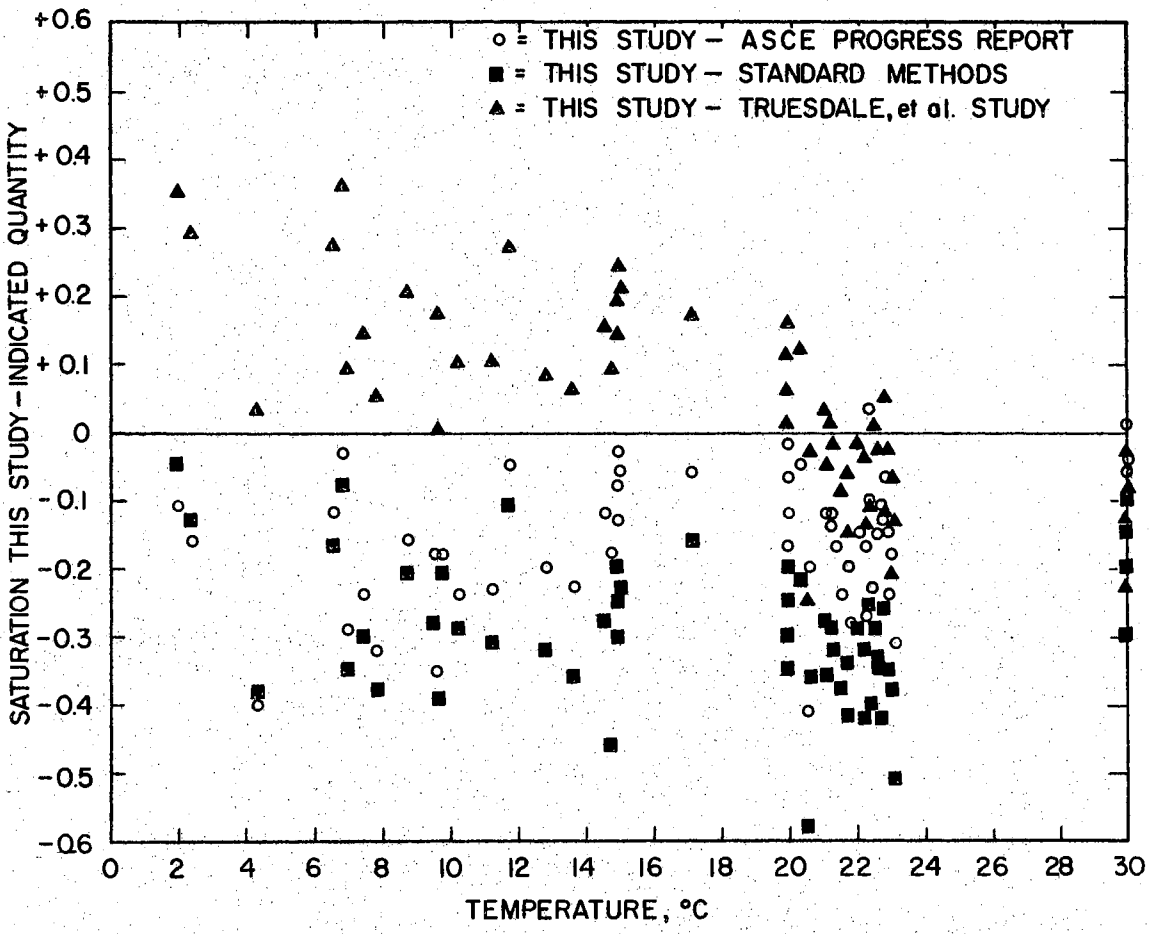


Figure 10 - Difference in dissolved oxygen saturation values observed in this study and values from indicated study.

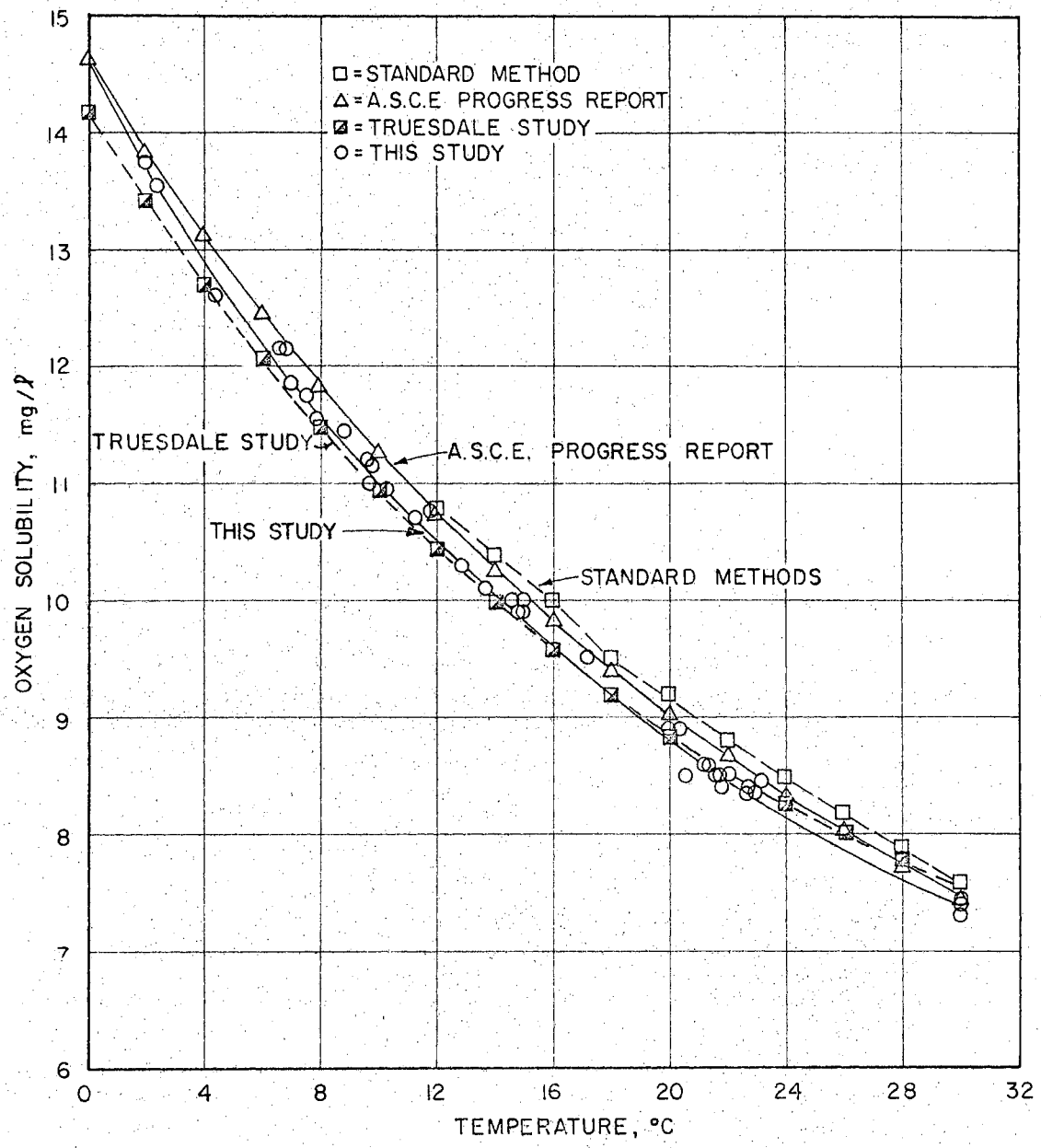


Figure 11 - Oxygen solubility in distilled water at 760 mm pressure as reported from the indicated study.

A least squares analysis of the results of the present research gave the following equation for the solubility of oxygen in distilled water or the tap water used in this research:

$$C_s = \frac{445}{30.2 + T} \tag{55}$$

where C_s is the oxygen solubility in mg/l, T is the temperature in degrees centigrade. The standard error of estimate was 0.08 mg/l for the data.

Table IV gives calculated oxygen solubilities based on the above equation, as well as those reported by three other sources.

Table V gives the chemical analysis of tap water from the Oklahoma State University water system which was used in this study. Conductivity measurements were made on the distilled water over a period of several months, and it was found to vary from about 1.1 to 1.8 micromhos.

B. Reaeration

1. Simulated Channel

Thirty-two reaeration experiments were conducted to establish the relationship between mean velocity and the reaeration rate constant. This relationship has been previously reported by Isaacs and Gaudy (2); however, the rims on the revolving walls were replaced during the interim which existed between that research and the present research. Therefore it was necessary that the relationship be re-established.

Twenty-four mean velocity measurements were made during the reaeration experiments. Several velocity measurements were made at each wall speed and water depth used in this study so as to give velocity data from before and after each set of experiments.

Table VI shows the point velocity values obtained at three wall

TABLE IV

SOLUBILITY OF OXYGEN IN DISTILLED WATER AT 760 mm PRESSURE AS REPORTED BY INDICATED STUDY

Temp. °C	This Study	Truesdale Study	ASCE Report	Standard Methods
0	14.73	14.16	14.65	14.6
1	14.26	13.77	14.25	14.2
2	13.82	13.40	13.86	13.8
3	13.40	13.05	13.49	13.5
4	13.01	12.70	13.13	13.1
5	12.64	12.37	12.79	12.8
6	12.29	12.06	12.46	12.5
7	11.97	11.76	12.14	12.2
8	11.65	11.47	11.84	11.9
9	11.36	11.19	11.55	11.6
10	11.07	10.92	11.27	11.3
11	10.81	10.67	11.00	11.1
12	10.55	10.43	10.75	10.8
13	10.31	10.20	10.50	10.6
14	10.07	9.98	10.26	10.4
15	9.84	9.76	10.03	10.2
16	9.63	9.56	9.82	10.0
17	9.43	9.37	9.61	9.7
18	9.23	9.18	9.40	9.5
19	9.04	9.01	9.21	9.4
20	8.86	8.84	9.02	9.2
21	8.69	8.68	8.84	9.0
22	8.52	8.53	8.67	8.8
23	8.36	8.38	8.50	8.7
24	8.21	8.25	8.33	8.5
25	8.06	8.11	8.18	8.4
26	7.92	7.99	8.02	8.2
27	7.78	7.86	7.87	8.1
28	7.65	7.75	7.72	7.9
29	7.51	7.64	7.58	7.8
30	7.39	7.53	7.44	7.6

TABLE V

CHEMICAL ANALYSES OF TAP WATER

Date (1967)	6-19	6-23	7-15	7-20	8-15	8-28	9-7
Acidity mg/l as $CaCO_3$	3.2	8.6	7.5	5.2	3.1	5.3	4.0
Alkalinity mg/l as $CaCO_3$	160	154	133	143	91	152	118
Chlorides mg/l as Cl^-	80	82	66	80	69	80	66
pH	7.85	7.6	7.5	7.7	7.5	7.6	7.6
Conductivity micromhos		600	550	540	560	560	540

Conductivity of distilled water = 1.1 to 1.8 micromhos.

TABLE VI

POINT VELOCITIES IN FEET PER SECOND FOR INDICATED DEPTH AND RIM SPEED

Point	12" Depth Rim Speed 6-4	12" Depth Rim Speed 9-6	12" Depth Rim Speed 12-8	18" Depth Rim Speed 4.5-3	18" Depth Rim Speed 6-4	18" Depth Rim Speed 9-6	18" Depth Rim Speed 12-8
A-1	0.614	0.872	1.194	0.492	0.616	0.962	1.228
A-2	0.635	0.830	1.228	0.501	0.611	0.933	1.291
A-3	0.645	0.859	1.268	0.511	0.629	0.930	1.319
A-4	0.687	0.949	1.325	0.526	0.648	0.949	1.342
A-5				0.549	0.669	0.954	1.399
A-6				0.566	0.727	0.999	1.455
B-1	0.595	0.817	1.154	0.477	0.616	0.843	1.171
B-2	0.585	0.804	1.126	0.482	0.616	0.856	1.183
B-3	0.603	0.825	1.154	0.488	0.606	0.846	1.211
B-4	0.624	0.901	1.200	0.496	0.611	0.869	1.228
B-5				0.499	0.598	0.901	1.256
B-6				0.517	0.648	0.904	1.291
C-1	0.574	0.817	1.114	0.465	0.608	0.862	1.165
C-2	0.561	0.814	1.091	0.458	0.582	0.822	1.137
C-3	0.553	0.811	1.097	0.452	0.585	0.785	1.137
C-4	0.550	0.817	1.103	0.458	0.585	0.804	1.143
C-5				0.463	0.587	0.896	1.160
C-6				0.475	0.608	0.888	1.171
D-1	0.606	0.872	1.171	0.484	0.632	0.904	1.205
D-2	0.611	0.875	1.205	0.475	0.616	0.893	1.200
D-3	0.585	0.862	1.165	0.480	0.608	0.869	1.222
D-4	0.598	0.864	1.120	0.475	0.627	0.906	1.257
D-5				0.477	0.619	0.880	1.262
D-6				0.496	0.645	0.935	1.257
Average	0.607	0.849	1.17	0.490	0.621	0.891	1.237

Note: Rim speed is given in revolutions per minute for inside and outside rims.

speeds for both a twelve and 18-inch water depth. The positions of the velocity measurements are shown in Figure 12. The velocity data given in Table VI indicate that the velocity did not vary greatly over the channel cross-section. The highest point velocities were observed near the channel walls and near the surface, while the lowest velocity occurred near the center and at the bottom of the channel. The same type of vertical velocity distribution is found in natural streams. Excellent agreement was found between successive velocity measurements at a point at any given wall speed.

Table VII gives a composite of the calculated mean velocity values together with the average velocity for each depth and rim speed used in this study. The average mean velocity was used in the reaeration rate constant determinations since the average value from several measurements is more nearly the true velocity than any single measurement.

The composite data for the thirty-two reaeration experiments conducted in the simulated channel are given in Table VIII. The data are listed by velocity-depth groups consistent with the designations used in Table VII. Column 3 in the table gives the inside wall and outside wall rotational speed, respectively, in revolutions per minute. The velocity data given in column 6 are the average values for the respective group of measurements. The kinematic viscosity values as given in column 7 may be found in most textbooks and reference books related to fluid properties. Column 8 gives the hydraulic mean depth or hydraulic radius which is the area of flow divided by the wetted perimeter. The Reynolds number, N_{Re}, is the ratio of inertia to viscous forces and is given by the following equation:

$$N_{Re} = \frac{UD\rho}{\mu} = \frac{UD}{\nu} \tag{56}$$

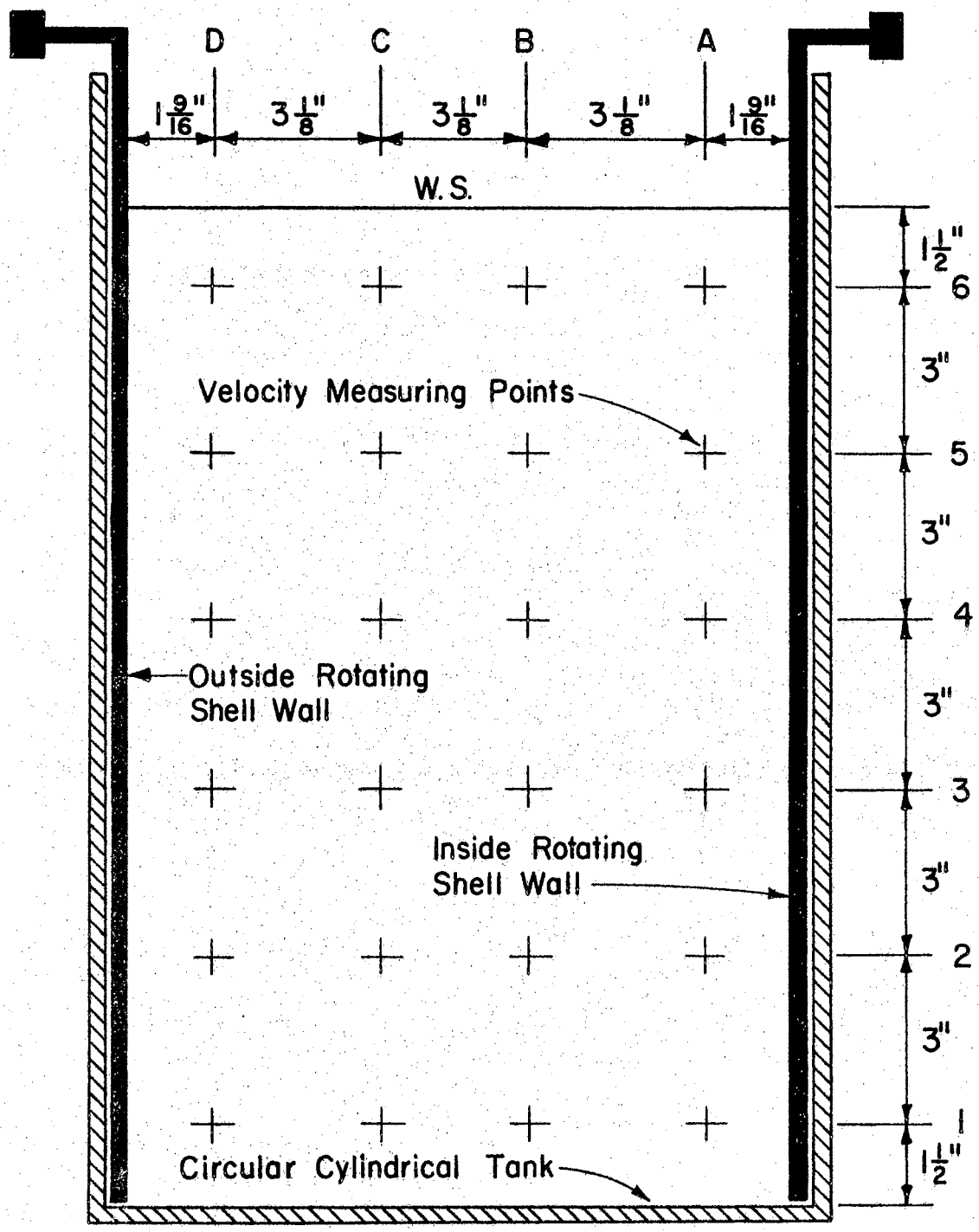


Figure 12 - Velocity measuring points for simulated channel.

TABLE VII

MEAN VELOCITY FOR SIMULATED CHANNEL

Group No.	Exp. No.	Rim Speed	Depth	Velocity
A	1	4.4-2.9	18"	0.474
	2			0.465
	3			0.460
	Average			0.466
B	1	4.5-3.0	18"	0.490
	2			0.490
	3			0.490
	Average			0.490
C	1	6-4	12"	0.596
	2			0.607
	3			0.600
	Average			0.601
D	1	6-4	18"	0.614
	2			0.624
	3			0.627
	4			0.622
	5			0.621
	Average			0.622
E	1	9-6	12"	0.842
	2			0.849
	3			0.882
	Average			0.858
F	1	9-6	18"	0.891
	2			0.896
	3			0.888
	Average			0.892
G	1	12-8	12"	1.17
	Average			1.17
H	1	12-8	18"	1.246
	2			1.253
	3			1.237
	Average			1.245

TABLE VIII

COMPOSITE DATA FOR REAERATION EXPERIMENTS IN SIMULATED CHANNEL

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
# Group	# Exp.	Rim Speed*	Depth ft	Temp °C	Vel. fps	$\nu \times 10^5$ ft^2/sec	R feet	$N_{Re} \times 10^{-4}$	f	G Sec^{-1}	$Gx10^{-3}$ hr^{-1}	K_{2-T} hr^{-1}	K_{2-20^o} hr^{-1}	k_{2-20^o} hr^{-1}	$G/H^{3/2}$ $x10^{-3}$	$U/H^{3/2}$
C	1	6 -4	1.0	21.4	0.601	1.046	0.343	1.97	0.0189	11.96	43.06	0.154	0.149	0.0647	43.06	0.601
	2	6 -4	1.0	21.6	0.601	1.046	0.343	1.97	0.0189	11.96	43.06	0.153	0.147	0.0638	43.06	0.601
	3	6 -4	1.0	21.8	0.601	1.046	0.343	1.97	0.0189	11.96	43.06	0.150	0.145	0.0630	43.06	0.601
D	4	6 -4	1.5	23.0	0.622	1.012	0.386	2.37	0.0181	11.81	42.52	0.083	0.077	0.0334	23.15	0.339
	5	6 -4	1.5	23.3	0.622	1.012	0.386	2.37	0.0181	11.81	42.52	0.083	0.077	0.0334	23.15	0.339
	6	6 -4	1.5	23.0	0.622	1.012	0.386	2.37	0.0181	11.81	42.52	0.087	0.081	0.0352	23.15	0.339
	7	6 -4	1.5	23.0	0.622	1.012	0.386	2.37	0.0181	11.81	42.52	0.086	0.080	0.0347	23.15	0.339
F	8	9 -6	1.5	23.8	0.892	0.992	0.386	3.47	0.0168	19.73	71.03	0.137	0.125	0.0543	38.67	0.486
	9	9 -6	1.5	23.6	0.892	0.992	0.386	3.47	0.0168	19.73	71.03	0.136	0.125	0.0543	38.67	0.486
	10	9 -6	1.5	23.9	0.892	0.992	0.386	3.47	0.0168	19.73	71.03	0.132	0.121	0.0526	38.67	0.486
	11	9 -6	1.5	24.3	0.892	0.992	0.386	3.47	0.0168	19.73	71.03	0.128	0.116	0.0504	38.67	0.486
E	12	9 -6	1.0	23.3	0.858	1.039	0.343	2.83	0.0175	19.70	70.92	0.232	0.214	0.0929	70.92	0.858
	13	9 -6	1.0	21.9	0.858	1.039	0.343	2.83	0.0175	19.70	70.92	0.230	0.220	0.0955	70.92	0.858
	14	9 -6	1.0	21.9	0.858	1.039	0.343	2.83	0.0175	19.70	70.92	0.213	0.204	0.0886	70.92	0.858
H	15	12 -8	1.5	21.9	1.245	1.039	0.386	4.63	0.0159	30.92	111.31	0.143	0.137	0.0595	60.59	0.678
	16	12 -8	1.5	21.8	1.245	1.039	0.386	4.63	0.0159	30.92	111.31	0.147	0.141	0.0612	60.59	0.678
	17	12 -8	1.5	22.0	1.245	1.039	0.386	4.63	0.0159	30.92	111.31	0.158	0.151	0.0656	60.59	0.678
G	18	12 -8	1.0	22.0	1.17	1.041	0.343	3.85	0.0165	30.44	109.58	0.299	0.285	0.1237	109.58	1.17
	19	12 -8	1.0	21.8	1.17	1.041	0.343	3.85	0.0165	30.44	109.58	0.304	0.291	0.1264	109.58	1.17
	20	12 -8	1.0	21.8	1.17	1.041	0.343	3.85	0.0165	30.44	109.58	0.299	0.286	0.1242	109.58	1.17
	21	12 -8	1.0	21.8	1.17	1.041	0.343	3.85	0.0165	30.44	109.58	0.292	0.279	0.1212	109.58	1.17
B	22	4.5-3	1.5	23.2	0.49	1.006	0.386	1.88	0.0191	8.50	30.60	0.069	0.064	0.278	16.66	0.267
	23	4.5-3	1.5	23.2	0.49	1.006	0.386	1.88	0.0191	8.50	30.60	0.074	0.069	0.0300	16.66	0.267
	24	4.5-3	1.5	23.2	0.49	1.006	0.386	1.88	0.0191	8.50	30.60	0.070	0.065	0.0282	16.66	0.267
	25	4.5-3	1.5	23.2	0.49	1.006	0.386	1.88	0.0191	8.50	30.60	0.071	0.066	0.0287	16.66	0.267
	26	4.5-3	1.5	23.2	0.49	1.006	0.386	1.88	0.0191	8.50	30.60	0.071	0.066	0.0287	16.66	0.267
F	27	9 -6	1.5	23.5	0.892	1.001	0.386	3.44	0.0168	19.64	70.70	0.134	0.123	0.0534	38.49	0.486
F	28	9 -6	1.0	20.8	0.858	1.067	0.343	2.76	0.0176	19.48	70.13	0.212	0.208	0.0903	70.13	0.858
D	29	6 -4	1.5	24.2	0.622	0.985	0.386	2.43	0.0182	12.00	43.20	0.072	0.065	0.0282	23.52	0.339
C	30	6 -4	1.0	22.8	0.601	1.017	0.343	2.02	0.0187	12.06	43.42	0.172	0.161	0.0699	43.42	0.601
A	31	4.4-2.9	1.5	23.7	0.474	0.997	0.386	1.84	0.0193	8.17	29.41	0.083	0.076	0.0330	16.01	0.258
	32	4.4-2.9	1.5	23.2	0.474	1.006	0.386	1.83	0.0193	8.13	29.28	0.076	0.071	0.0308	15.94	0.258

where U is the mean velocity, D is a characteristic length (for open channel systems the hydraulic radius is used), and ν is the kinematic viscosity. The Reynolds number is dimensionless, and any consistent system of units may be employed in its use.

The dimensionless friction factor, f, is related to the Reynolds number and the character of the channel. There have been various equations proposed for calculating the friction factor for flow in smooth and rough pipes and channels (12). The friction factor values found in column 10 of the composite data were calculated by the Prandtl-von Karman equation for smooth channels, which is

$$\frac{1}{\sqrt{f}} = 2 \log \left[N_{Re} \sqrt{f} \right] + 0.40 \qquad (57)$$

Since the mean velocity is related to the friction factor which, in turn, is related to velocity, it is noted that the equation requires a trial and error solution. For this reason, nomograms are a more popular means of evaluating the friction factor. One form of these nomograms is commonly termed "Moody Curves." These may be found in textbooks on hydraulics (64).

The velocity gradients, G, given in columns 11 and 12, were calculated from Equation 40, which is

$$G = \sqrt{\frac{f}{8} \frac{U^3}{\nu D}}$$

The characteristic length for expressing the depth D for open channel flow is the hydraulic mean depth. The units of G are sec^{-1}, as given in column 11. However, G is given in hr^{-1} in column 12, which agrees with the units of K_2 and these values are used in the regression analyses. The lb-ft/sec system is used in the analyses; however, since the

friction factor is dimensionless, the equation is equally applicable to either the metric or English system of measurement, since time units are common to both systems.

The reaeration rate constants given in column 13 were calculated from the reaeration data for the respective experiments. The K_2 values were adjusted to a standard temperature of 20°C by the reaeration rate-temperature relation proposed by the ASCE Committee on Sanitary Engineering Research (65). The relationship is given by

$$K_{2-T} = K_{2-20^o}\ 1.0241^{T-20} \tag{58}$$

where T is the temperature in degrees centigrade, K_{2-T} is the reaeration rate constant at the respective temperature, and K_{2-20^o} is the rate at 20°C.

The data given in columns 13 and 14 were obtained by using natural logarithms, and the reaeration rate constants given in column 15 are for use with common logarithms (k = 0.4343K).

The data from this research were analyzed to give the reaeration rate in terms of the mean velocity as proposed by Isaacs and Gaudy (2), and also to give the reaeration rate constant in terms of the velocity gradient, G hr^{-1}.

The relation between the reaeration rate constant and velocity was found to be

$$K_{2-20^o} = 0.003 + 0.2417 \left[U/H^{3/2} \right] \tag{59}$$

where K_{2-20^o} is the reaeration rate in $hours^{-1}$ at 20°C, U is the mean velocity in ft/sec, and H is the depth of flow in feet. The plot of the reaeration rate constant versus $U/H^{3/2}$ is given in Figure 13. The correlation coefficient for the data was 0.992. The intercept of 0.003 is

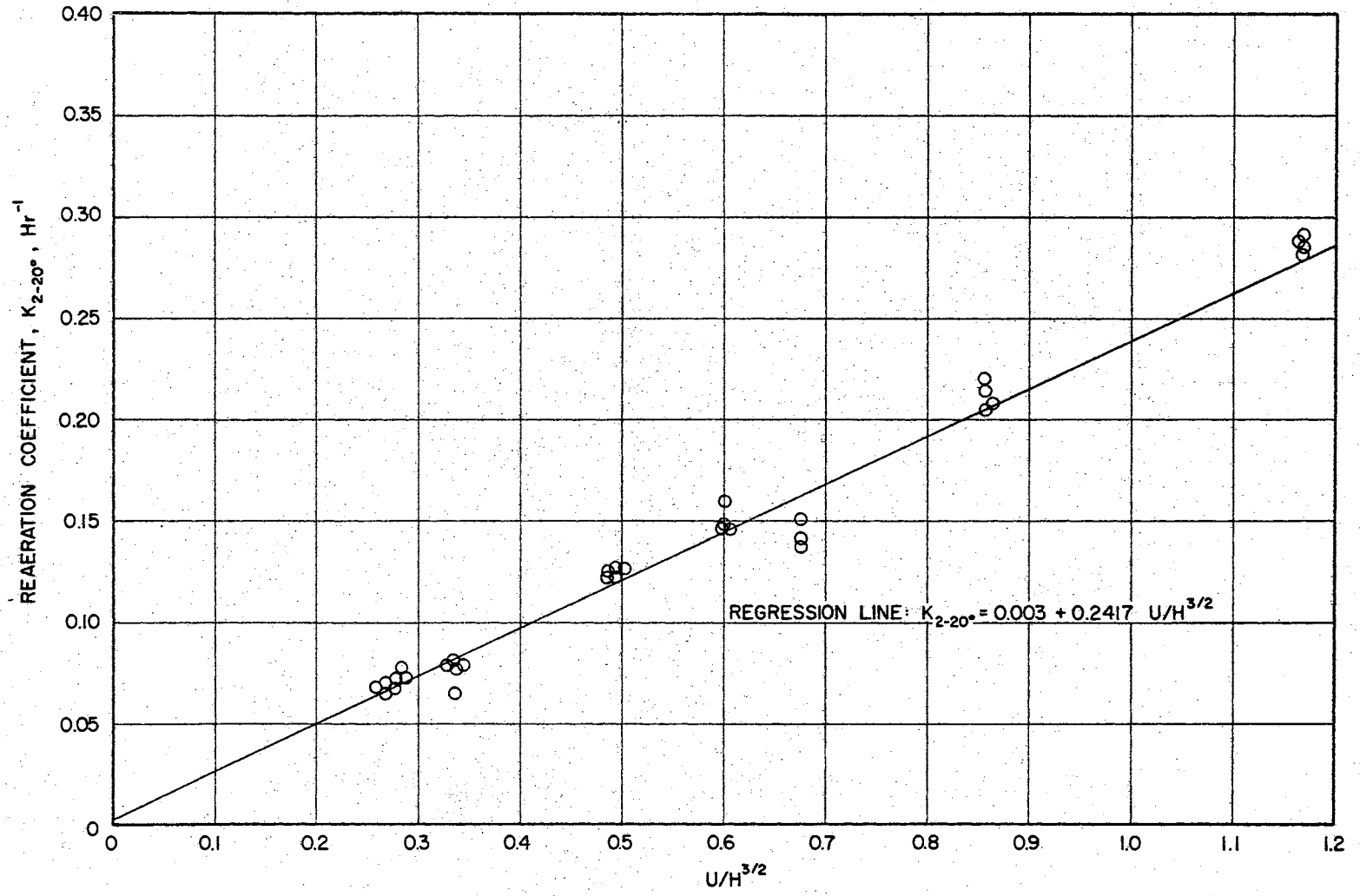


Figure 13 - Regression line for relationship between reaeration rate in simulated channel and mean velocity.

small and can be omitted without causing a significant change in the calculated value of K_2. This gives the following equation:

$$K_{2\text{-}20^o} = 0.2417 \left[U/H^{3/2}\right] \tag{60}$$

A plot of the reaeration coefficient versus $G/H^{3/2}$ is given in Figure 14. The regression equation for K_2, $hour^{-1}$ in terms of the velocity gradient was

$$K_{2\text{-}20^o} = 0.0292 + 2.367 \times 10^{-6} \left[G/H^{3/2}\right] \tag{61}$$

where G is in $hours^{-1}$, and the depth H is in feet. The intercept of 0.0292 is not insignificant in this case and cannot be omitted.

It is emphasized that the equations reported herein are for turbulent flow and therefore do not apply when the velocity gradient is zero. The reaeration rate constant at zero G was found by experimentation to be 0.0097 $hour^{-1}$.

The data from the present research were combined with data previously obtained with the experimental apparatus by Isaacs and Gaudy (2). A plot of the combined data is shown in Figure 15, and the regression equation for these data was given by

$$K_{2\text{-}20^o} = 0.0430 + 2.666 \times 10^{-6} \left[G/H^{3/2}\right] \tag{62}$$

where K_2 and G each have dimensions of $hour^{-1}$, and H is in feet. The correlation coefficient was 0.987.

The regression of $K_{2\text{-}20^o}$ on $U/H^{3/2}$ for the combined data was

$$K_{2\text{-}20^o} = -0.0283 + 0.3252 \left[U/H^{3/2}\right] \tag{63}$$

and the correlation coefficient was 0.989.

It seems evident from the correlation coefficients for Equations 59

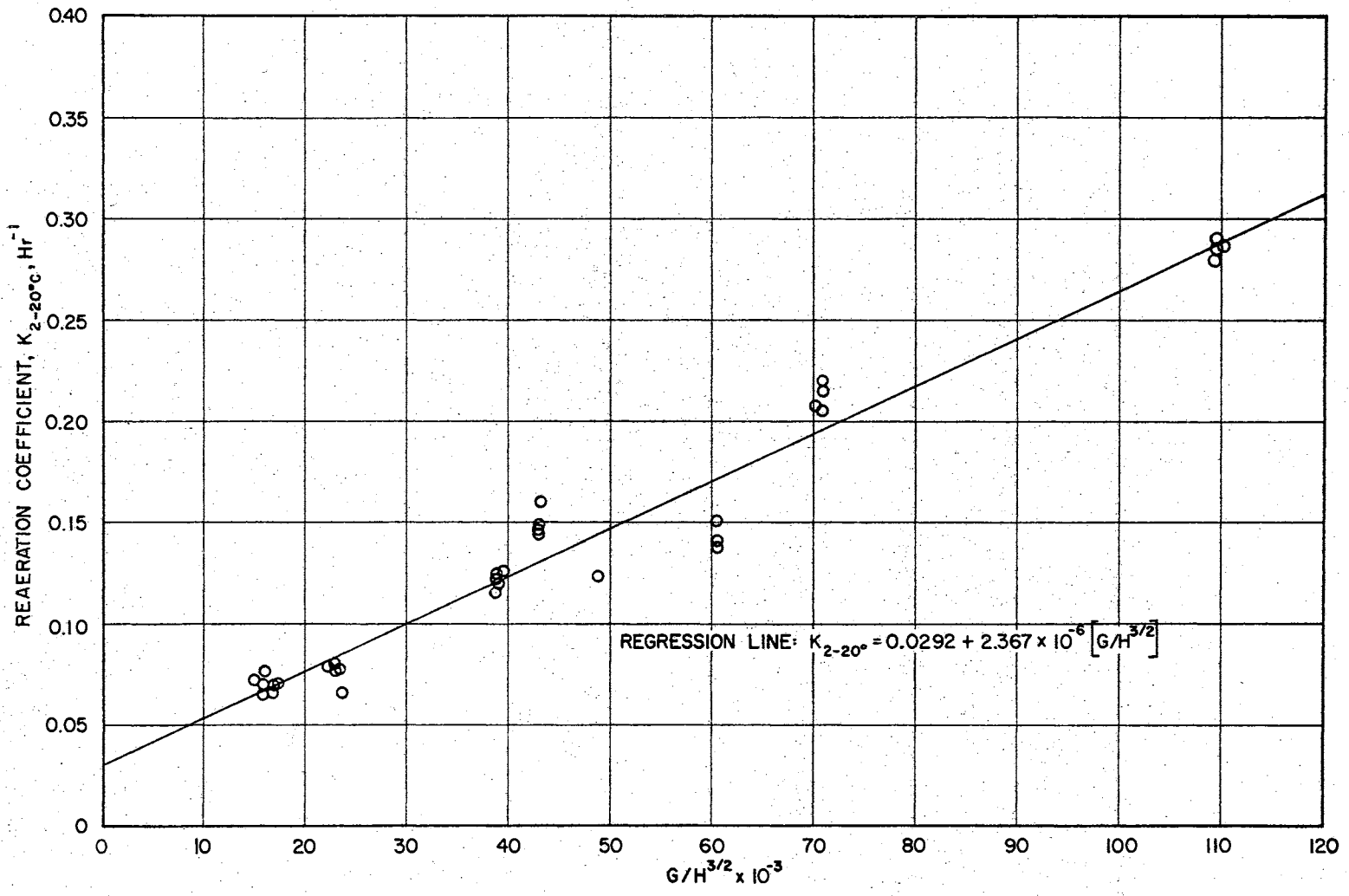


Figure 14 - Regression line for relationship between reaeration rate in simulated channel and velocity gradient.

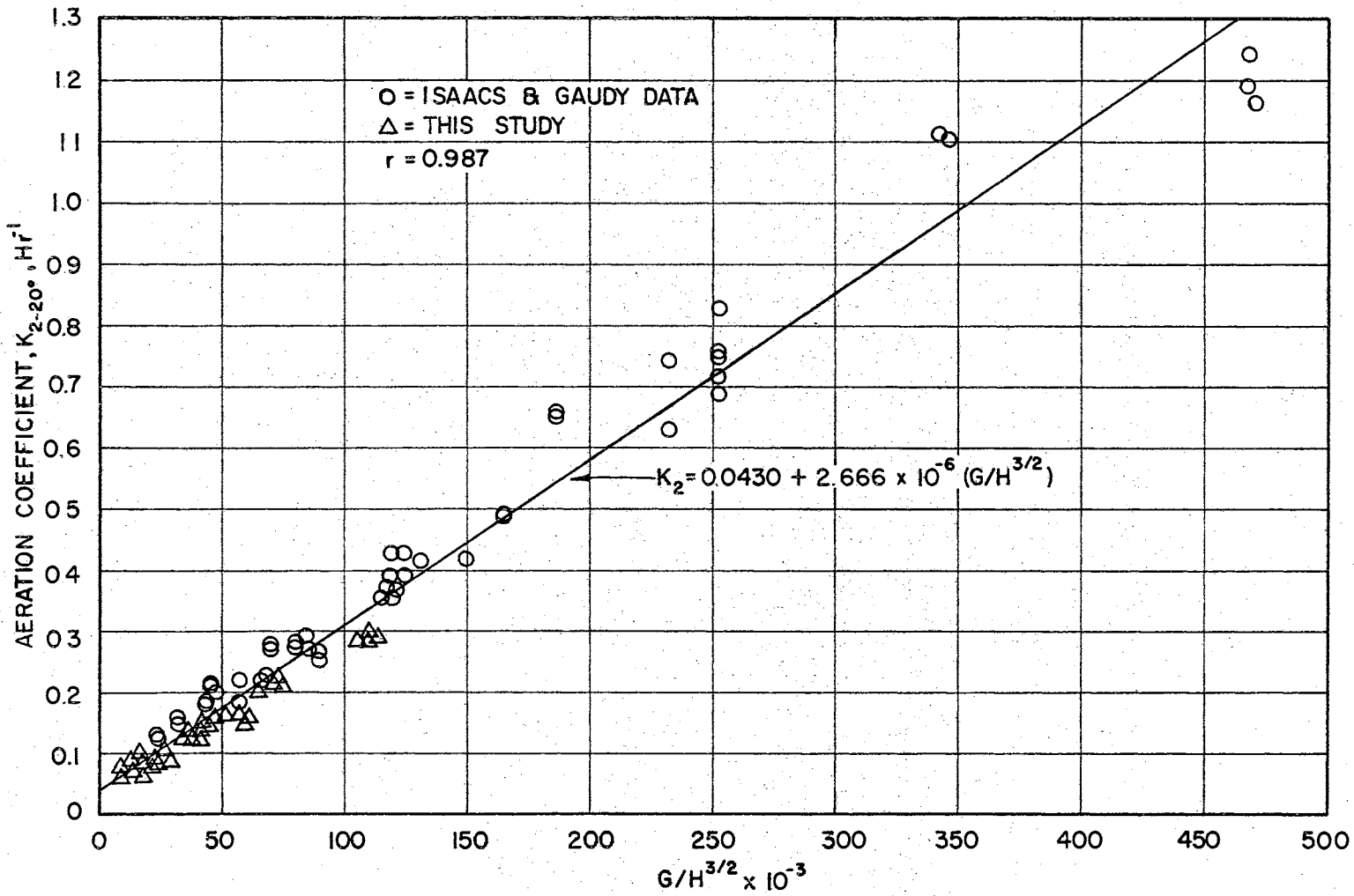


Figure 15 - Regression line for combined data from this research and that reported by Isaacs.

through 63 that the reaeration data correlates equally well with either the velocity gradient, G, or the mean velocity, U.

2. Stirred Tank

Seventy-nine reaeration experiments were conducted in the stirred tank reactor. The experiments covered a range of impeller speeds from 184 to 736 rpm, and reaeration rates from 0.089 to 1.25 hr^{-1} (log base e).

The impeller speed was calibrated with the drive micrometer position as given in Chapter IV of this thesis. The data are presented in Figure 16, and the impeller speed was given by

$$\text{Shaft speed, rev/min} = 36.8 \left[\text{dial position}\right] \tag{64}$$

The composite data for the reaeration experiments are given in Table IX. The power input to the system, P, ft-lb/sec, as given in column 4 of Table IX is for a 4-inch square-pitch marine impeller. The following equation for power input was developed from data reported by the equipment manufacturer (66), using the relationship given in Equation 47:

$$P, \frac{\text{ft-lb}}{\text{sec}} = 0.150 \times 10^{-6} N^3 \tag{65}$$

or

$$\log P = -6.832 + 3.0 \log N \tag{66}$$

where N is the impeller speed in revolutions per minute. The water viscosity as given in column 6 may be found in hydraulic reference material. Column 7 gives the reaeration rate constants for the respective experiments. The K_2 values are adjusted to $20^{o}C$ by Equation 58 and presented in column 8. The data in columns 7 and 8 are for use with natural logarithms, and the data in column 8 have been adjusted for use with common logarithms and presented in column 9.

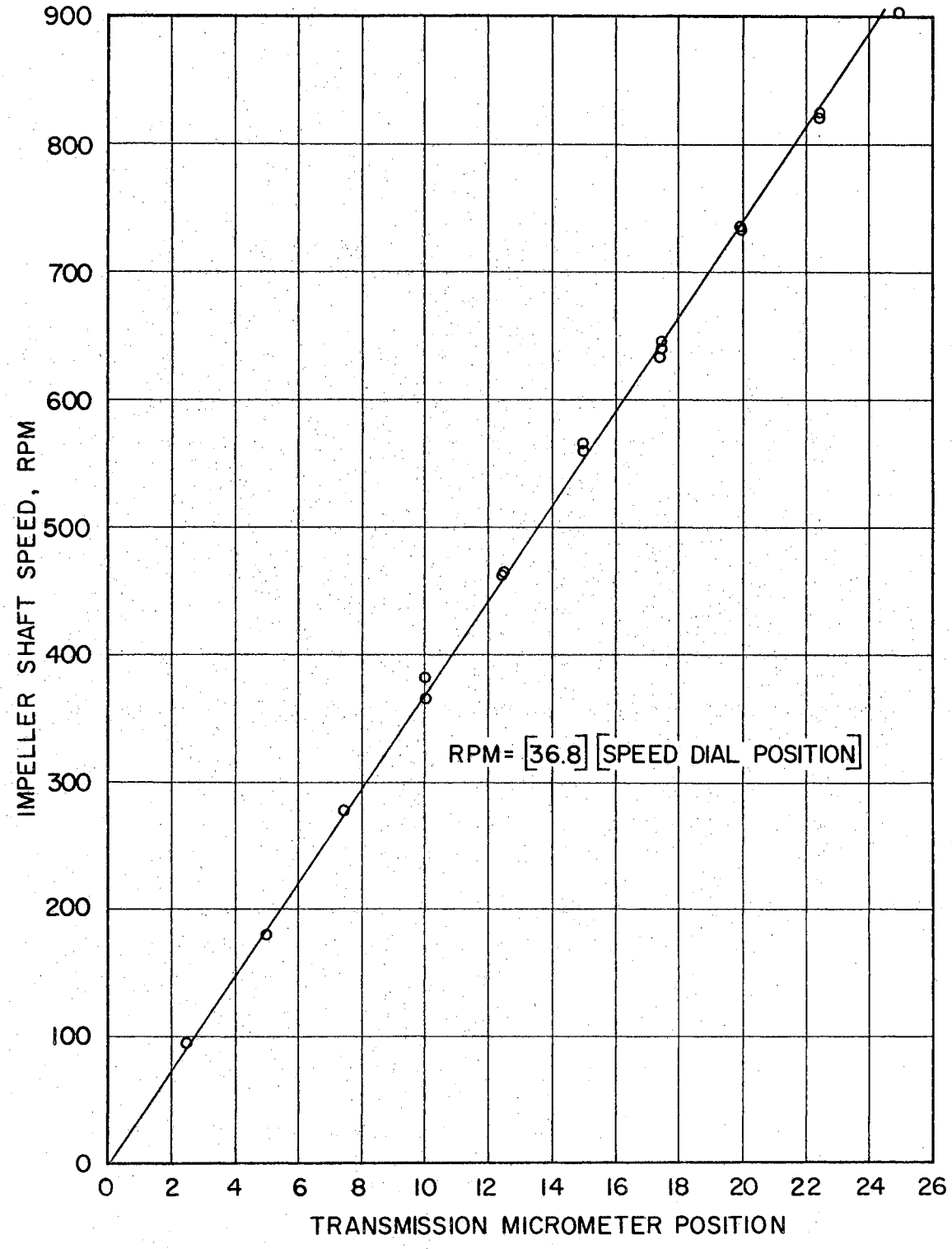


Figure 16 - Impeller speed for drive mechanism used on stirred tank.

TABLE IX

COMPOSITE DATA FOR REAERATION EXPERIMENTS IN STIRRED REACTOR

1	2	3	4	5	6	7	8	9	10	11
Exp. No.	Speed Dial	Impeller rpm	P ft-#/sec	Temp °C	$\mu \times 10^4$ lb/ft-sec	$K_{2\text{-}T}$ hr^{-1}	$K_{2\text{-}20^o}$ hr^{-1}	$k_{2\text{-}20^o}$ hr^{-1}	$G \times 10^{-5}$ hr^{-1}	Log $(K_2 \times 10^2)$
1	10	368	7.500	5	10.206	0.117	0.158	0.364	13.905	1.199
2	10	368	7.500	5	10.206	0.097	0.139	0.320	13.905	1.143
3	10	368	7.500	5	10.206	0.105	0.150	0.345	13.905	1.176
4	10	368	7.500	5	10.206	0.102	0.146	0.336	13.905	1.164
5	10	368	7.500	5	10.206	0.095	0.136	0.313	13.905	1.133
6	10	368	7.500	5	10.206	0.102	0.146	0.336	13.905	1.164
7	15	552	25.293	5	10.206	0.337	0.481	1.108	25.536	1.682
8	15	552	25.293	5	10.206	0.326	0.466	1.073	25.536	1.668
9	15	552	25.293	5	10.206	0.340	0.486	1.119	25.536	1.687
10	15	552	25.293	5	10.206	0.335	0.479	1.103	25.536	1.680
11	5	184	0.936	10	8.801	0.070	0.089	0.205	5.290	0.949
12	5	184	0.936	10	8.801	0.074	0.095	0.219	5.290	0.978
13	5	184	0.936	10	8.801	0.074	0.094	0.216	5.290	0.973
14	5	184	0.936	10	8.801	0.073	0.093	0.214	5.290	0.969
15	10	368	7.500	10	8.801	0.151	0.191	0.440	14.974	1.281
16	10	368	7.500	10	8.801	0.142	0.181	0.417	14.974	1.258
17	10	368	7.500	10	8.801	0.141	0.178	0.410	14.974	1.250
18	10	368	7.500	10	8.801	0.144	0.183	0.421	14.974	1.262
19	15	552	25.293	10	8.801	0.345	0.438	1.009	27.499	1.641
20	15	552	25.293	10	8.801	0.343	0.436	1.004	27.499	1.640
21	15	552	25.293	10	8.801	0.340	0.432	0.995	27.499	1.635
22	15	552	25.293	10	8.801	0.343	0.435	1.002	27.499	1.639
23	20	736	59.980	10	8.801	0.740	0.939	2.163	42.346	1.973
24	20	736	59.980	10	8.801	0.742	0.942	2.169	42.346	1.974
25	20	736	59.980	10	8.801	0.771	0.979	2.255	42.346	1.991
26	20	736	59.980	10	8.801	0.756	0.959	2.209	42.346	1.982
27	5	184	0.936	15	7.692	0.081	0.091	0.210	5.658	0.959
28	5	184	0.936	15	7.692	0.082	0.092	0.212	5.658	0.964
29	5	184	0.936	15	7.692	0.078	0.088	0.203	5.658	0.948
30	5	184	0.936	15	7.692	0.080	0.090	0.207	5.658	0.954
31	10	368	7.500	15	7.692	0.145	0.163	0.375	16.017	1.212
32	10	368	7.500	15	7.692	0.144	0.162	0.373	16.017	1.210
33	10	368	7.500	15	7.692	0.129	0.145	0.334	16.017	1.161
34	10	368	7.500	15	7.692	0.139	0.157	0.362	16.017	1.193
35	15	552	25.293	15	7.692	0.351	0.396	0.912	29.414	1.598
36	15	552	25.293	15	7.692	0.350	0.394	0.907	29.414	1.595
37	15	552	25.293	15	7.692	0.323	0.364	0.838	29.414	1.561
38	15	552	25.293	15	7.692	0.337	0.380	0.875	29.414	1.580
39	20	736	59.980	15	7.692	0.721	0.812	1.870	45.296	1.910
40	20	736	59.980	15	7.692	0.767	0.864	1.990	45.296	1.936
41	20	736	59.980	15	7.692	0.750	0.845	1.946	45.296	1.927
42	20	736	59.980	15	7.692	0.738	0.831	1.914	45.296	1.920
43	5	184	0.936	20	6.779	0.103	0.103	0.237	6.027	1.013
44	5	184	0.936	20	6.779	0.105	0.105	0.242	6.027	1.021
45	5	184	0.936	20	6.779	0.116	0.116	0.267	6.027	1.064
46	5	184	0.936	20	6.779	0.105	0.105	0.242	6.027	1.021
47	10	368	7.500	20	6.779	0.200	0.200	0.461	17.062	1.301
48	10	368	7.500	20	6.779	0.192	0.192	0.442	17.062	1.283
49	10	368	7.500	20	6.779	0.197	0.197	0.454	17.062	1.294
50	15	552	25.293	20	6.779	0.431	0.431	0.993	31.332	1.634
51	15	552	25.293	20	6.779	0.401	0.401	0.924	31.332	1.603
52	20	736	59.980	20	6.779	1.090	1.090	2.510	48.250	2.037
53	20	736	59.980	20	6.779	1.067	1.067	2.457	48.250	2.027
54	20	736	59.980	20	6.779	1.252	1.252	2.883	48.250	2.097
55	20	736	59.980	20	6.779	1.136	1.136	2.616	48.250	2.055
56	10	368	7.500	25	6.014	0.191	0.170	0.392	18.114	1.230
57	10	368	7.500	25	6.014	0.196	0.174	0.401	18.114	1.240
58	10	368	7.500	25	6.014	0.188	0.167	0.385	18.114	1.223
59	10	368	7.500	25	6.014	0.193	0.171	0.394	18.114	1.233
60	15	552	25.293	25	6.014	0.428	0.380	0.875	33.266	1.580
61	15	552	25.293	25	6.014	0.410	0.364	0.838	33.266	1.561
62	15	552	25.293	25	6.014	0.363	0.323	0.744	33.266	1.509
63	15	552	25.293	25	6.014	0.389	0.345	0.794	33.266	1.538
64	10	368	7.500	25	6.014	0.193	0.171	0.394	18.114	1.233
65	10	368	7.500	25	6.014	0.194	0.172	0.396	18.114	1.235
66	15	552	25.293	25	6.014	0.440	0.390	0.898	32.266	1.591
67	15	552	25.293	25	6.014	0.523	0.464	1.069	32.266	1.667
68	15	552	25.293	25	6.014	0.451	0.400	0.921	32.266	1.602
69	15	552	25.293	25	6.014	0.421	0.373	0.859	32.266	1.572
70	15	552	25.293	25	6.014	0.504	0.447	1.029	32.266	1.650
71	7.5	276	3.162	22.5	6.380	0.130	0.122	0.281	11.420	1.086
72	7.5	276	3.162	23.0	6.303	0.142	0.132	0.304	11.489	1.121
73	7.5	276	3.162	22.5	6.380	0.139	0.131	0.302	11.420	1.114
74	12.5	460	14.62	23.0	6.303	0.283	0.263	0.606	24.705	1.420
75	12.5	460	14.62	22.8	6.334	0.283	0.265	0.610	24.644	1.423
76	17.5	644	40.18	23.4	6.247	0.732	0.675	1.554	41.138	1.829
77	17.5	644	40.18	22.8	6.334	0.742	0.693	1.596	40.855	1.841
78	17.5	644	40.18	22.9	6.319	0.690	0.644	1.483	40.903	1.809
79	17.5	644	40.18	22.7	6.349	0.794	0.744	1.713	40.807	1.872

The velocity gradient data given in column 10 were computed from Equation 41, which is

$$G = 3600\sqrt{\frac{Pg_c}{V\mu}}$$

A semi-logarithmic plot of the reaeration rate constant versus the velocity gradient is shown in Figure 17. The regression equation for the data is

$$K_{2\text{-}20^o} = 0.0697 \times 10^{0.2503 \times 10^{-6}G} \qquad (67)$$

The correlation coefficient for the equation was 0.987. The reaeration coefficient, K_2 ($hour^{-1}$) is for use with natural logarithms.

Since the flow pattern in stirred vessels is related to the geometric and kinematic parameters of the reactor and impeller, the relationships found from this research cannot be extended to other installations unless dynamic similitude is maintained. However, this does not impose undue restrictions on the use of the equations presented in this report, since the conditions adopted for this research are in accord with recommended conditions for stirred tanks (56), and should be used in all operations where aeration in mechanically stirred vessels is achieved through turbulence.

C. Deoxygenation Studies

1. General Comments

The experiments on deoxygenation responses were designed to evaluate the relationships which exist for biological degradation in closed quiescent systems with those occurring in open turbulent systems. For presenting the results, the experiments have been grouped according to substrate and type of seed used. The data are presented so as to show

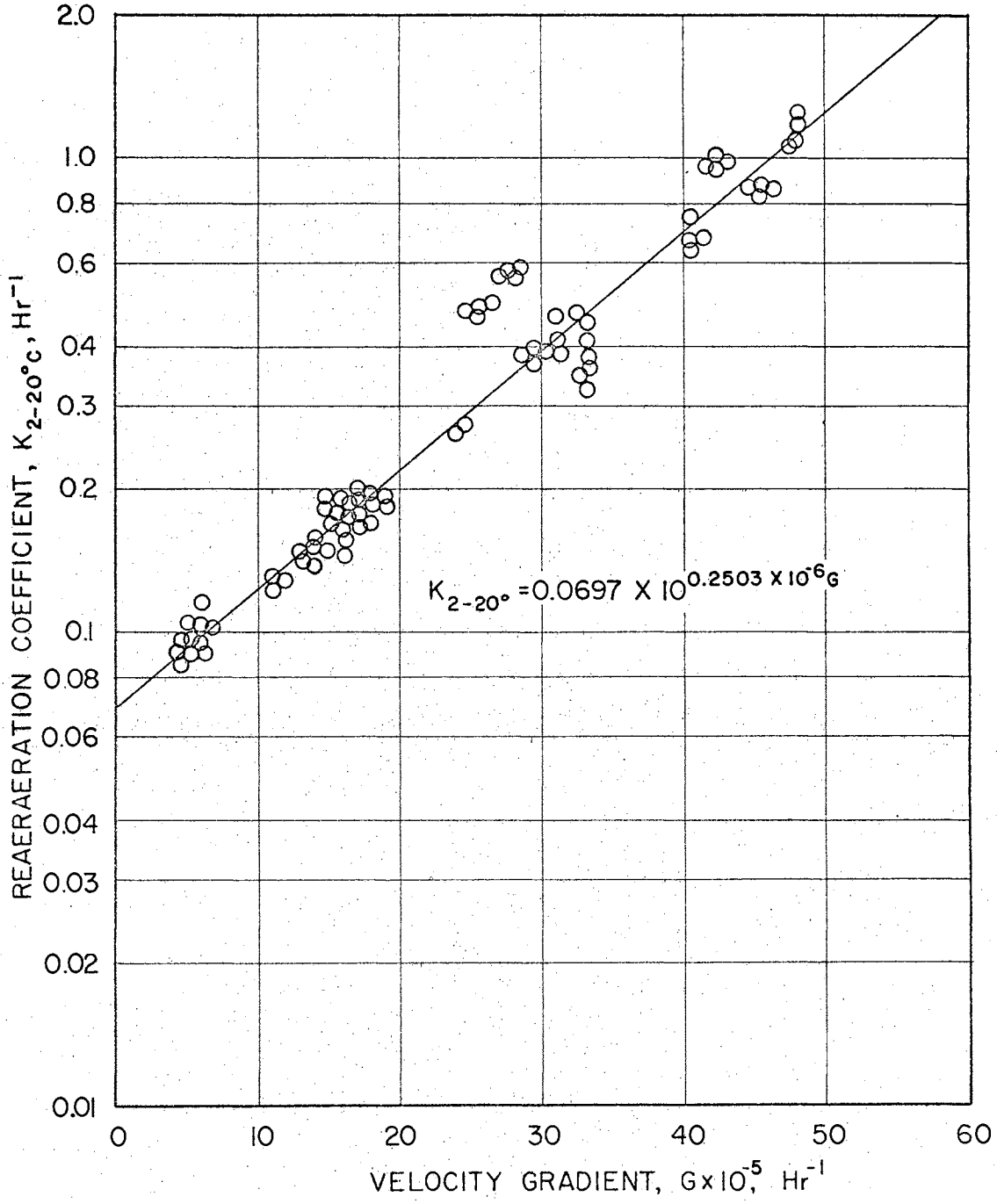


Figure 17 - Regression line for reaeration rate in stirred tank.

the relationship which existed between the simulated channel and the stirred tank, the oxygen uptake in the simulated channel and the bottle systems, the stirred and quiescent bottle systems.

The summarized data for the deoxygenation experiments are presented in Table X. The notations used in the table are as follows:

1. System designation

   A = simulated river channel

   B = stirred tank

   C = bottle system

2. Substrate designation

   G+GA = glucose-glutamic acid, mg COD/l

   S = settled sewage collected from the primary clarifier effluent launder, Stillwater, Oklahoma, sewage treatment plant, ml/l

   M = non-fat dry milk, mg/l

   manufacturer's analysis: 36.7 % protein
   51.0 % lactose
   0.8 % fat
   8.0 % mineral
   3.5 % moisture

3. Seed designation

   S = settled sewage

   AS = settled sewage acclimated to substrate

4. BOD designation

   Y_p = oxygen uptake to plateau

   Y_5 = 5-day oxygen uptake

   L_a = "first stage" or "carbonaceous stage" oxygen uptake

   K_1 and k_1 = rate constant for portion of oxygen uptake curve that was approximately defined by a first order decreasing relationship

TABLE X

SUMMARIZED DATA FOR DEOXYGENATION EXPERIMENTS

Group	Exp #	System	Substrate	Seed	Substrate Conc.	Initial COD	Initial Carbo.	Lag Hours	Y_P (Plateau)	Y_5 (5-day)	L_a mg/l	Y_P/COD	Y_5/COD	K_1 $Hour^{-1}$	k_1 Day^{-1}	k_i Day^{-1}
I	A	A	G+GA	S	15+15	30	15	14	11.0	23.0	25.8	0.37	0.76	0.0241	0.252	2.06
		B			15+15	30	15.5	12	11.0	26.0	30.8	0.37	0.86	0.0153	0.159	2.22
		C			8+ 8	15	8	36	-	15.4	18.3	-	0.55	0.0205	0.214	-
	B	A	G+GA	S	15+15	30	15	14	10.5	19.2	20.1	0.35	0.64	0.0355	0.370	1.62
		B			15+15	30	16	14	12.0	20.4	-	0.40	0.68	-	-	1.66
		C			8+ 8	20	-	40	-	13.1	16.4	-	0.44	0.0232	0.242	0.95
	C	A	G+GA	S	15+15	29.5	15	19	11.9	22.3	26.7	0.40	0.76	0.0132	0.137	2.97
		B			15+15	30	15	12	11.7	23.7	31.9	0.39	0.79	0.0104	0.109	2.10
		C			7+ 7	16.5	7.6	50	-	10.1	12.7	-	0.34	0.010	0.104	-
	D	A	G+GA	S	15+15	31	7.5	18	12.0	19.9	24.7	0.39	0.64	0.0093	0.0975	2.39
		B			15+15	30	7.5	15	12.5	28.4	32.4	0.42	0.95	0.0176	0.184	2.18
		C			7+ 7	15.9	4.0	50	-	11.8	-	-	0.36	-	-	-
	E	A	G+GA	S	15+15	30	15	12	12.0	22.1	23.8	0.40	0.74	0.0212	0.220	2.32
		B			12+12	25	13.5	12	10.0	21.2	29.7	0.40	0.84	0.0123	0.129	2.42
		C			9+ 9	18	7.0	24	-	13.0	18.6	-	0.44	0.0086	0.089	1.46
	F	A	G+GA	S	15+15	30.3	15.1	30	9.0	20.3	20.1	0.30	0.67	0.049	0.510	2.06
		B			12+12	25.7	11.0	24	12.0	23.6	20.0	0.47	0.92	0.037	0.383	2.19
		C			8+ 8	16.0	7.7	48	-	15.2	16.1	-	0.51	0.047	0.487	1.09
II	G	A	G+GA	AS	15+15	28.4	15.2	24	11.8	20.6	22.3	0.42	0.72	0.025	0.26	2.92
		B			12+12	26.8	13.5	24	11.1	19.5	20.4	0.41	0.73	0.029	0.30	2.92
		C			5+ 5	10.5	5.5	24	-	18.4	-	-	0.65	-	-	-
	H	A	G+GA	AS	15+15	30.8	14.4	24	11.5	17.4	20.0	0.37	0.57	0.0133	0.140	2.18
		B			14+14	28.0	13.2	12	12.0	26.0	-	0.43	0.93	-	-	2.09
		C			5+ 5	10.6	4.9	36	-	18.2	22.0	-	0.61	0.0110	0.115	1.23
	I	A	G+GA	AS	15+15	30.0	19	12	11.0	20.7	23.4	0.37	0.69	0.0172	0.179	1.90
		B			12+12	22.0	14.6	12	10.5	23.7	23.5	0.48	1.01	0.0370	0.383	1.90
		C			6+ 6	12.6	9.3	12	-	20.0	-	-	0.67	-	-	-
III	J	A	S	S	250	52	2.7	0	12.5	27.6	28	0.24	0.53	0.022	0.230	-
		B			200	48	2.7	0	9.6	19.3	19.3	0.20	0.40	0.021	0.218	-
		C			45	5.8	2.5	20	-	16.1	18.3	-	0.50	0.024	0.253	-
	K	A	S	S	230	46.5	1.4	0	11.5	24.9	33.4	0.25	0.54	0.012	0.122	-
		B			300	60.8	1.4	7	12.5	35.7	38.9	0.21	0.59	0.025	0.257	-
IV	L	A	M	S	50	56	25	36	23.3	30.0	-	0.42	0.54	-	-	1.64
		B			60	64	24	60	25.9	35.8	-	0.40	0.56	-	-	1.86
	M	A	M	S	50	53	19	0	17.0	29.2	30.7	0.32	0.55	0.023	0.240	2.25
		B			40	45	16	0	19.6	40.7	50.2	0.43	0.90	0.014	0.146	2.21
		C			20	22.6	7.2	45	-	18.0	19.2	-	0.34	0.054	0.565	0.48
V	N	A	M	AS	50	50.2	17	42	18.4	24.7	24.3	0.37	0.49	0.059	0.617	1.80
		B			40	47.0	15.6	12	15.9	40.0	-	0.34	0.85	-	-	1.13
		C			20	19.0	5.4	96	-	14.5	-	-	0.29	-	-	-
	O	A	M	AS	50	38.3	20.7	48	18.5	23.3	25.6	0.48	0.61	0.031	0.324	1.27
		B			40	30.0	17.1	48	15.7	21.6	23.2	0.52	0.72	0.029	0.304	1.59
VI	P	A	G+GA	S	30	31.5	13.5	36	11.3	19.6	20.7	0.36	0.62	0.033	0.341	2.19
		C			30	34.7	14.8	36	11.1	23.6	23.7	0.32	0.68	0.038	0.402	2.15

k_i = rate constant for increasing rate portion of oxygen uptake curve

2. Group I - Experiments Using Sewage Seed and Glucose-Glutamic Acid Substrate

The first group includes experiments A through F, which are the experiments conducted using glucose and glutamic acid or sodium glutamate as substrate and settled sewage as seed. The seed was collected from the primary clarifier effluent launder at the Stillwater, Oklahoma, sewage treatment plant, and aerated for about fifteen hours before using. This group of experiments extends over a period from early March to mid-August, thus including biological populations existing at the plant during both cold and warm seasons. Figures 18 through 27 show pertinent 5-day metabolic responses of the four systems for this group of experiments.

The oxygen uptake for the simulated channel and the stirred tank were essentially the same. The mean lag period for the two systems was 16.3 hours with a minimum of twelve hours and a maximum of thirty. The longer lag periods were associated with lower initial viable counts.

In both open systems the oxygen uptake curve shows a lag period followed by an increasing rate of oxygen uptake which was found to be defined by a first order increasing rate relationship. This logarithmic increasing oxygen utilization rate corresponded to the log growth phase of the bacterial growth curves. This phase of the oxygen uptake was found in all cases to correspond to the period of substrate removal. The beginning of the plateau region of the oxygen uptake curve occurred at the point of substrate exhaustion and maximum viable counts.

The beginning of the oxygen plateau occurred at the point of

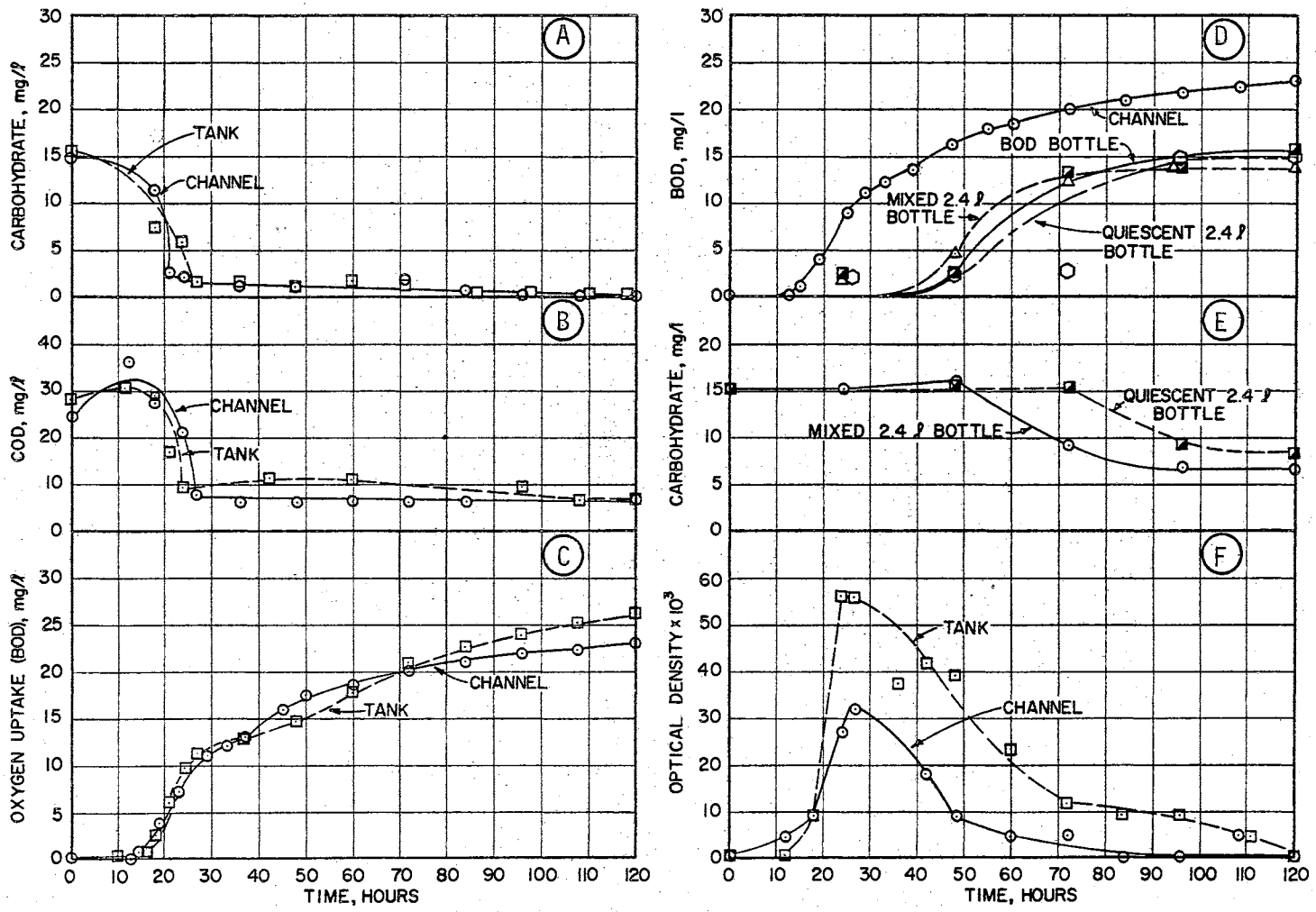


Figure 18 - Changes in system parameters using glucose-glutamic acid substrate and settled sewage seed collected on 3-21-1968 (Experiment A).

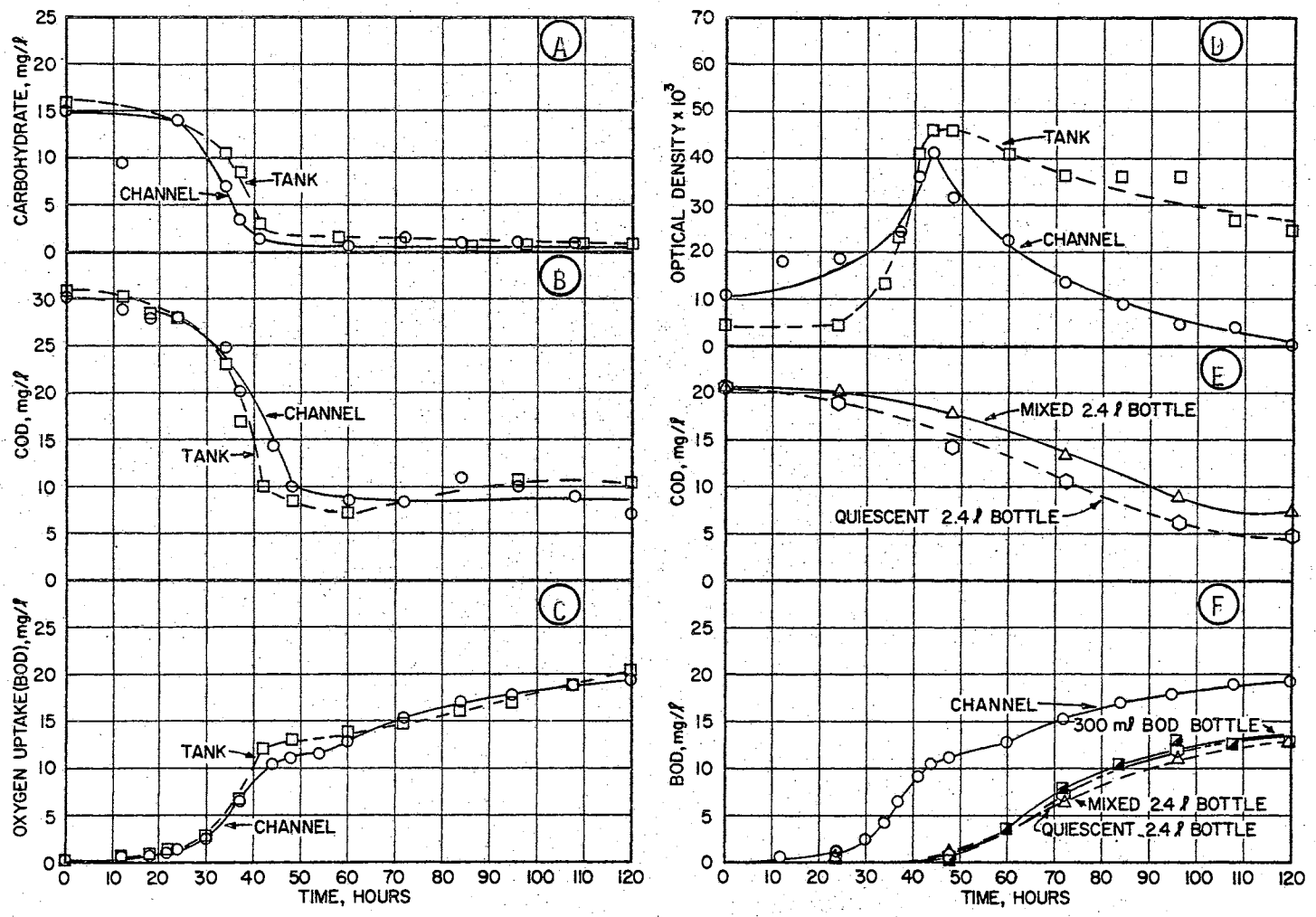


Figure 19 - Changes in system parameters using glucose-glutamic acid substrate and settled sewage seed collected on 4-4-1968 (Experiment B).

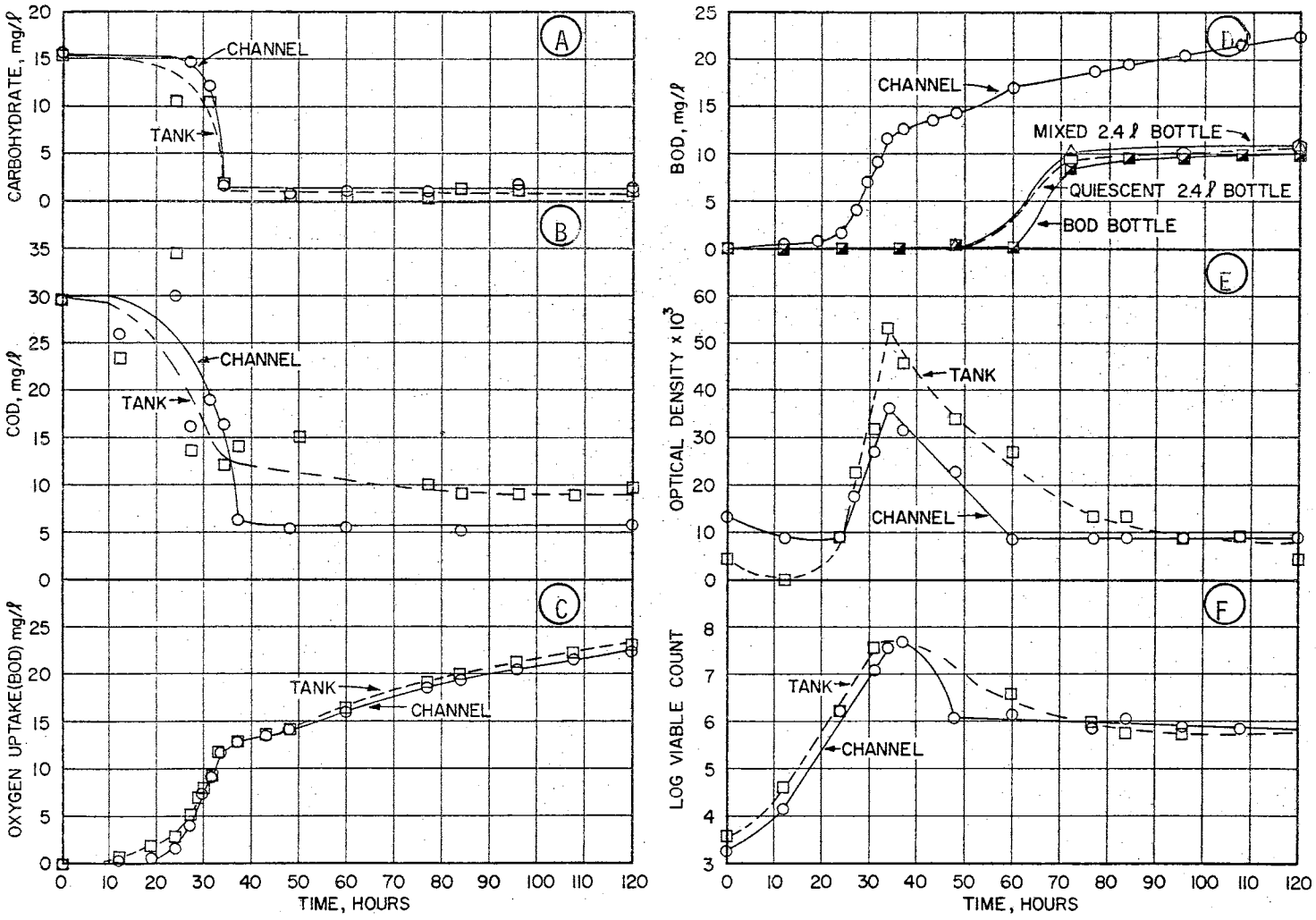


Figure 20 - Changes in system parameters using glucose-sodium glutamate substrate and sewage seed collected on 4-10-1968 (Experiment C).

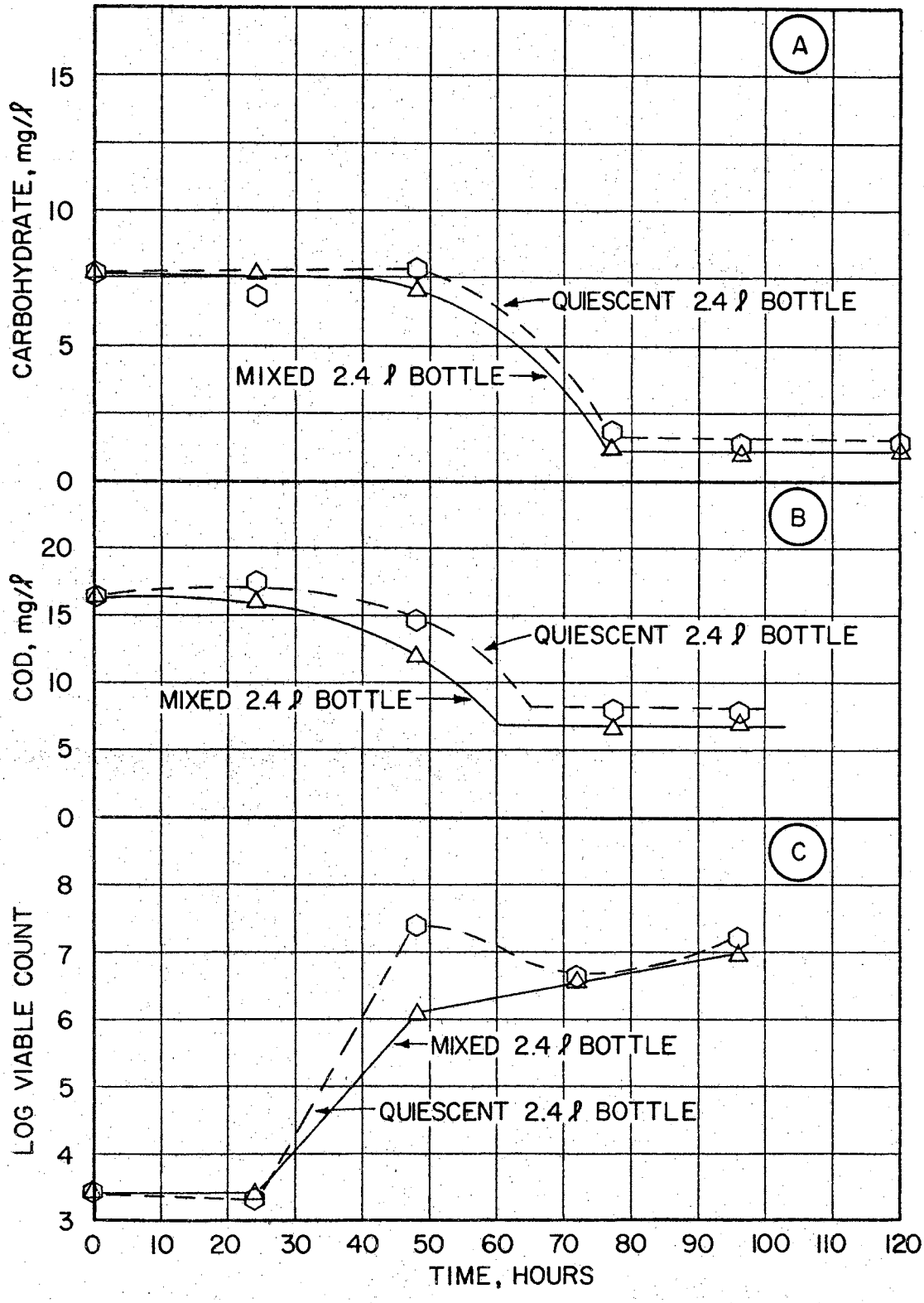


Figure 21 - Changes in bottle system parameters using glucose-sodium glutamate substrate and sewage seed collected on 4-10-1968 (Experiment C).

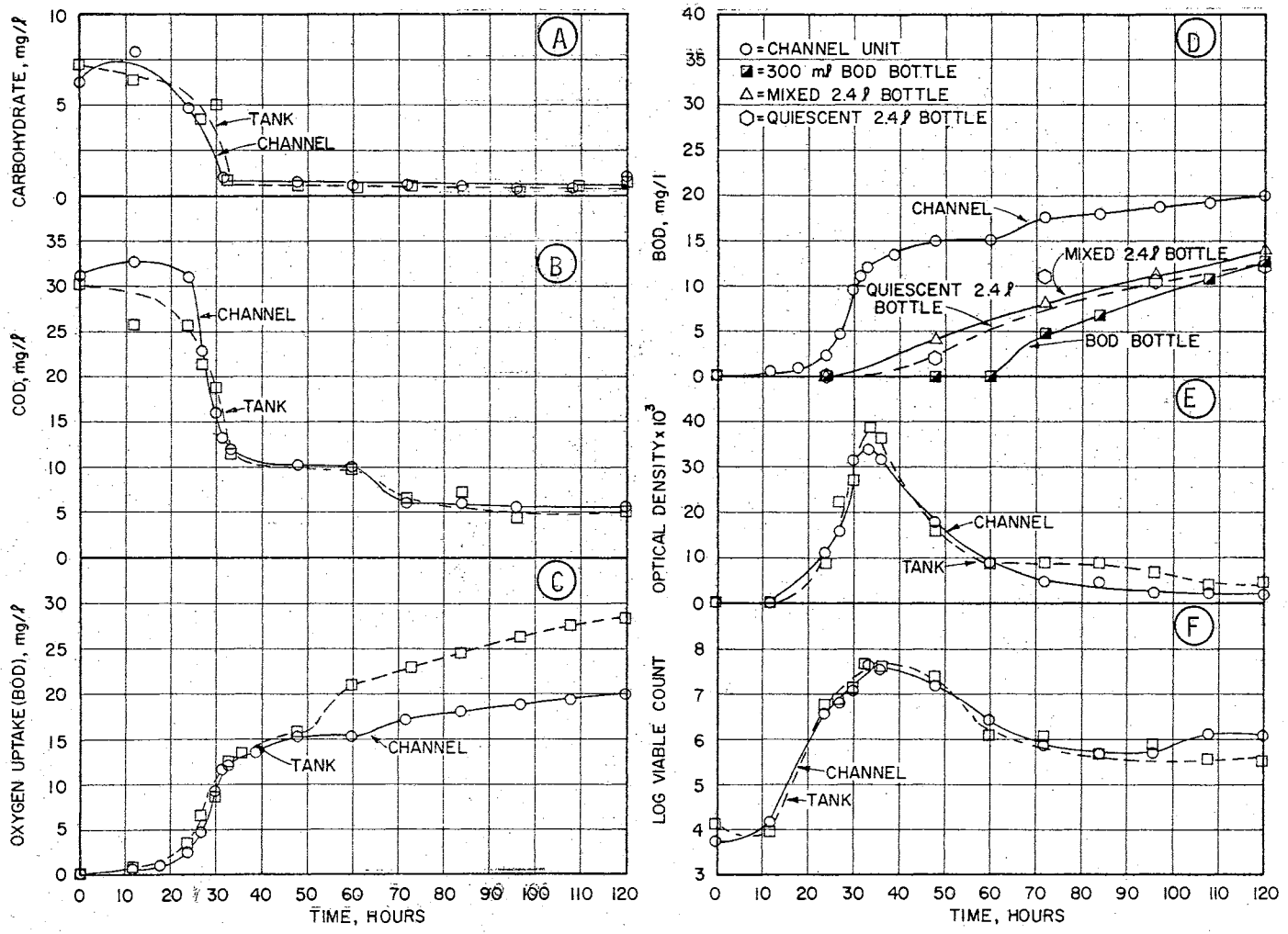


Figure 22 - Changes in system parameters using glucose-sodium glutamate substrate and sewage seed collected on 4-16-1968 (Experiment D).

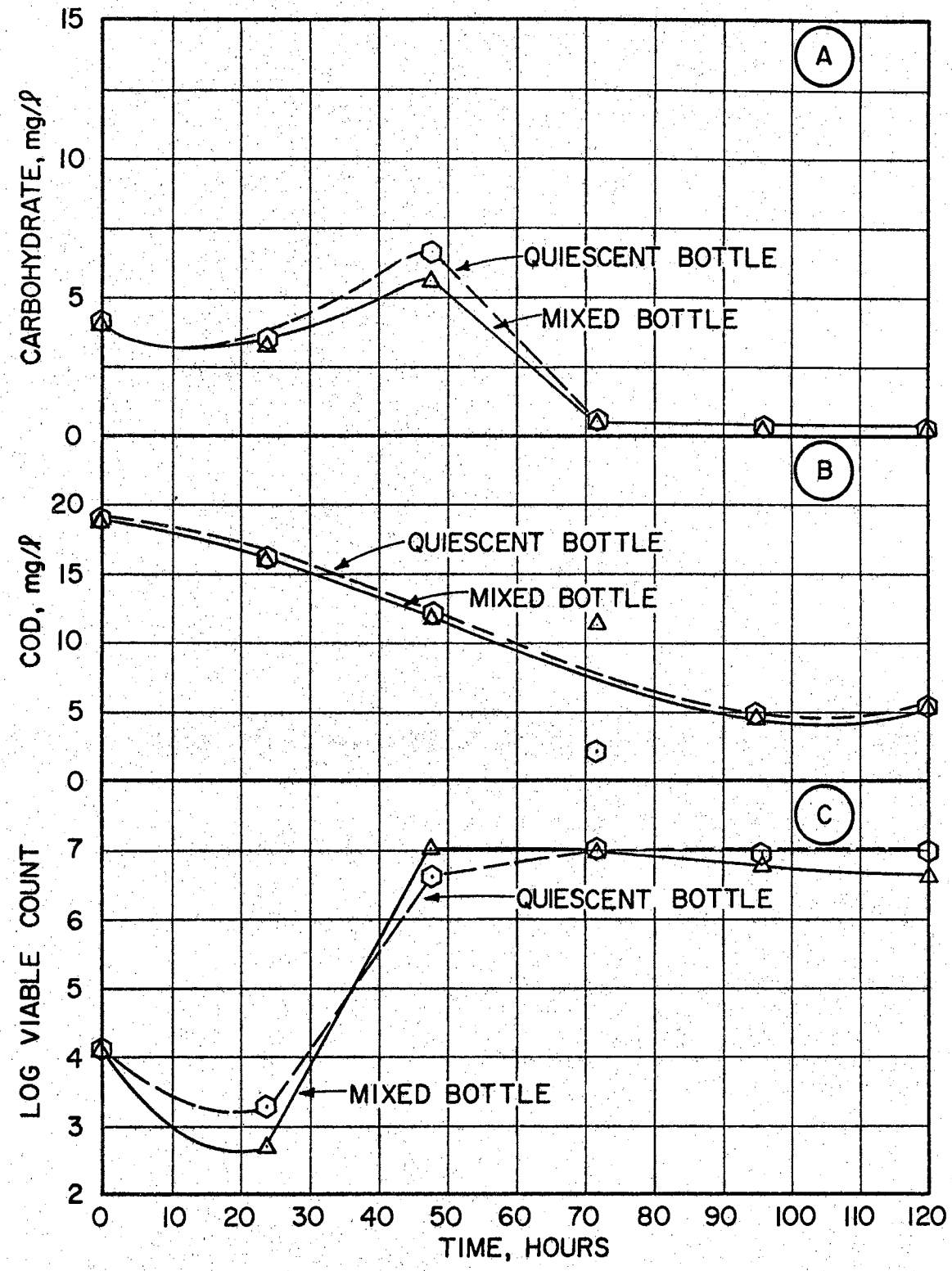


Figure 23 - Changes in bottle system parameters using glucose-sodium glutamate substrate and sewage seed collected 4-16-1968 (Experiment D).

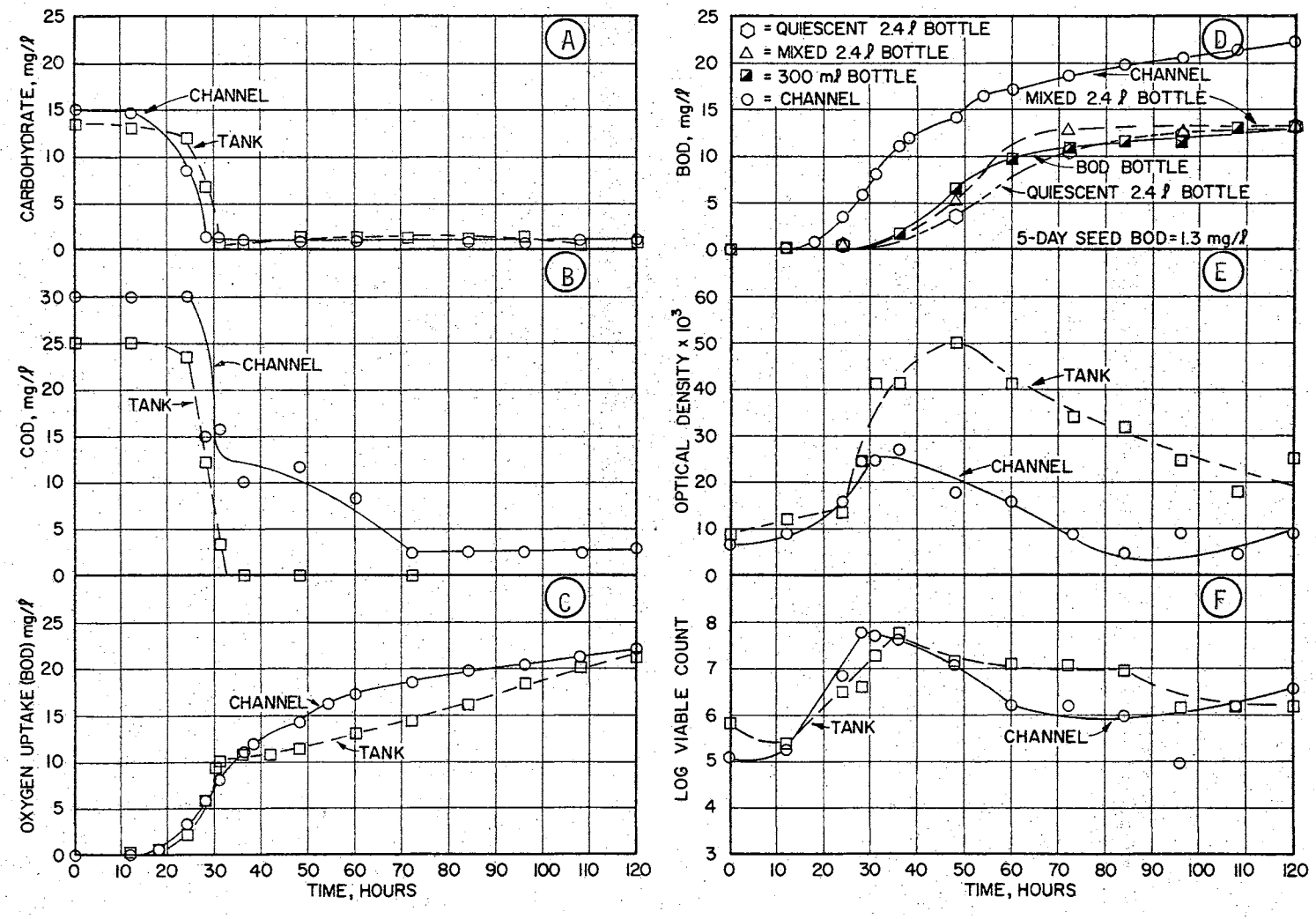


Figure 24 - Changes in system parameters using glucose-sodium glutamate substrate and sewage seed collected on 7-17-1968 (Experiment E).

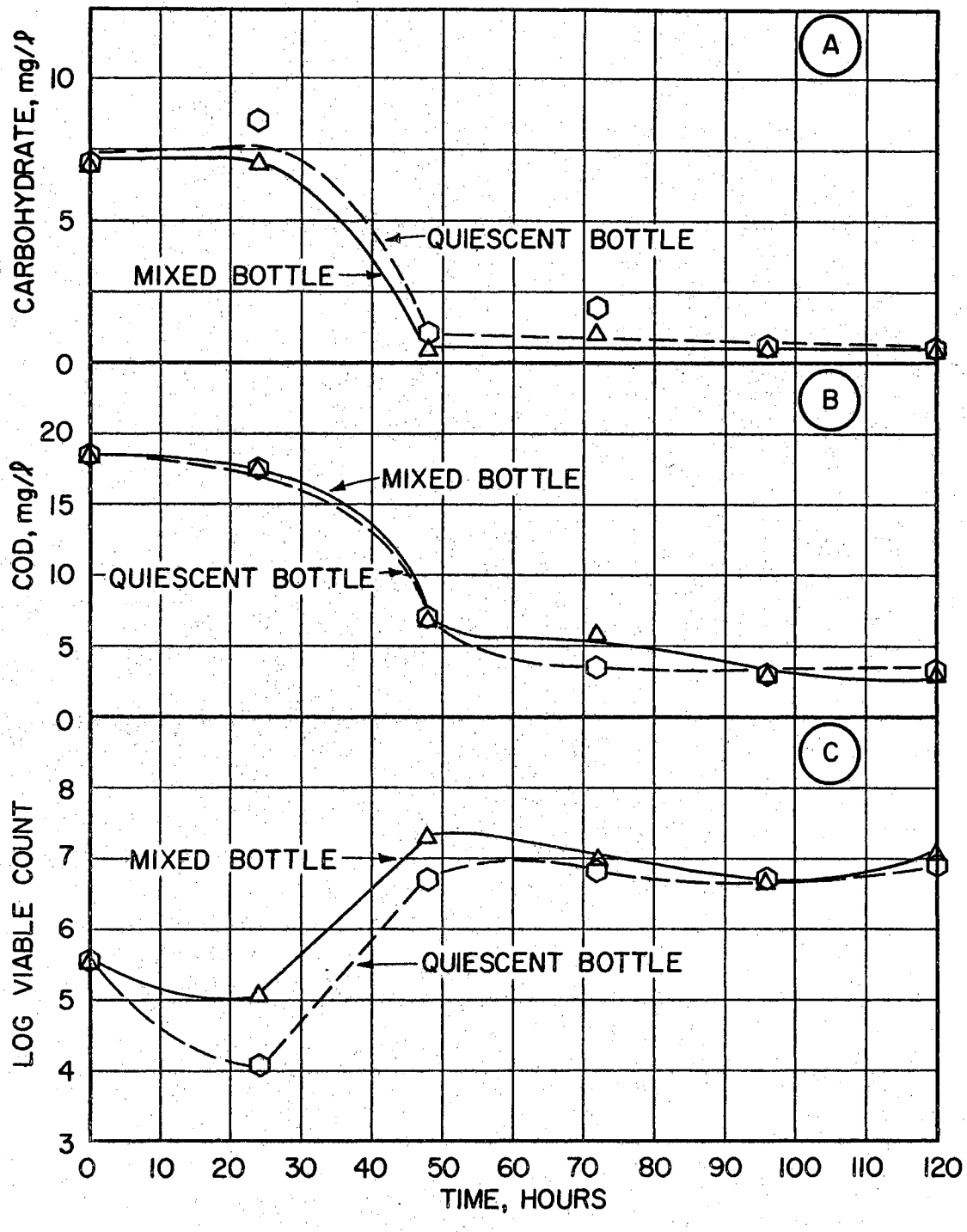


Figure 25 - Changes in bottle system parameters using glucose-sodium glutamate substrate and sewage seed collected on 7-17-1968 (Experiment E).

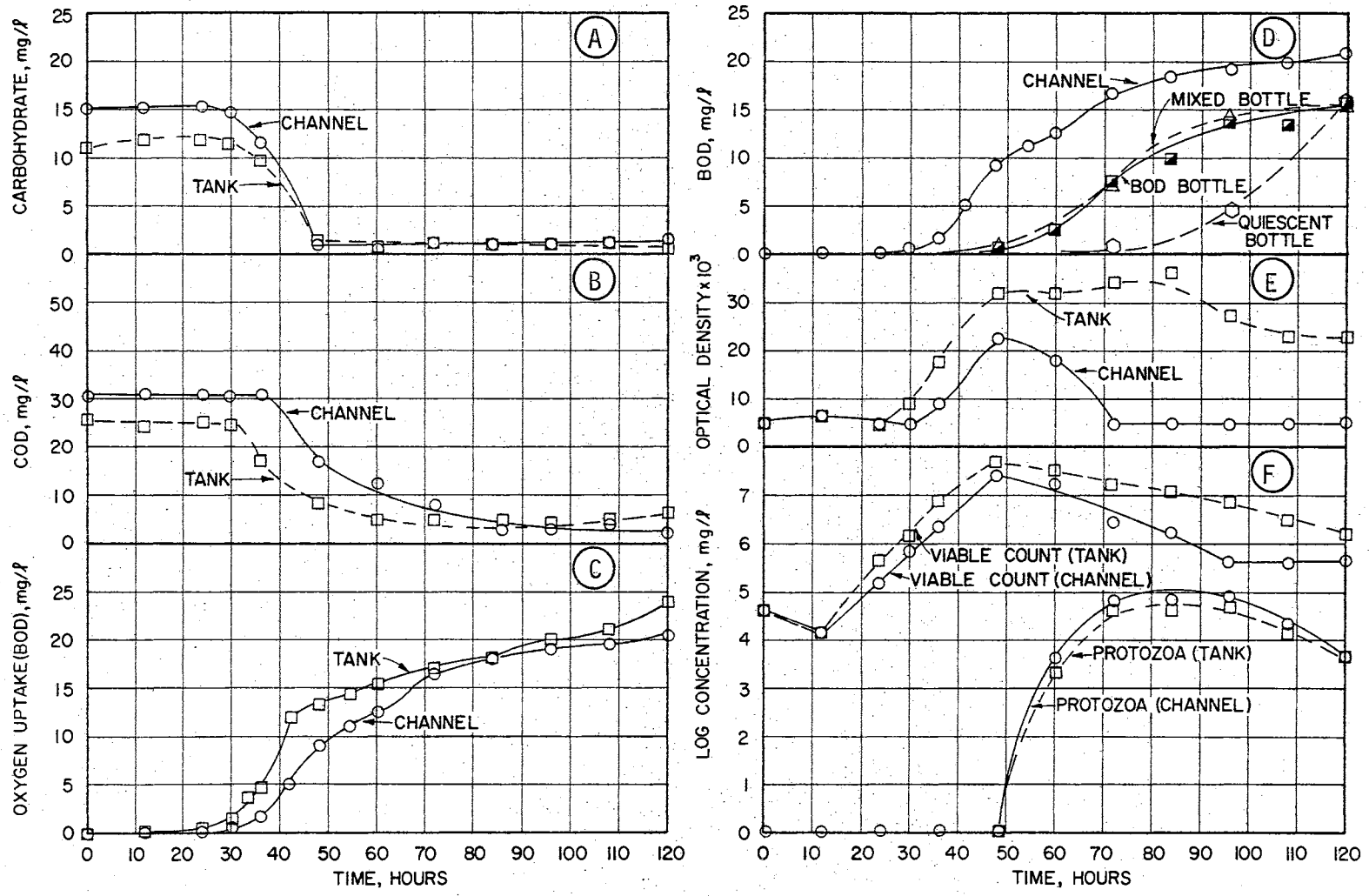


Figure 26 - Changes in system parameters using glucose-glutamic acid substrate and sewage seed collected on 8-16-1968 (Experiment F).

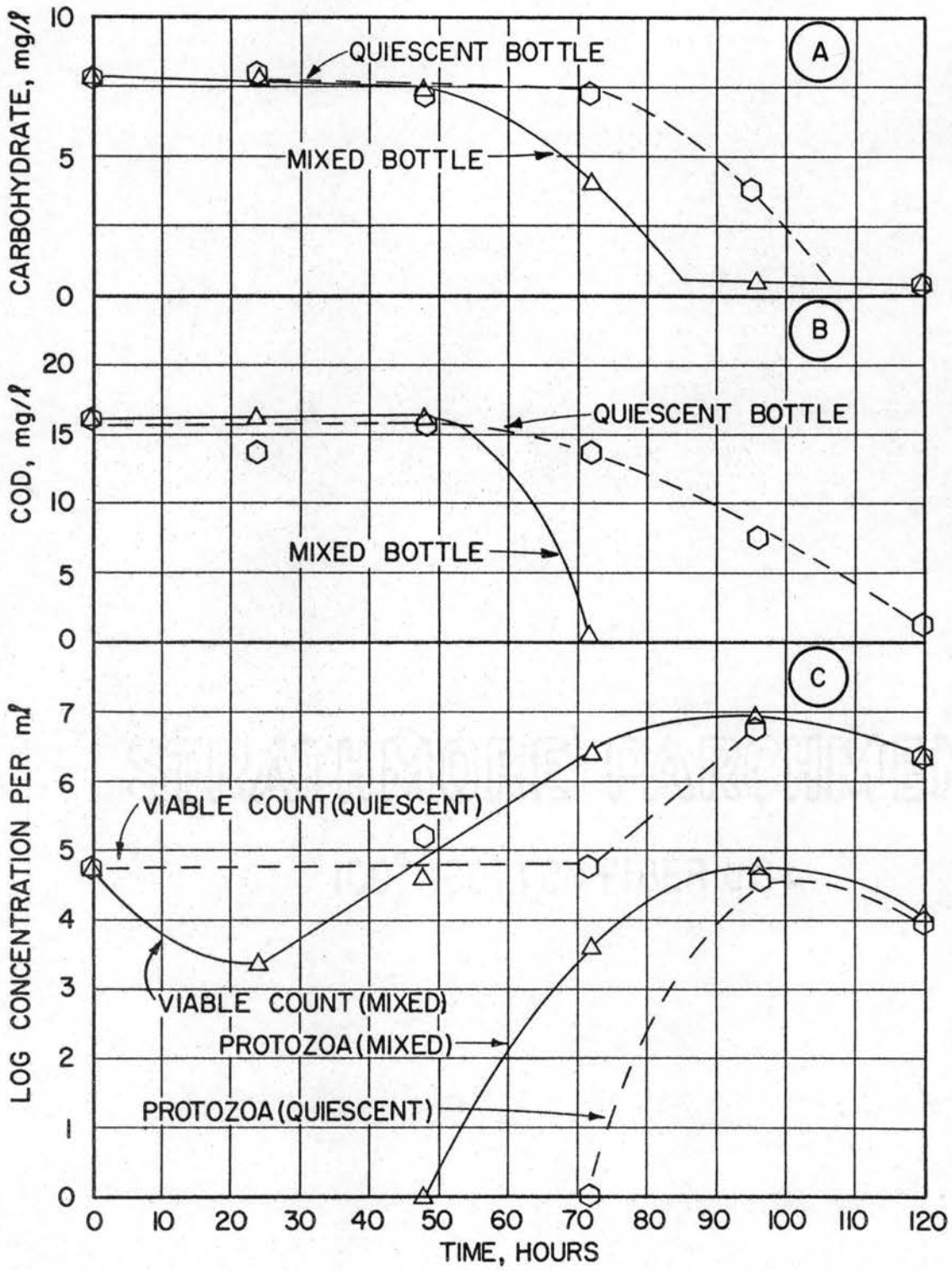


Figure 27 - Changes in bottle system parameters using glucose-glutamic acid substrate and sewage seed collected on 8-16-1968 (Experiment F).

minimum dissolved oxygen concentration in the reactor (see Figure 51 at the end of this section). The sag point as defined by the oxygen sag equation (Equation 8) is a position on the oxygen content curve representing the condition where K_1L equals K_2D. The transition across this point as defined by the sag equation is a continuous function where as the BOD remaining, L, becomes smaller the product K_1L goes from greater than to less than the product of K_2D. However, as shown by these experiments, the system goes from a proliferating to an endogenous condition at the sag point. In other words, the low point in the sag always occurred at the point where the exogenous substrate was exhausted and the rate of oxygen uptake was decreasing at a rapid rate at this time, giving a rather abrupt change from decreasing to increasing in the dissolved oxygen content of the reactor liquid at this point.

Following the removal of the exogenous substrate, there was a rapid recovery in the oxygen content of the liquid during a period where the rate of oxygen utilization was very low. This period generally lasted about ten hours and resulted in a plateau in the oxygen uptake curve. Bhatla and Gaudy (45) have proposed that the plateau in the oxygen uptake curve represents the oxygen uptake by the bacteria during a stationary growth phase. The results found in these experiments also indicate that the plateau begins at the point of exogenous substrate depletion which occurred at the point of maximum bacteria growth.

The plateau was followed by a region of increasing oxygen demand of short duration. However, the influence of this demand on the oxygen depletion of the water was insignificant. This secondary demand was followed by a decreasing uptake rate of oxygen utilization of long duration. This last decreasing rate extended in most cases to the

termination of the experiment at five days. This last portion of the oxygen uptake curve was the only part that was defined, even in the broadest terms, by a first order decreasing rate.

The average oxygen uptake at the plateau was 39 per cent of the theoretical COD, and the value varied only from 30 per cent to 47 per cent. This represents the oxygen uptake during the growth period and it was the only portion of the oxygen uptake curves related directly to the initial substrate concentration. An oxygen uptake of approximately 40 per cent of the theoretical at the plateau has also been reported by Gaudy, Bhatla, and Abu-Niaaj (67), and by Busch (38).

The average 5-day uptake for the open systems in this group was 77 per cent with a range from 64 per cent to 95 per cent. These values are slightly higher than the 70 per cent theoretical demand reported by Ballinger and his associates (68) of the Analytical Reference Service, U. S. Public Health Service. However, this study also reported a standard deviation of approximately 20 per cent in the 5-day BOD. Hence it seems apparent that wide variations are to be expected in the 5-day results.

The average decreasing deoxygenation rate constant was 0.232 day^{-1} for the open mixed systems in this group of experiments. However, the value varied from 0.098 to 0.510 day^{-1}.

The increasing oxygen uptake rate for the experiments in group 1 was 2.2 day^{-1} with a range from 1.62 to 2.97 day^{-1}. For experiments A, C, D, E, and F, the average increasing rate constant was 2.3 day^{-1} with a range from 2.06 to 2.97 day^{-1}. The average increasing rate constant for the five experiments (2.2 day^{-1}) was 9.5 times the average decreasing rate constant of 0.232 for the same group of

experiments. Thus it is seen that the decreasing rate constant was insignificant in the oxygen balance of the open systems, but that the critical period for the systems was during the time of exogenous substrate utilization where the oxygen uptake rate was an increasing function. Furthermore, from these data it was concluded that the term "k_1L_a" has no validity in an oxygen uptake expression, since the decreasing rate portion of the oxygen uptake curve is unrelated to the initial substrate. In fact, the substrate is exhausted prior to this portion of the curve.

The oxygen uptake in the bottle systems was 43 per cent of the initial COD for the 5-day period. This compares with an average uptake of 77 per cent of the theoretical for the open systems. One major cause of this difference was the longer lag period experienced with the bottle systems. The average lag period for this group of experiments was forty hours for the bottle systems, compared with an average of only 16.3 hours for the open systems. Furthermore, there was no indication of phasic uptake in the bottles. There was an increasing rate of oxygen uptake during the substrate utilization, but the uptake curves appear to level off at a low rate of oxygen uptake at the point of substrate depletion, and there was no definite indication of a secondary demand. This may have been caused by a lower level, or lack of predator activity because of the lower bacteria population achieved in bottle systems. Wilson and Harrison (42) found that the oxygen uptake prior to the plateau was not affected by cell concentration, but that the endogenous phase was related to the number of cells present. The plateau in the open systems corresponded to the plateau observed in the bottle systems but the lack of a secondary demand in the bottle systems resulted in a

much lower 5-day oxygen demand. Because of the long lag period, the development of the predator population in most cases was delayed to very near the end of the experiment. Thus the secondary uptake in the bottle systems was apparently too small to be detected.

In general, the metabolic patterns were similar in the mixed and quiescent 2.4 liter bottles, and there was no difference in the 2.4 liter bottles and the standard 300 ml BOD bottles. While it has been reported by Lordi and Heukelekian (69) that the first stage BOD was approximately 42 per cent higher in stirred systems than in quiescent systems, mixing appeared to have no effect on the kinetics observed in this research. However, they found that the nitrification occurred two to three days earlier under stirred open conditions than under quiescent closed conditions.

Mixing can logically be expected to contribute to deoxygenation in at least two ways. Mixing brings the organisms into contact with the substrate, and provides uniform substrate concentration throughout the liquid. In a quiescent system this contact is achieved through the motility of the organism and molecular and eddy diffusion of the substrate. Microscopic examination of the biological solids taken from the BOD bottles in this research showed large numbers of mobile bacteria. The oxygen uptake data from the present research indicate that for the dilute substrate concentrations such as exist in the BOD bottle, bacteria motility and substrate diffusion are sufficient to prevent any inhibition of substrate utilization rates. This was shown not only in the oxygen uptake rates, but also in the substrate depletion data and in the biological counts. None of these parameters show any difference in biological kinetics between the mixed bottle and the quiescent bottle.

Attempts were made to measure biological solids; however, only a few hundred ml of sample was required to completely clog the 0.45 μ filter and it was not possible to obtain a sufficient quantity of solids for weighing. During the logarithmic growth phase, filtering times as great as twenty-four hours were required to filter a one liter sample volume. Attempts at concentrating the solids by centrifugation were unsuccessful because of the low solids concentration.

Optical density measurements are reported for the two open systems. The optical density was read at 540 mμ using a 3/4 inch diameter sample tube. However, at these low concentrations the results reported are not sufficiently accurate to permit the determination of solids. Research in this laboratory has shown that optical density values lower than about 0.070 (85 per cent transmittance) are unreliable for estimating solids, since the relationship between solids and optical density is not linear in this range. The relative values indicated by the optical density curves were in agreement with other parameters measured. The optical density data indicate the same lag periods and growth patterns as observed for the oxgen uptake and viable count data.

For experiments C, D, E, and F, the mean viable count increase for the two open systems was from about 3000 organisms/ml to 45 million organisms/ml. Thus the initial count was less than 0.01 per cent of the final count. The average bacteria growth from the time of seeding to the end of the growth phase was approximately 45 million organisms/ml as determined by the viable count. For an average wet cell weight of 10^{-12} grams, this gives a wet cell growth of 45 mg/l or a dry cell weight of 9 mg/l (cell 80 per cent moisture). This gives a cell COD of (1.41x 9) =12.7 mg/l [cell COD = 1.41 cell mass (70)]. This is

approximately 42 per cent of the applied COD. This gives about 80 per cent recovery of the applied COD at the plateau, with 39 per cent accounted for by the oxygen uptake and 42 per cent by the cell mass. However, the viable count may be low due to clumping, and the average cell weight and percent moisture could have sufficient variation to account for this deficiency in the materials balance.

Protozoa counts were also included for Experiment F as shown in Figures 26 and 27. The protozoa growth lags the bacteria growth. It appears from this and later experiments that there was a threshold level of bacteria required to support protozoa growth. It was noted that the protozoa growth was accompanied by a decrease in the viable count. The protozoa growth period also corresponds to the second phase of oxygen uptake. No specific attempt was made to identify the protozoa; however, some of the predominate types present were those belonging to the family Ochromonadidae, the stalked family Aloricata, and the family Parameciidae. Nematodes were also present in small numbers. The protozoa included both free swimmers and stalked forms attached to particles of microbial floc. The larger species of free swimmers were the last to appear and the first to disappear during the growth cycle. The major predators appeared to be the large number of stalked species which fed in and adjacent to the floc particles.

3. Group II - Experiments Using Glucose-Glutamic Acid Substrate and Acclimated Sewage Seed

The second group includes experiments G, H, and I, which are the experiments conducted using glucose and glutamic acid or sodium glutamate as substrate, and acclimated sewage seed. The data for these experiments are shown in Figures 28 through 33.

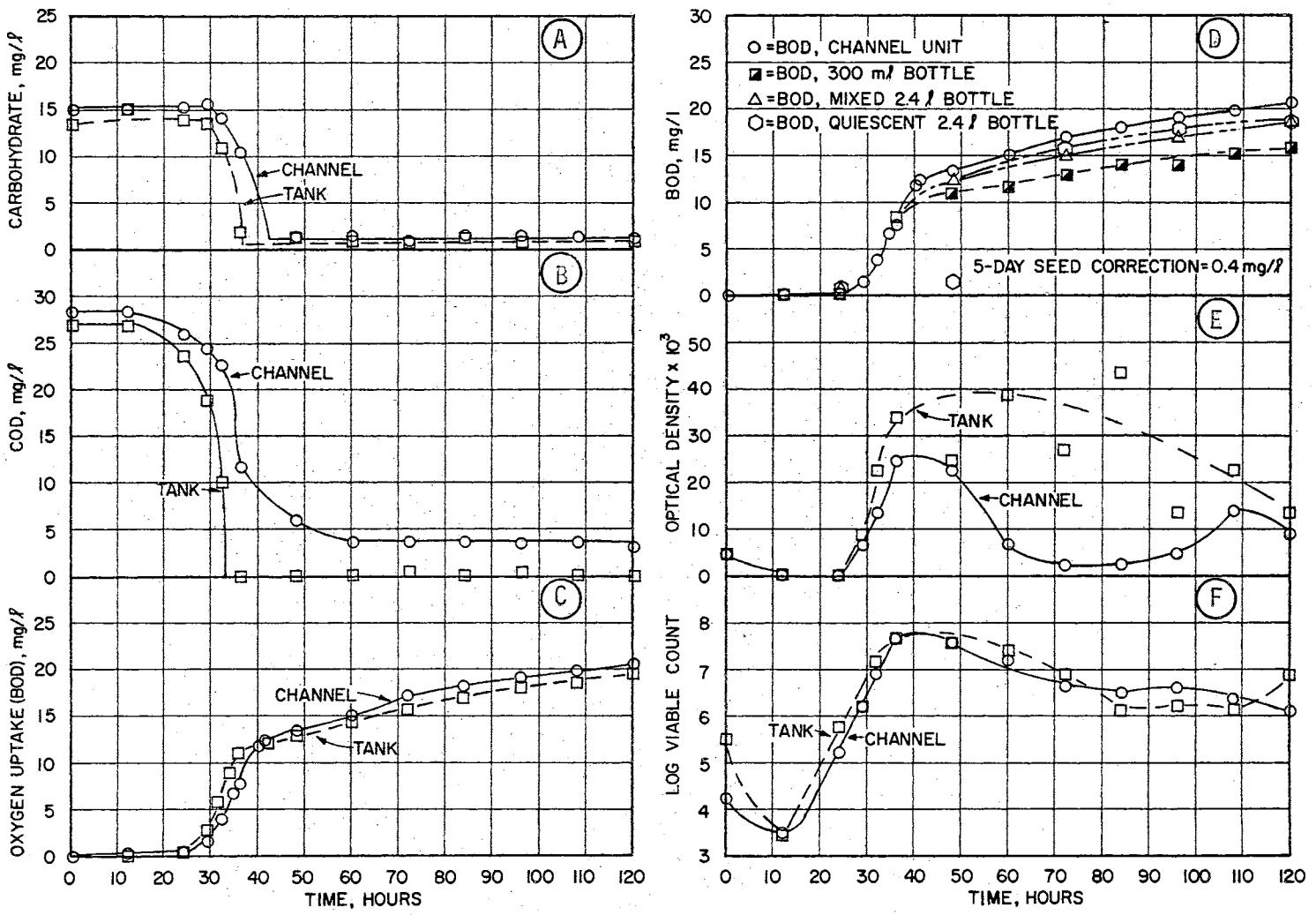


Figure 28 - Changes in bottle system parameters with glucose-sodium glutamate substrate and acclimated sewage seed collected on 7-17-1968 (Experiment G).

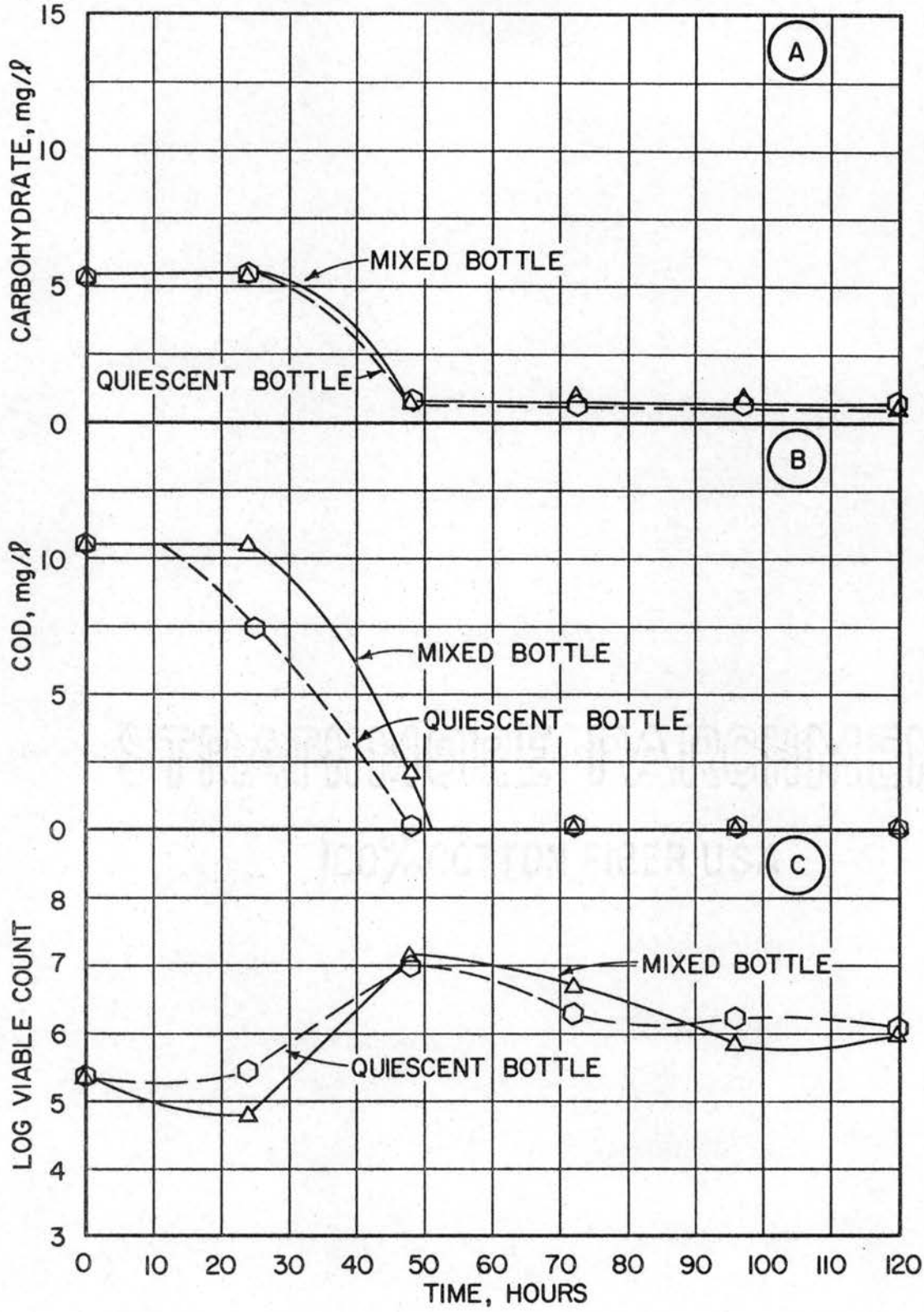


Figure 29 - Changes in bottle system parameters with glucose-sodium glutamate substrate and acclimated sewage seed collected on 7-17-1968 (Experiment G).

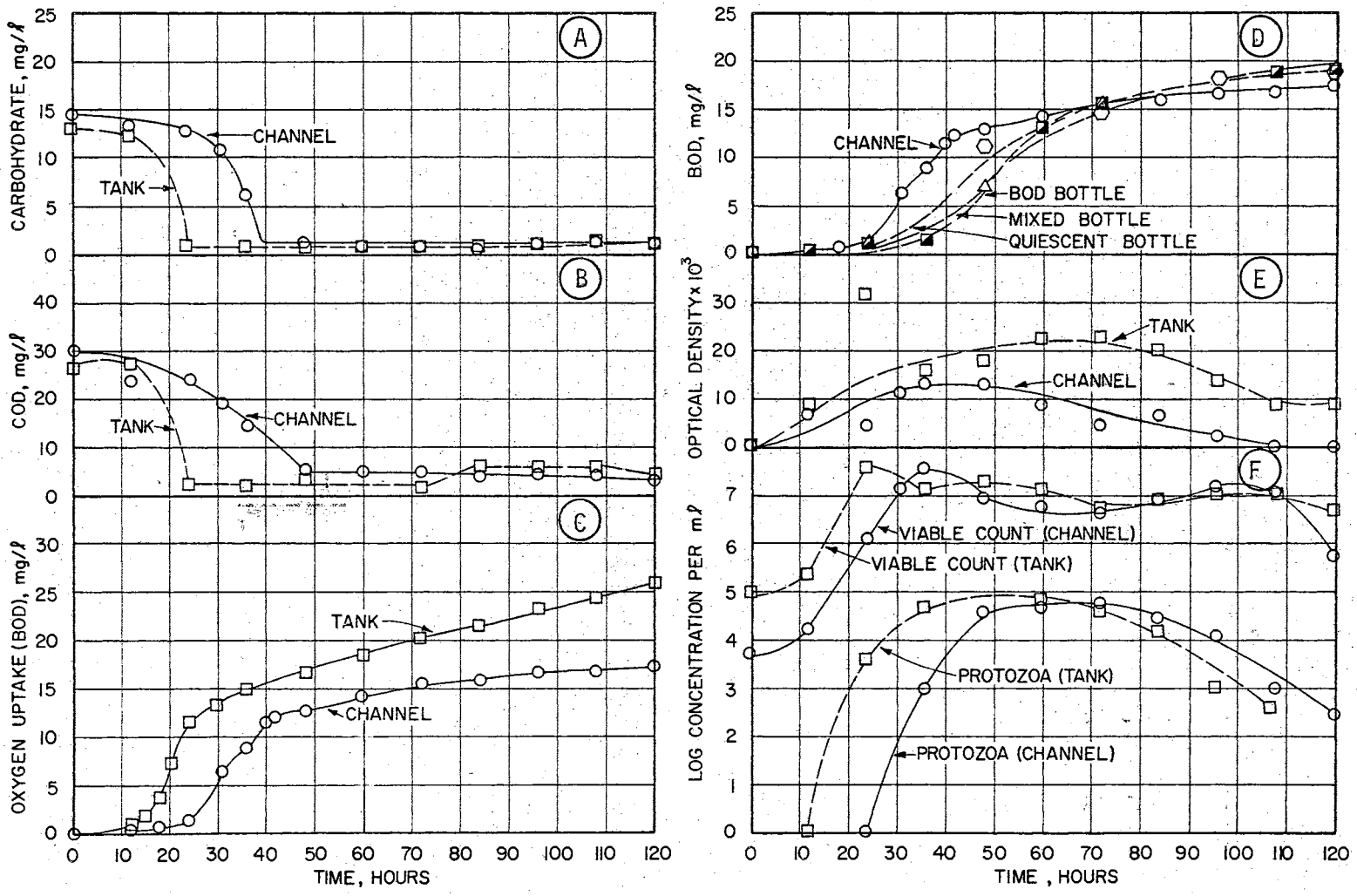


Figure 30 - Changes in system parameters using glucose-sodium glutamate substrate and acclimated sewage seed with hay infusion from sewage seed collected on 7-17-1968 (Experiment H).

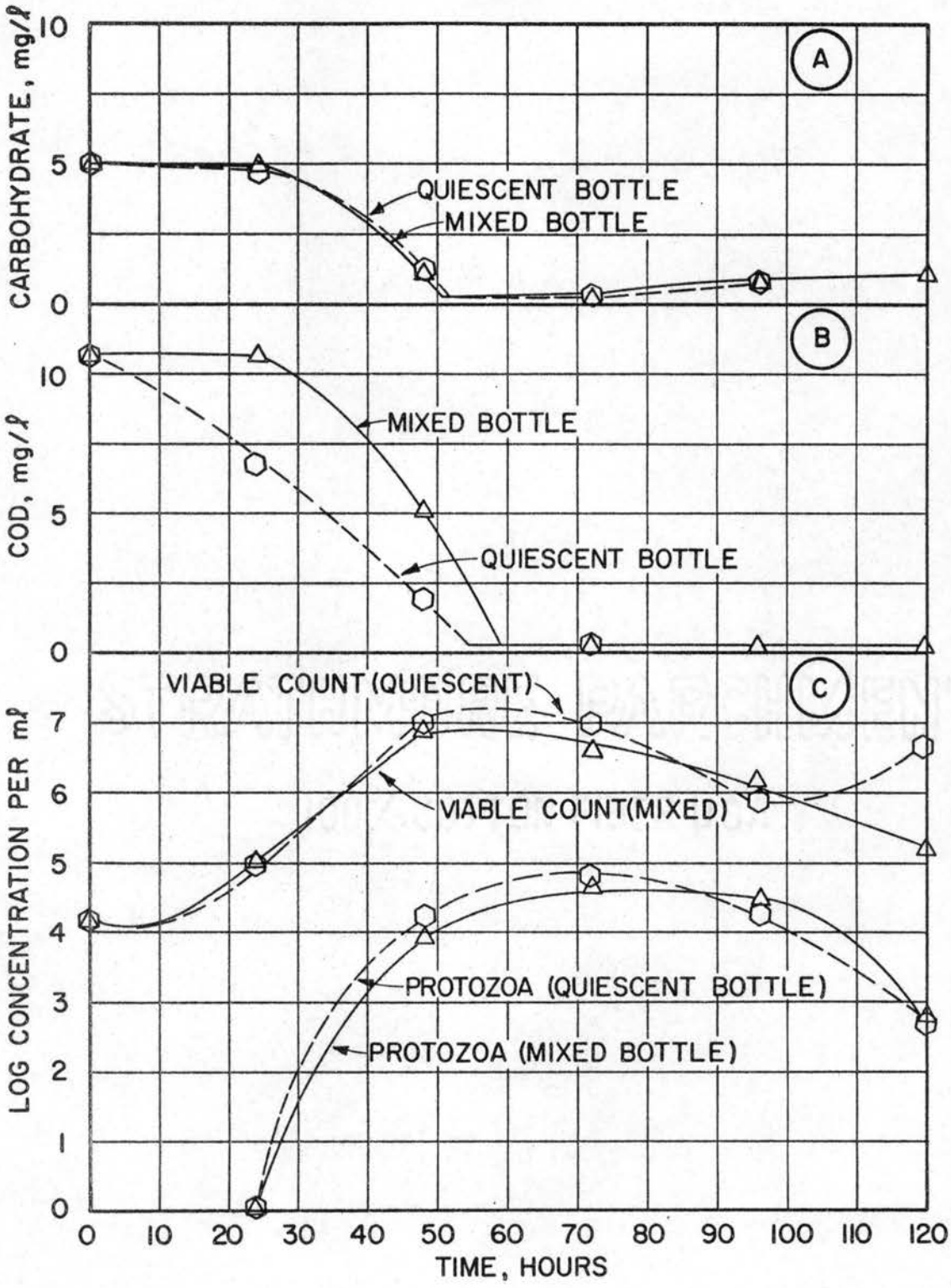


Figure 31 - Changes in bottle system parameters using glucose-sodium glutamate substrate and acclimated sewage seed with hay infusion from sewage seed collected on 7-17-1968 (Experiment H).

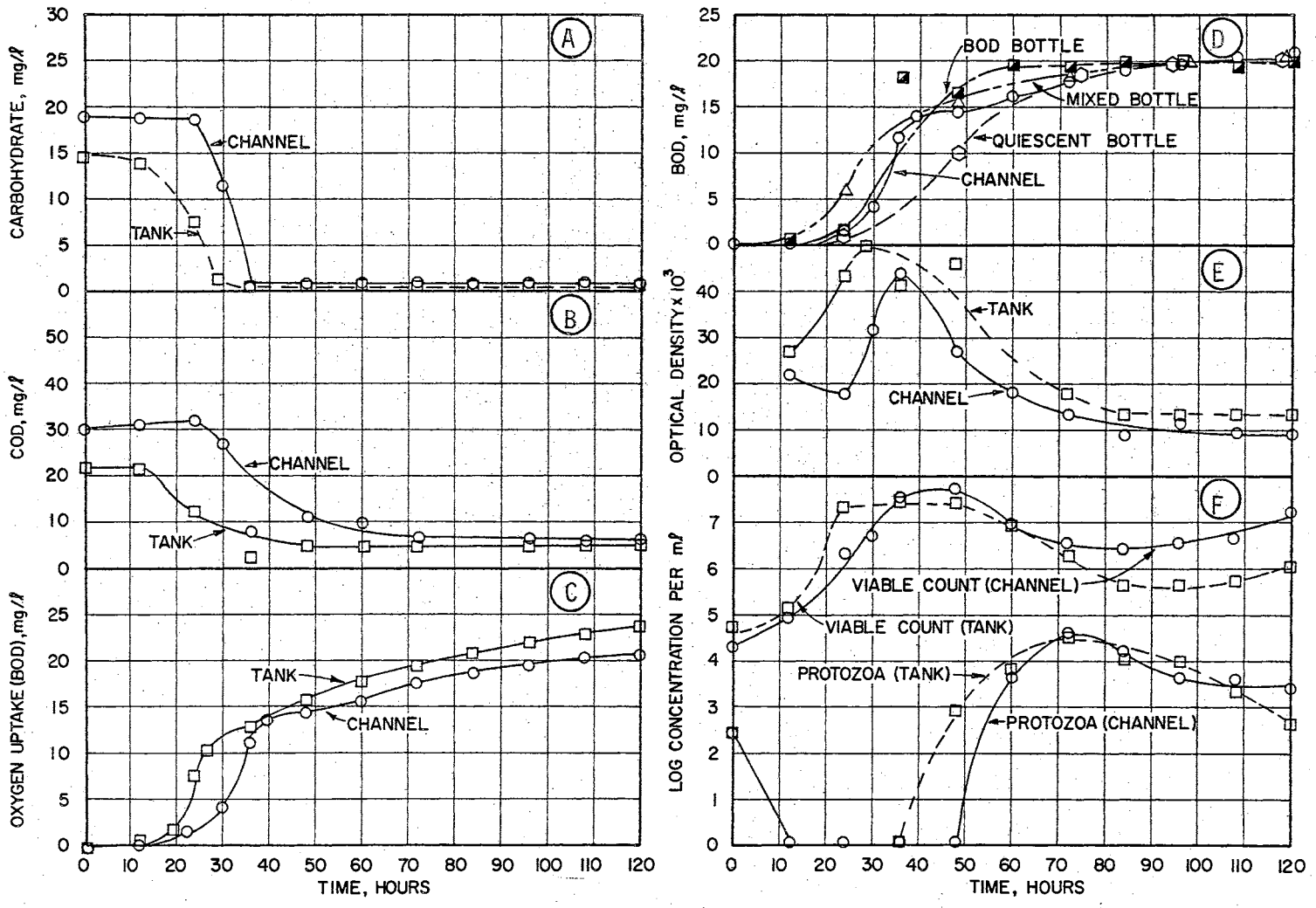


Figure 32 - Changes in system parameters using glucose-sodium glutamate substrate and acclimated sewage seed collected on 8-16-1968 (Experiment I).

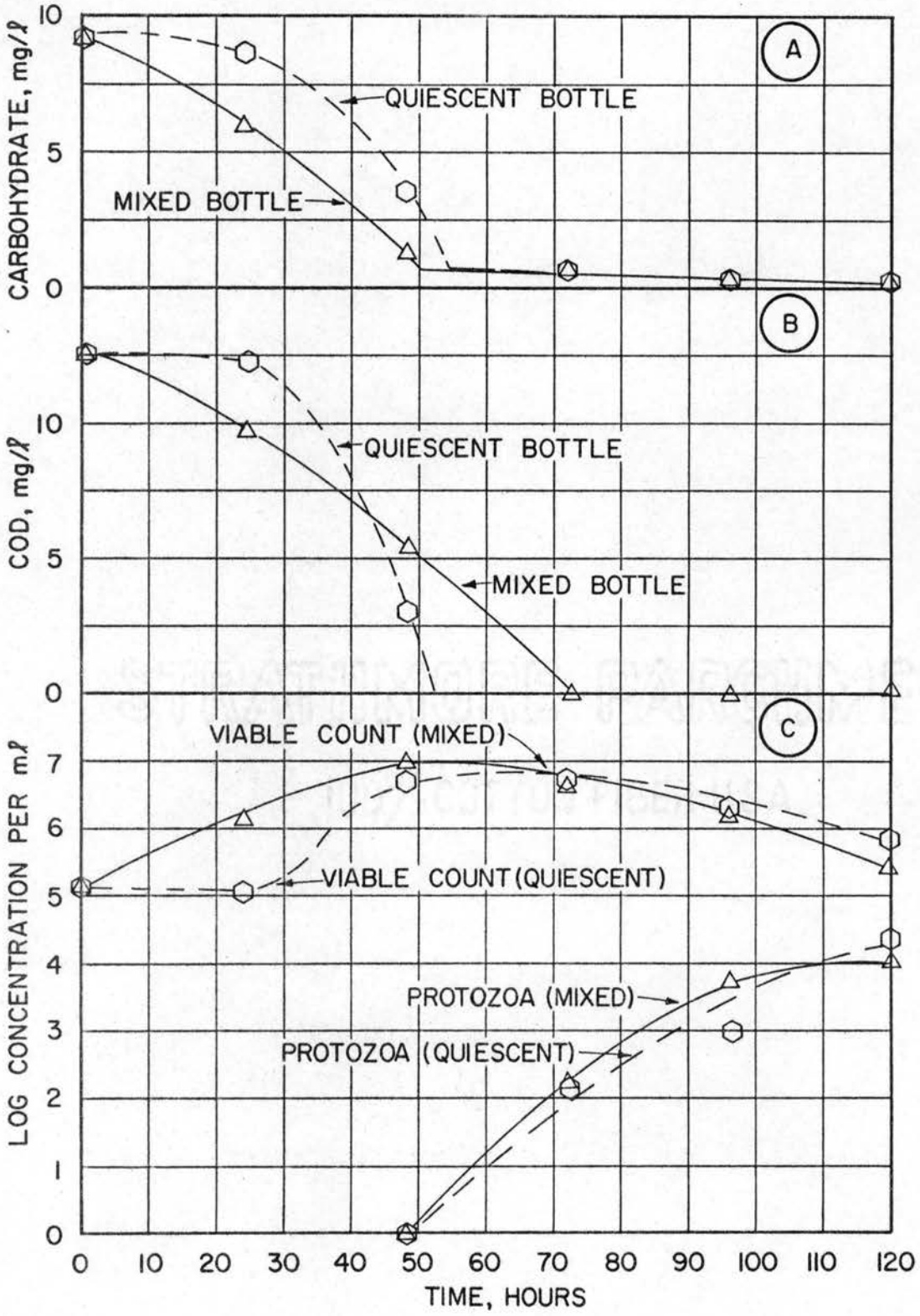


Figure 33 - Changes in bottle system parameters using glucose-sodium glutamate substrate and acclimated sewage seed collected on 8-16-1968 (Experiment I).

The seed was collected from the primary clarifier effluent launder at the Stillwater, Oklahoma, sewage treatment plant, and fed on the glucose-glutamic acid substrate for one week before using as seed for experiment G (Figures 28 and 29). A hay infusion was prepared by boiling some hay in water and adding the liquid to the remaining seed from experiment G which had been acclimated for one week. The seed was then fed the same substrate for an additional week before using with experiment H. Jahn (61) has reported that this is helpful in increasing the growth of paramecium, hypotrichs, and many small ciliates which feed on bacteria.

The daily feeding rate of 50 mg/l of both glucose and glumatic acid was sufficient to give a heavy growth of protozoa. There was no significant effect detected from the addition of the hay infusion. There was an increase in the large free swimmers and nematodes, but these are thought to have developed as a result of the prolonged acclimation period.

There was less variety in the plate colonies from the acclimated seed than from the sewage seed. The plates obtained at zero time for experiment G showed only two types of colonies. Approximately two-thirds of the colonies were white and uniform in size, and the other one-third was blue. There was some change in pigmentation of the colonies as the experiment progressed. Most of the colonies plated at 120 hours from the open systems were white, with a few red, green, and blue ones being noted. The colonies plated from the bottle systems were mostly blue, with a few white ones on the plates.

The lag period was twenty-four hours for all systems in experiment G, which was longer than the average for the open system experiments in

group I using sewage seed. This appears to indicate that the "lag" does not entirely represent an acclimation period, but that it was also affected by low bacterial numbers. There was a considerable reduction in viable count during the lag period (see 0 and 12-hour counts shown in Figure 28-F).

The viable count peaks for all systems occurred at the same time as the substrate was exhausted and the oxygen uptake plateau began, as was observed for experiments using non-acclimated seed. The higher viable count in the acclimated seed gave a shorter lag period for the bottle systems. In experiments G, H, and I, the lag period was shortened to twenty-four hours for the bottle systems as compared with an average lag of forty hours for the five experiments in group I. The higher bacteria counts in the closed systems appears to have been sufficient to cause a secondary uptake for the bottle systems, giving an oxygen uptake approaching that observed for the open systems. Not only was the lag period the same for both the open and closed systems, but the wide difference in the 5-day oxygen uptake for the open and closed systems that was observed for the experiments in group I was not found in this group of experiments. This appears to give additional support to the concept that the second phase of oxygen uptake is related to predator activity, since the bacterial and protozoa growth also occurs much earlier in the bottle system for this group of experiments than in the group I experiments.

The seed inoculum for the stirred tank in experiment H was higher than that used in the simulated channel. This produced a shorter lag period for the stirred tank than was found for the simulated channel. The higher inoculum of biological solids also appears to mask the

plateau which was less evident in the curves shown in part C of Figures 28, 30, and 32, than was found for the experiments in group I.

A die-off or inactivation was observed for the protozoa in both the open and closed systems (Figures 32-F and 33-C) during the lag period. This was apparently caused by the reduction in bacterial population when the seed was diluted to 5 ml/l when the systems were seeded. Dead or inactive protozoa and nematodes were visible in the samples taken for microscopic examination until near the end of the log growth phase. This inactivation appeared to occur very rapidly following the seeding of the units. Approximately forty-five minutes elapsed between the time of seeding and the microscopic examination, and except for experiment I there was no protozoa activity at the time of this initial microscopic examination.

The average oxygen uptake at the plateau was 39 per cent of the theoretical O_2 demand value. This is the same average per cent as was observed for the group I experiments. The average 5-day BOD was 66 per cent of the theoretical for the simulated channel experiments in this group.

4. Group III - Experiments Using Settled Sewage as Substrate

Two experiments, J and K, were conducted using settled sewage as substrate. The settled sewage was collected from the effluent launder of the primary clarifier at the Stillwater, Oklahoma, sewage treatment plant. The time of flow to the plant plus inplant time was estimated to be about five hours. An additional one and one-half hours were required to collect and transfer the sewage to the units. Thus the initial samples were for sewage approximately seven hours old. The 5-day responses observed in these experiments for the selected parameters

are shown in Figures 34, 35, and 36.

The oxygen uptake for the open systems was essentially defined by a first order decreasing rate formulation. The k_1 rates varied from 0.122 day^{-1} to 0.257 day^{-1}. The k_1 rates for the open system data shown in Figures 34 and 36 were calculated on the basis of a first order decreasing rate reaction for the entire duration of the experiment. It is seen from Table X that the rate constants are 0.230 and 0.218 day^{-1} for the channel and tank, respectively. The decreasing rate constants for experiment K were 0.122 and 0.257 day^{-1} for the channel and tank, respectively.

Figures 34-A and 36A indicate that there was no exogenous carbohydrate in the sewage at the beginning of the experiment. Both total and filtrate COD are shown for both experiments. There was little change indicated in the soluble COD during the experiment, and it appears that a small residual COD exists in sewage that may be caused by biologically stable compounds. McWhorter and Heukelekian (40) have also reported a residual COD when using glucose as substrate. There was a significant decrease in total COD during the first couple of days of the experiment.

The viable count increased from about two million to twenty million organims/ml during the first day of the experiment. This increase was then followed by a gradual decrease in viable count during the following four days.

Hoover and his associates (35) proposed in 1952 that the substrate assimilation phase of biochemical reactions is often completed before the sample is introduced into the BOD bottle. The results of these experiments also indicate that most of the biological growth had

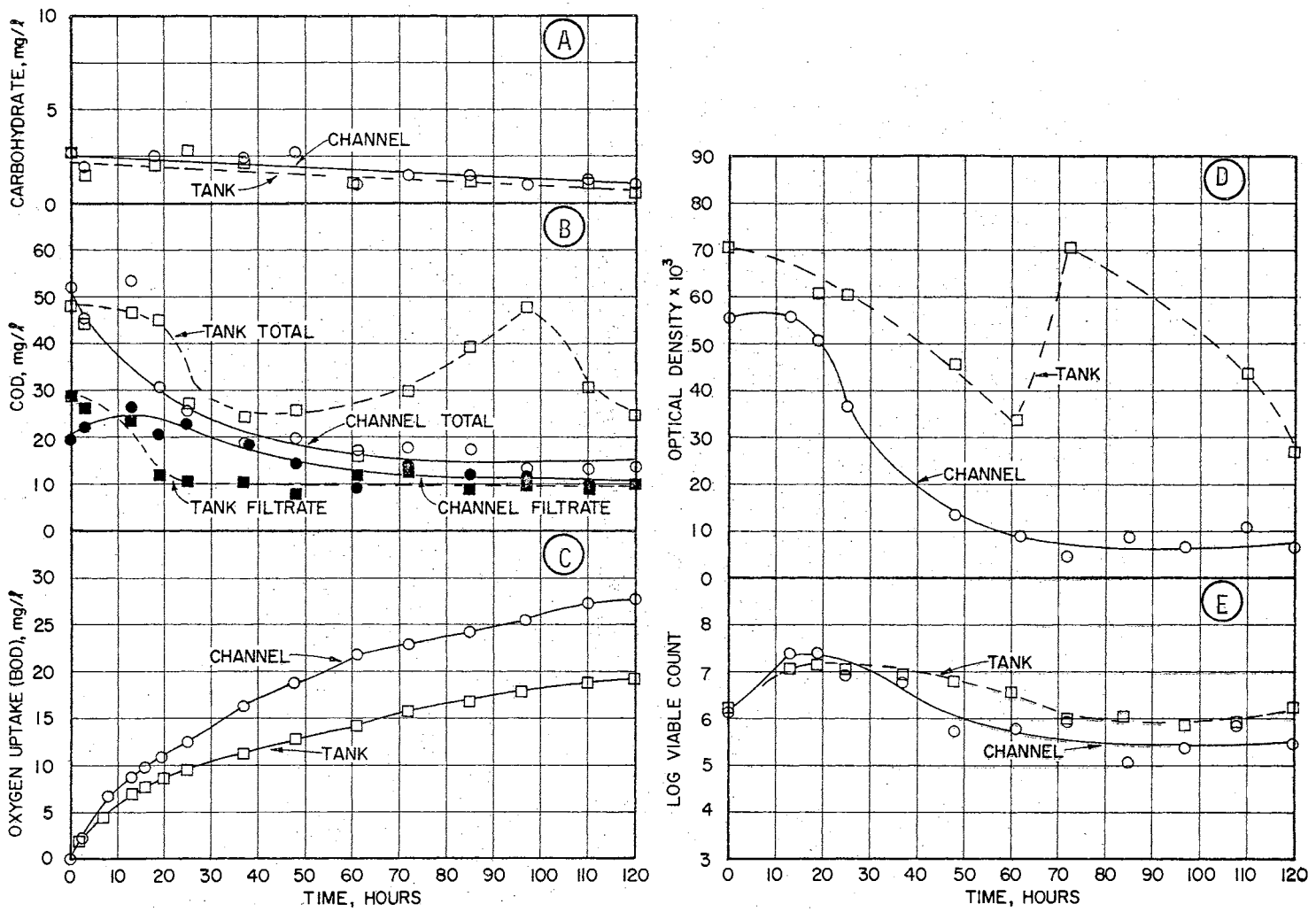


Figure 34 - Changes in system parameters using sewage collected on 4-22-1968 (Experiment J).

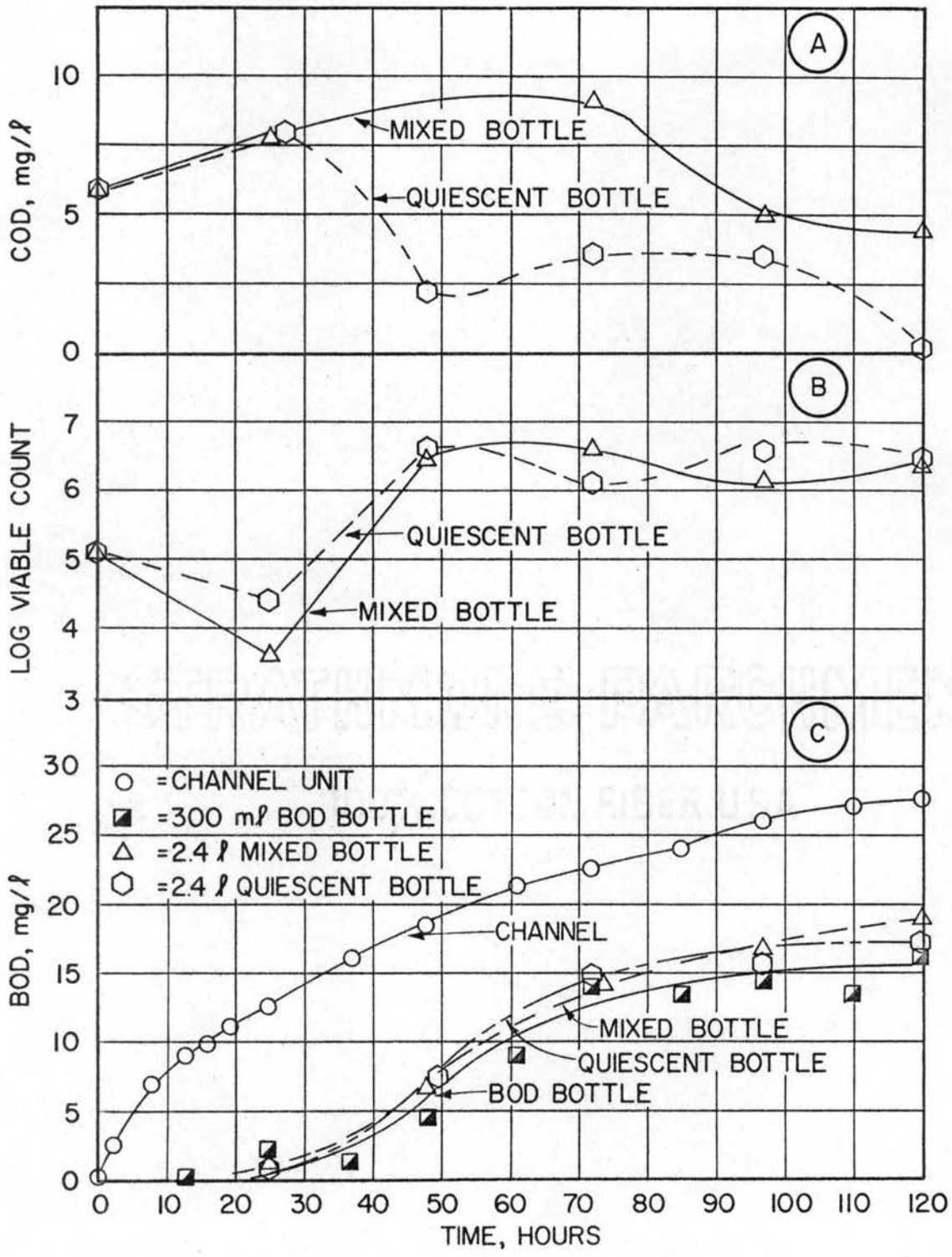


Figure 35 - Changes in bottle system parameters using sewage collected on 4-22-1968 (Experiment J).

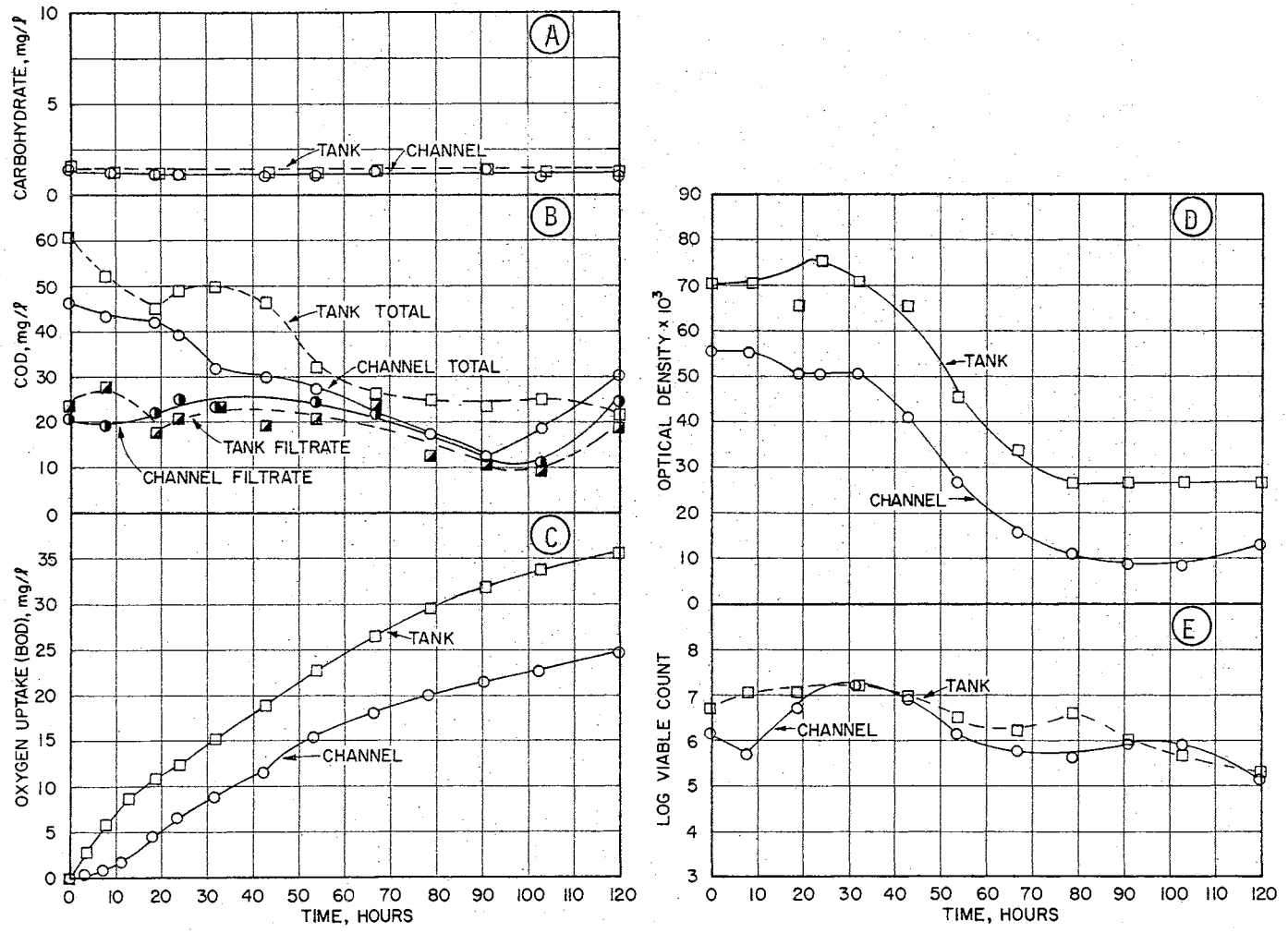


Figure 36 - Changes in system parameters using sewage collected on 4-28-1968 (Experiment K).

occurred prior to the beginning of the experiment. Since the higher oxygen demands were found (from other experiments in the present research) to be associated with the period of biological growth, it is indicated that the critical period of oxygen uptake had occurred prior to the beginning of the experiment.

Gaudy, et al. (46) have also reported decreasing oxygen uptake rates for systems having high biological solids to substrate ratios. This type of oxygen uptake was also reported for nonproliferating biological systems (71). Thus it appears that systems having high biological solids and low substrate concentrations exhibit oxygen uptake rates that are essentially defined by decreasing first order rate kinetics.

As shown in Figure 35-C, the bottle systems exhibited a lag period of about twenty hours, whereas there was no lag period found in the tank or channel system. Since there was no difference in the open and closed systems other than dilution, there was no other apparent reason for the lag. The lag period in the closed systems was followed by a normal oxygen uptake curve as observed in the experiments of the other groups.

The sewage contained a sufficient quantity of clay and other inorganics to affect the optical density readings. Much of this material settled to the bottom of the channel during the experiment. After about the third day of the experiments, the sewage was essentially clear, as shown by the low optical density data.

5. Group IV - Experiments Using Dry Milk as Substrate and Sewage Seed

It was deemed desirable to study the response of a complex substrate in the four systems selected for this research. Therefore, Experiments L and M were conducted using non-fat dry milk as substrate

and settled sewage as seed. The data for these experiments are given in Figures 37, 38, and 39.

The general nature of the response of the complex waste was the same as that observed for the glucose-glutamic acid substrate. The oxyten uptake exhibited a lag, followed by an increasing rate which occurred at the same time as the substrate was removed and the bacteria were exhibiting logarithmic growth. The increasing oxygen uptake rate was followed by a plateau and a secondary demand as was observed for the experiments in group I.

An exceptionally long lag was found for experiment L (Figure 37). In fact, the lag period was so long for the bottle systems that no oxygen uptake was exhibited during the 5-day experimental period. No carbohydrate was removed in the bottle system, and no biological growth was exhibited in the viable counts. The longer lag periods observed for the bottle system appeared to be caused by the lower substrate concentrations, since the seed material was the same for all systems.

The fraction of the initial COD removed at the plateau was 42 and 40 per cent for the simulated channel and stirred tank, respectively, in experiment L. For experiment M the plateau occurred at 32 and 43 per cent COD removal for the two open systems. The rate constant, k_1, was also found to be of the same magnitude as observed for experiments in groups I and II.

The oxygen uptake for the bottle systems in experiment M (Figure 38-D) shows a longer lag period and a lower 5-day oxygen demand than was observed for the open units. Here, as in the experiments in group I, the oxygen demand for the bottle systems corresponds to the plateau value for the open systems, indicating that the second phase of oxygen

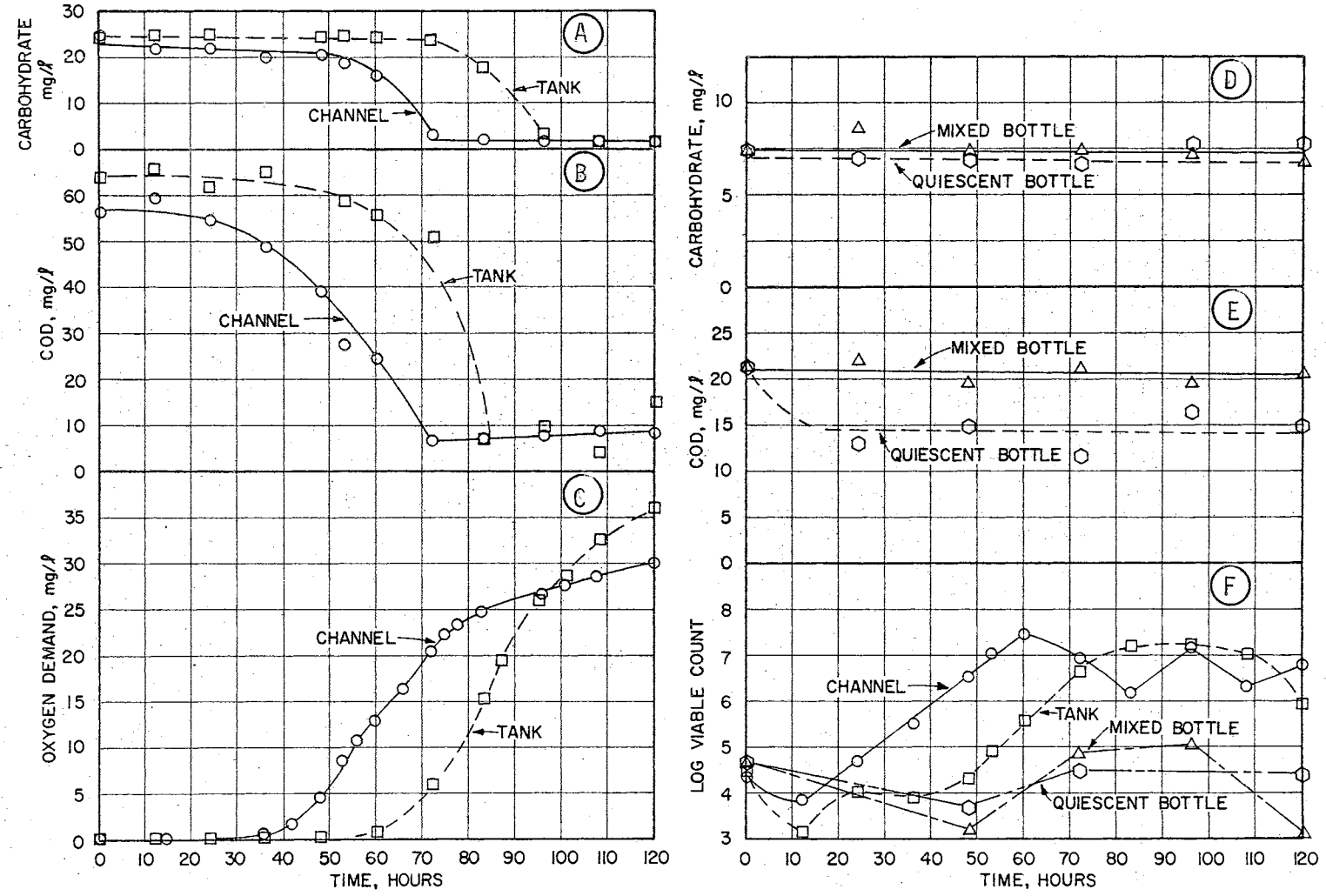


Figure 37 - Changes in system parameters using dry milk substrate and sewage seed collected on 5-4-1968 (Experiment L).

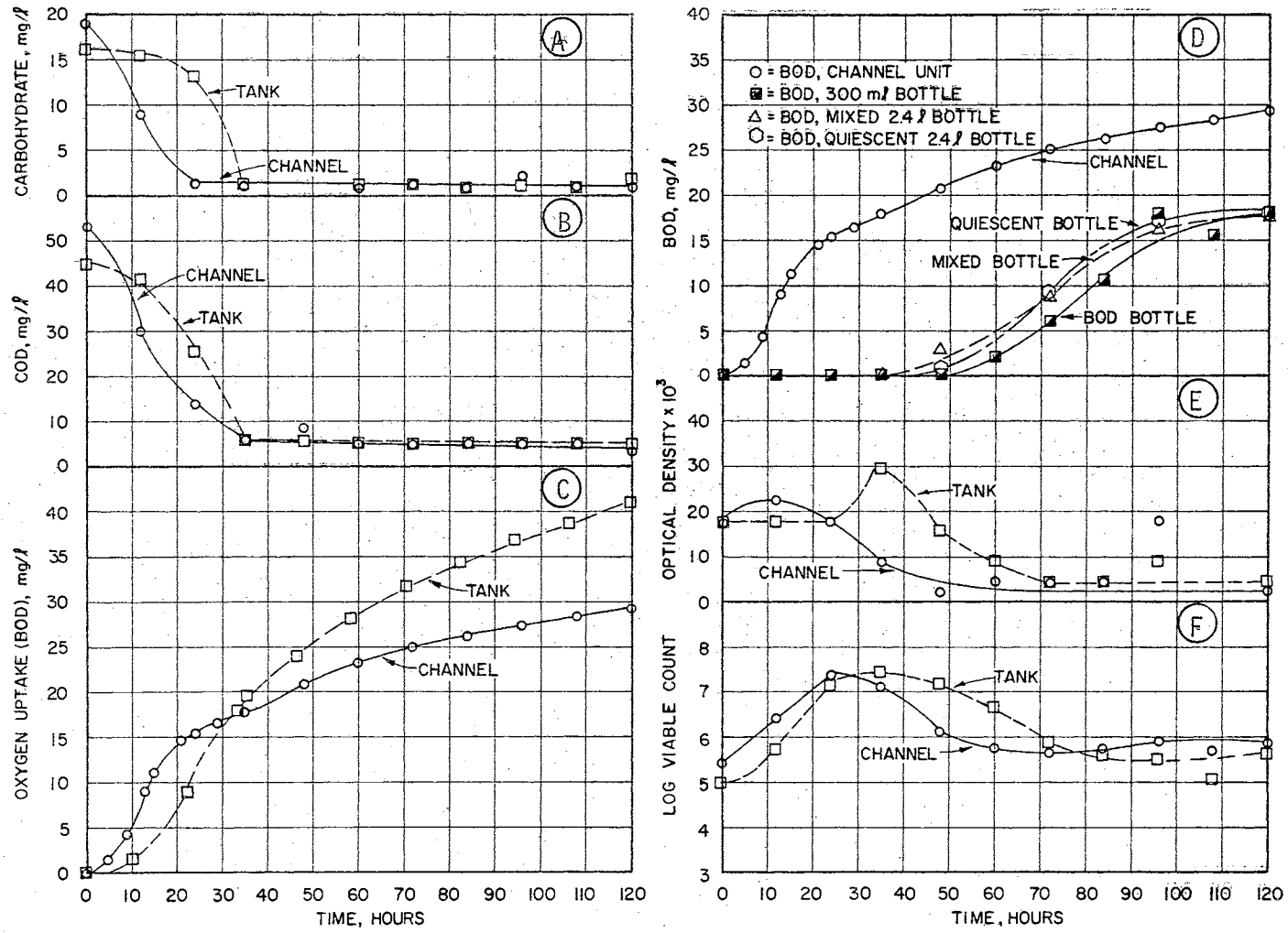


Figure 38 - Changes in system parameters using dry milk substrate and sewage seed collected on 5-12-1968 (Experiment M).

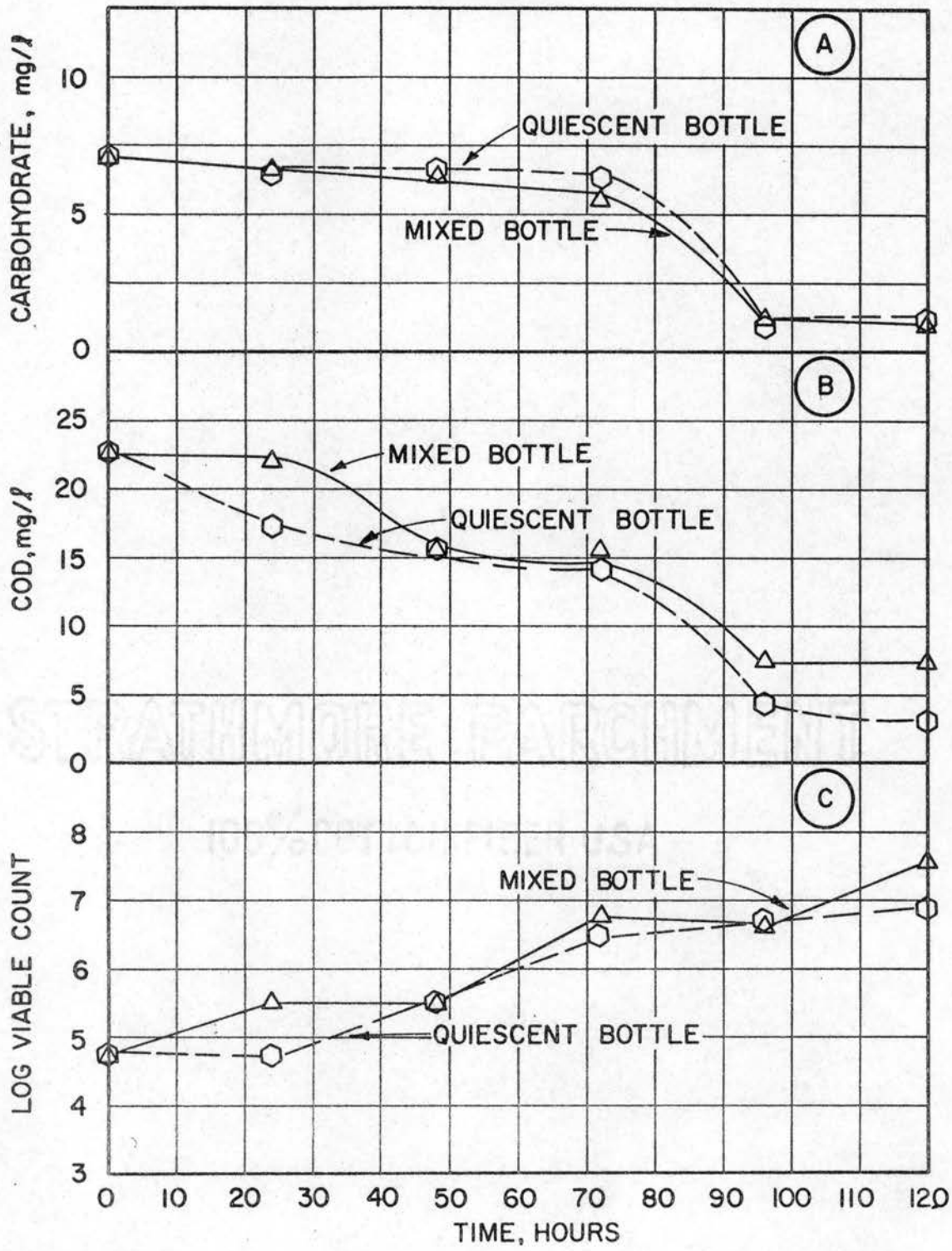


Figure 39 - Changes in bottle system parameters using dry milk substrate and sewage seed collected on 5-12-1968 (Experiment M).

uptake was probably delayed in the more dilute system.

In summary, it seems apparent that while seed composition may vary sufficiently to cause different lag periods, the rate of oxygen uptake during the substrate removal phase and the ratio of the oxygen uptake to initial COD are consistently of the same magnitude.

6. Group V - Experiments Using Dry Milk as Substrate and Acclimated Sewage Seed

Group V includes experiments N and O which are the experiments conducted using non-fat dry milk as substrate and acclimated sewage seed. The data for these experiments are shown in Figures 40 through 43.

Because of the long lag periods experienced in experiment L, which could have been caused by the low solids concentration or the need for an acclimation period, the sewage seed used in these experiments was grown on dry milk substrate for one week prior to beginning the experiments. Microscopic examination of the seed showed high concentrations of protozoa and nematodes. The bacterial count in the systems was about 2×10^5 after adding 5 ml of seed/l. However, acclimation of the seed to the substrate did not eliminate the lag period; in fact, there is no apparent explanation for the difference in the lag period observed for the two open systems as shown in Figure 40-C. The initial conditions were the same for the two reactors as shown by the initial COD, carbohydrate, and viable count (Figure 40). There was a decrease in viable count for the simulated channel and the bottle systems during the first day of the experiment. The protozoa activity ceased during this period, and dead or inactive protozoa and nematodes were observed by microscopic examination of samples.

The experiment was repeated about three weeks later, using a

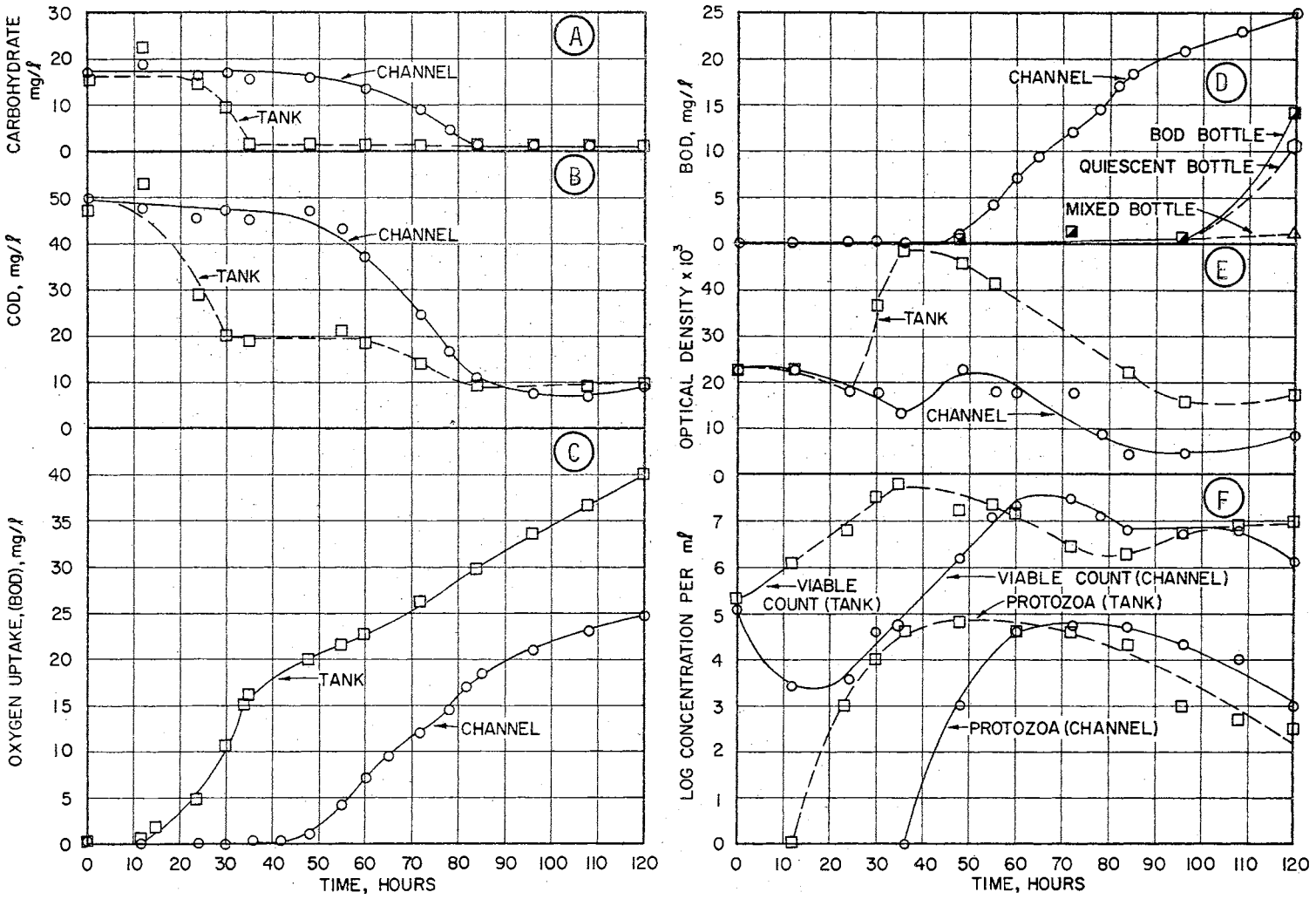


Figure 40 - Changes in system parameters using dry milk substrate and acclimated seed with hay infusion from sewage collected on 7-28-1968 (Experiment N).

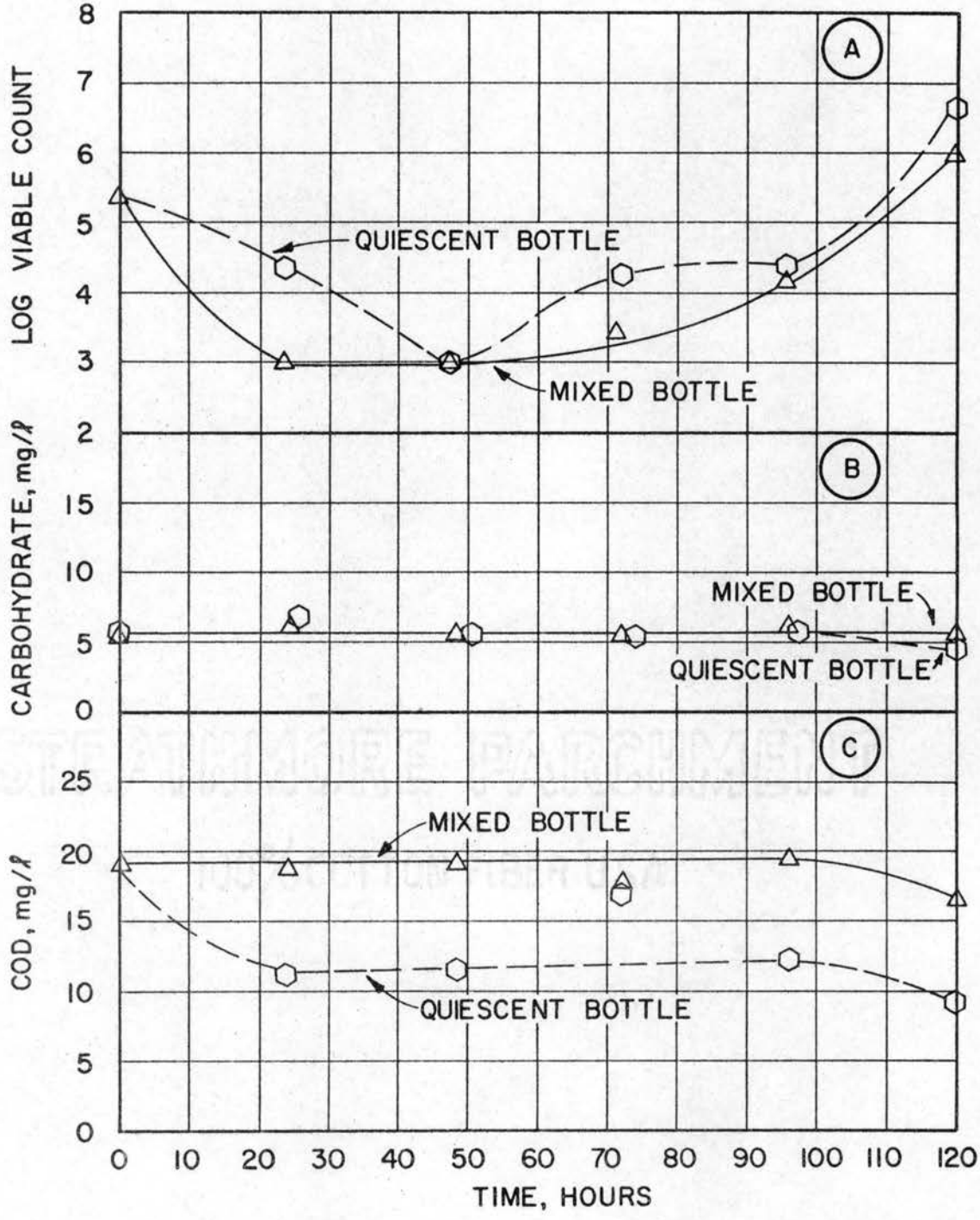


Figure 41 - Changes in bottle system parameters using dry milk substrate and acclimated seed with hay infusion from sewage collected on 7-28-1968 (Experiment N).

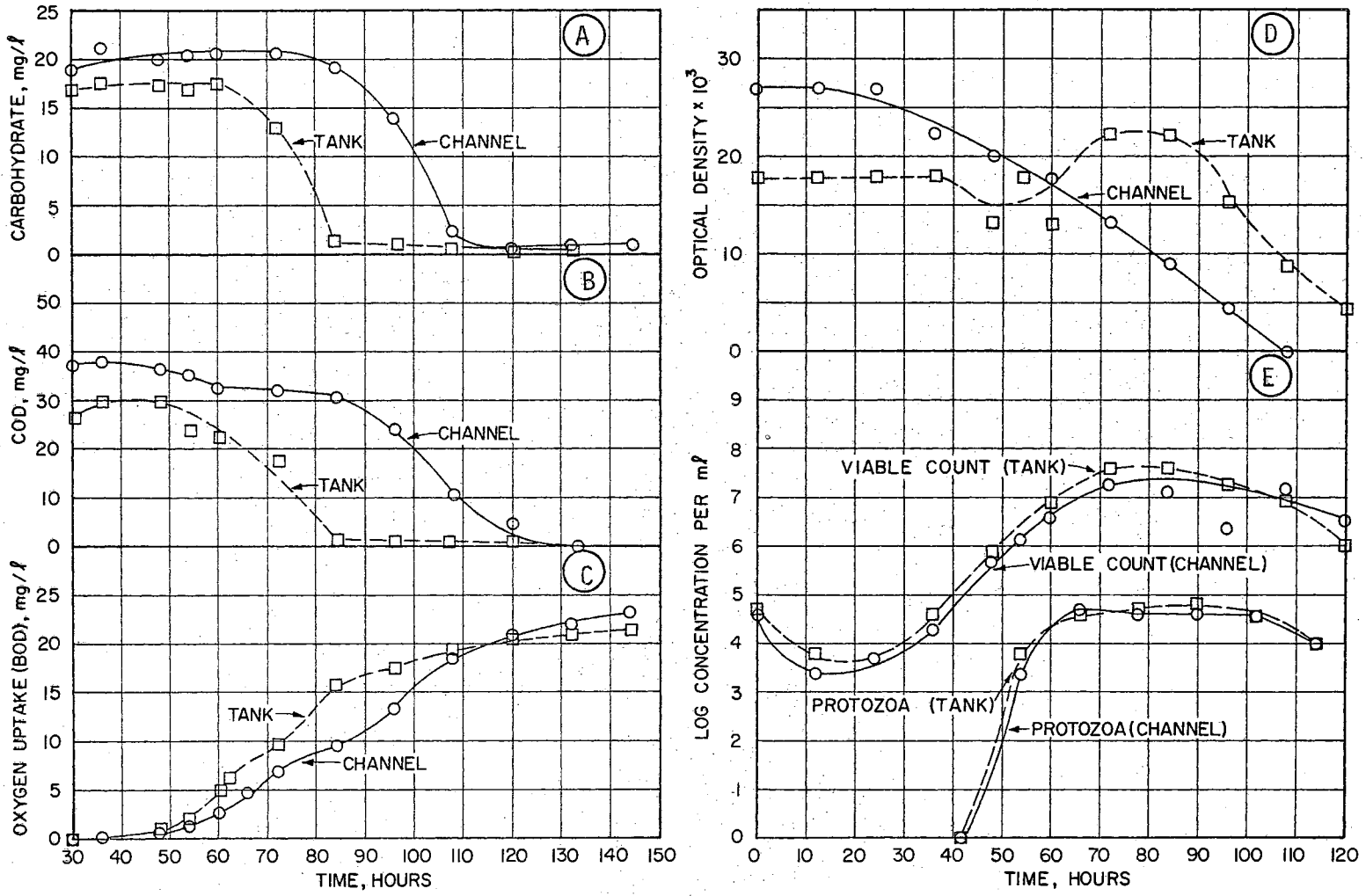


Figure 42 - Changes in system parameters using dry milk substrate and acclimated seed from sewage collected on 8-17-1968 (Experiment 0).

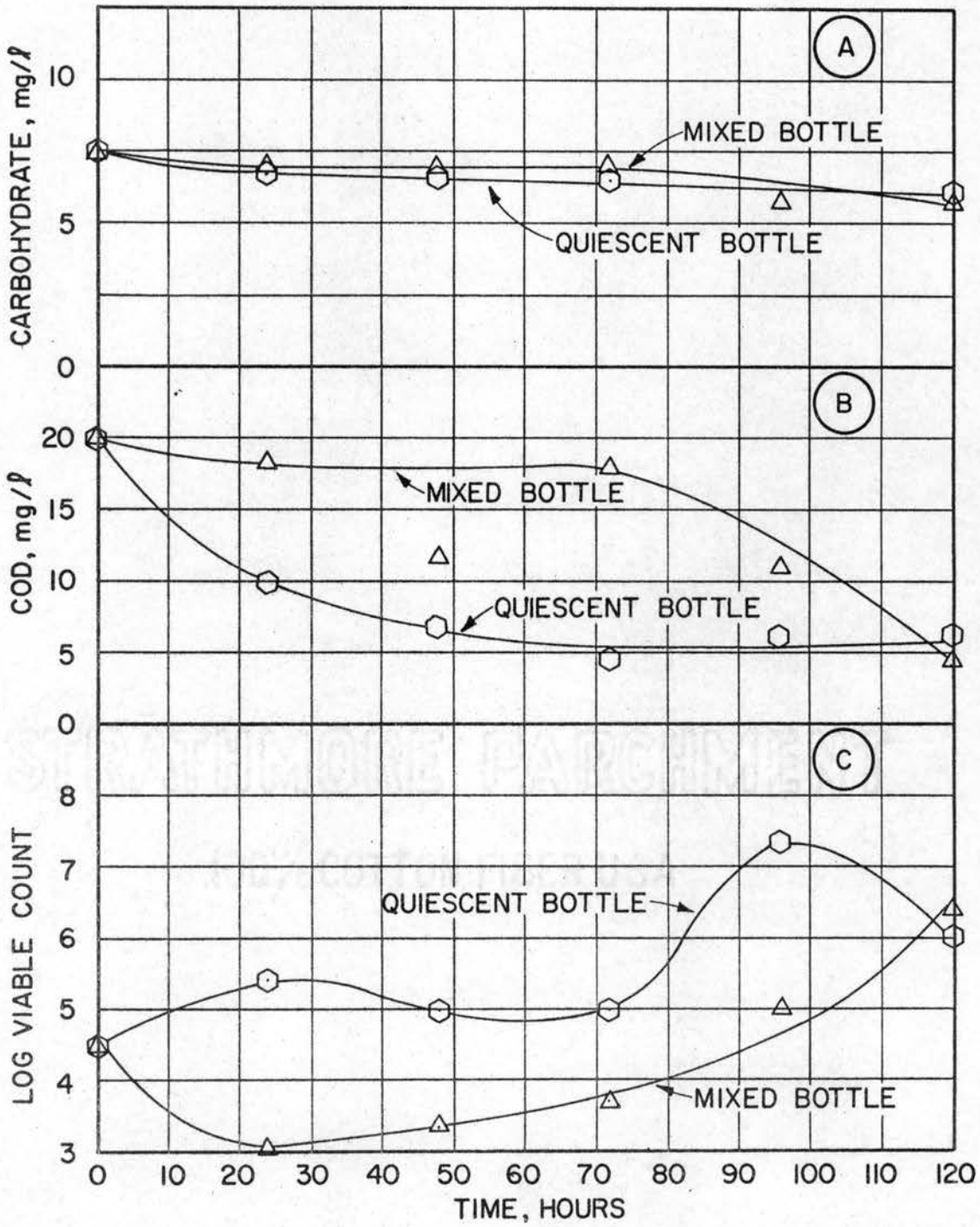


Figure 43 - Changes in bottle system parameters using dry milk substrate and acclimated seed from sewage collected on 8-17-1968 (Experiment 0).

different acclimated seed. The results of this experiment are shown in Figures 42 and 43 (experiment O). The initial viable count was of the same magnitude as was observed for experiment N. A decrease in the viable count occurred during the first day of aeration (Figure 42-E) as was found for experiment N.

The growth pattern observed for the experiments in this group and for group II experiments where acclimated seed was also used, indicate that the lag periods not only represent an acclimation period, but it appears that the lag period may also be related to dilution, i.e., initial number of feeding organisms. It is seen from experiments N and O that a seed growing on a substrate exhibits a significant lag period when both the seed and substrate are diluted.

7. Group VI - Relation of Response in Channel and Bottle Systems for Equal Substrate Concentrations

The results of the previous experiments indicate that the longer lag periods and lower increasing oxygen uptake rates observed in the closed systems were caused by a lower substrate concentration. Therefore it was decided to aerate the dilution water for the bottle system with oxygen, thus raising the oxygen concentration to a sufficient level to permit the use of a higher substrate concentration in the bottles.

Experiment P was run using the simulated channel and the bottle systems which included the standard 300 ml BOD bottles, the 2.4 liter mixed bottles, and the 2.4 liter quiescent bottles. The dilution water was aerated with compressed oxygen and the seed and substrate were added, giving an initial COD in the bottle system of 34.7 mg/l and a COD of 31.5 mg/l in the channel.

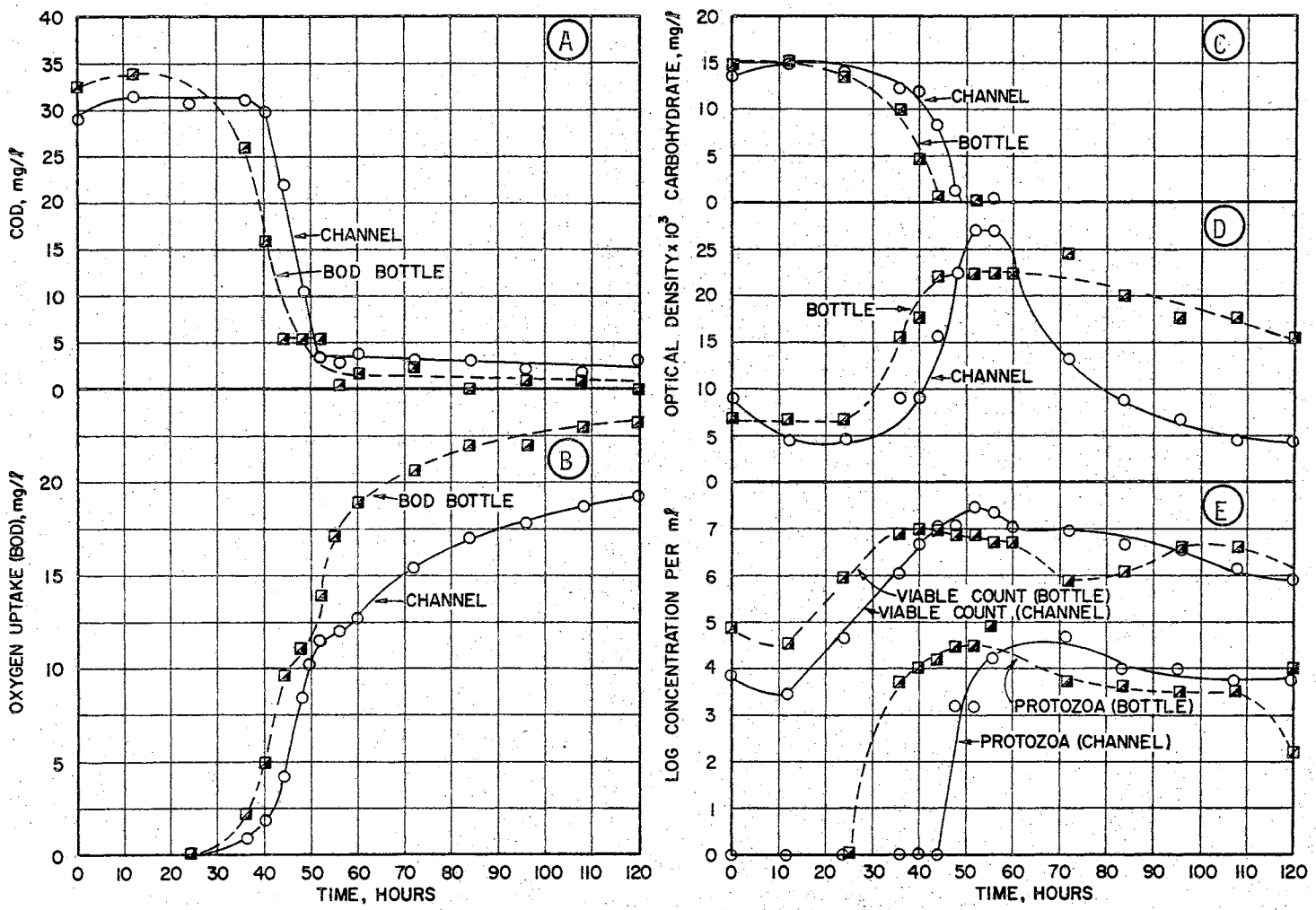
The relative response of the channel and the 300 ml BOD bottle system is given in Figure 44. It is seen that the lag period for the bottle system is now essentially the same as was observed for the channel. Therefore, it seems that the lag period is related to the substrate concentration. The initial COD in the BOD bottles was slightly higher than that of the channel, and this also gave a slightly shorter lag period. The increasing rate constants for the two systems shown in Figure 44 are the same. The plateau occurred at essentially the same position and at the time corresponding to the substrate depletion and maximum bacterial counts.

The earlier bacteria growth in the BOD bottles appeared to induce an earlier protozoa growth and higher second phase oxygen uptake. The lower initial viable count in the channel appears to have delayed the onset of protozoa growth in that system; however, as seen from Table X, there is only a small difference in either the k_i or the k_1 rate constant for the two systems. The percent COD removed at the plateau was 30 per cent for the channel, and 32 per cent for the bottle system. Sixty-two per cent of the COD was removed in the channel in five days, and 68 per cent was removed in the bottle system.

Figure 45 shows the observed 5-day response in the three types of bottles used in this research. It is seen that there was no significant difference in the response observed for the quiescent bottle and the mixed bottle for the relatively low degree of agitation employed.

8. Group VII - Bottle Systems Employing Various Substrate Concentrations

The results of Experiment P (Figures 44 and 45) indicated that the lag period and oxygen uptake rates are related to substrate concentration. Therefore, experiments were designed to determine the effect of



Experiment 44 - Observed response in simulated channel and BOD bottle when the same substrate concentration was applied (Experiment P).

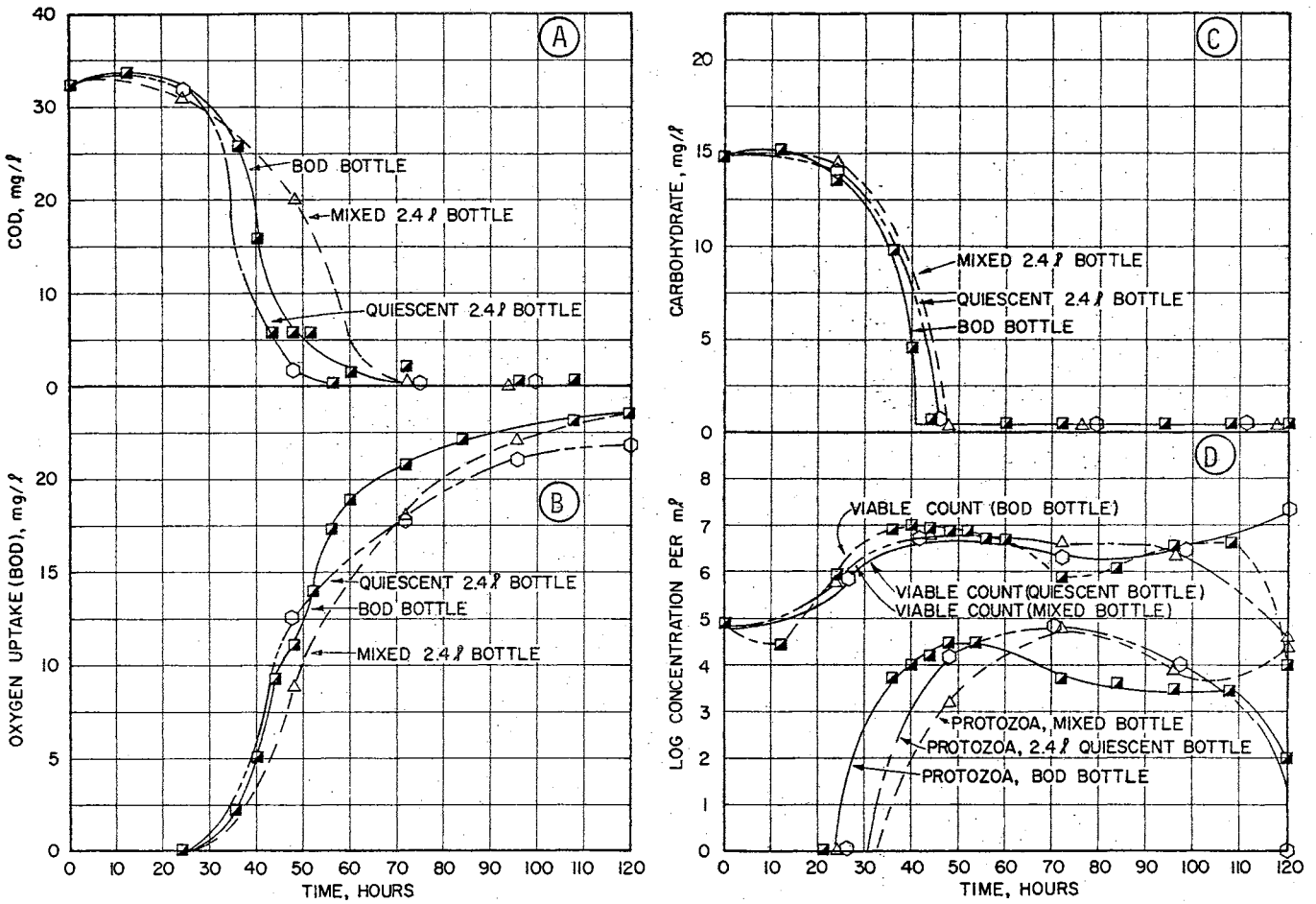


Figure 45 - Observed response in mixed and quiescent bottle systems employing the same seed and substrate concentration (Experiment P).

substrate concentration on the lag period and the increasing oxygen uptake rate. These experiments are designated Q and R, and the data are shown in Figures 46 through 49.

Four systems employing a glucose-glutamic acid substrate and sewage seed were established, using standard BOD bottles for incubation. The dilution water was aerated with compressed oxygen, which gave an initial oxygen concentration of 29 mg/l for experiment Q. This oxygen concentration was not sufficient to supply the oxygen requirements throughout the substrate utilization period, but the objective of these experiments was to determine the effect of substrate concentration on the system kinetics during the increasing oxygen uptake period. Thus this oxygen concentration was sufficient to permit the employment of substrate concentrations to well above the range found in receiving streams.

The initial COD concentrations for experiment Q are shown in Table XI and Figure 46-D. The results of experiment Q are shown in Figures 46 and 47. There was essentially no oxygen used during the first twelve hours of incubation. The increasing rate of oxygen uptake was found to be related to the substrate concentration. The optical density data, which are a measure of growth, also indicated a relationship between growth rate and substrate concentration.

The oxygen uptake data shown in Figure 46-B are plotted on a semi-logarithmic scale in Figure 47. It is seen from the data that the oxygen uptake during the substrate removal phase was defined by a first order increasing function of the following form:

$$\frac{dY}{dt} = K_i Y \tag{68}$$

where Y is the oxygen uptake, and K_i is the increasing rate constant. The rate constants for the four systems are given in Table XI.

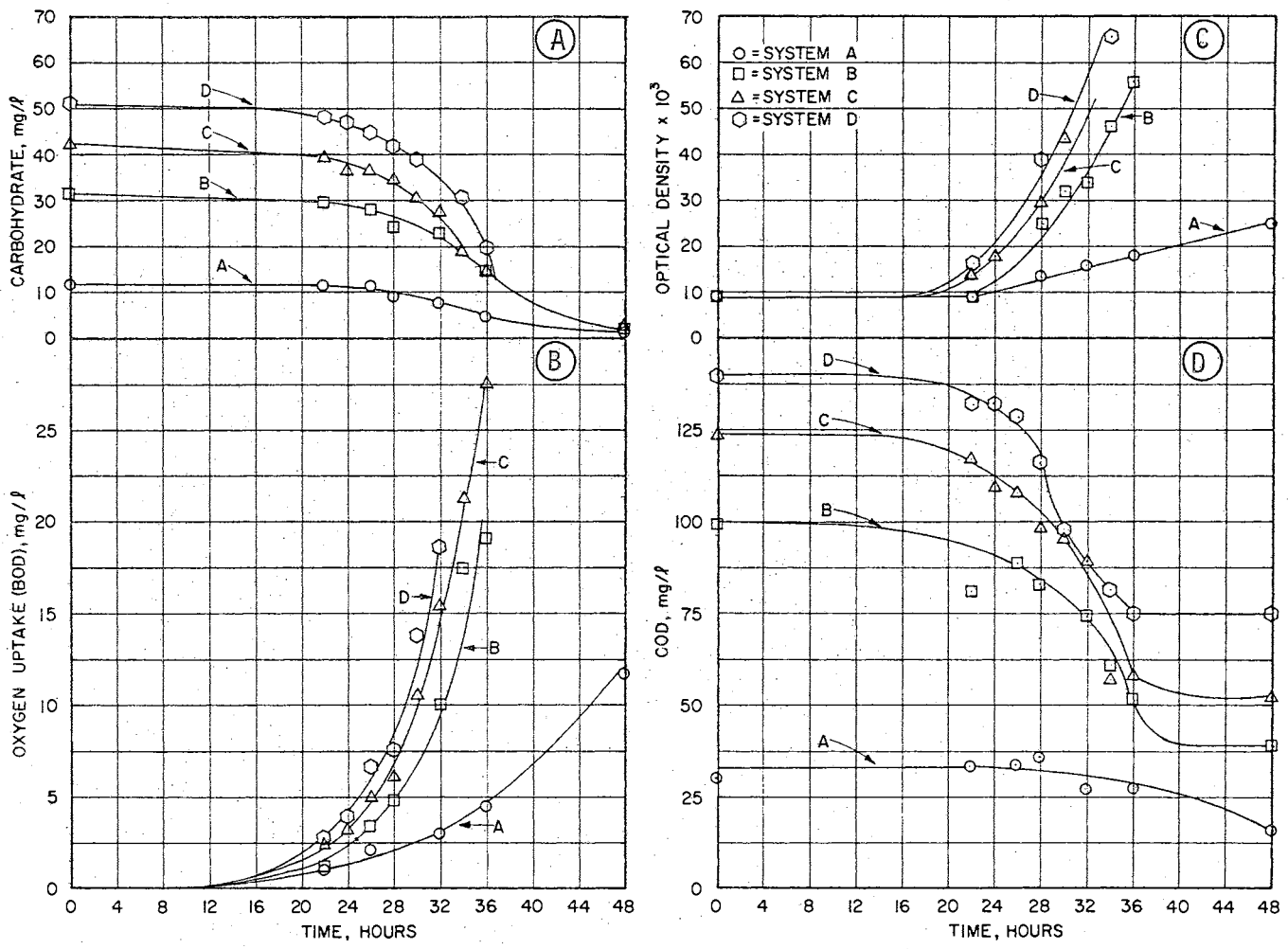


Figure 46 - Observed response of bottle systems when employing various initial substrate concentrations with sewage seed (Experiment Q).

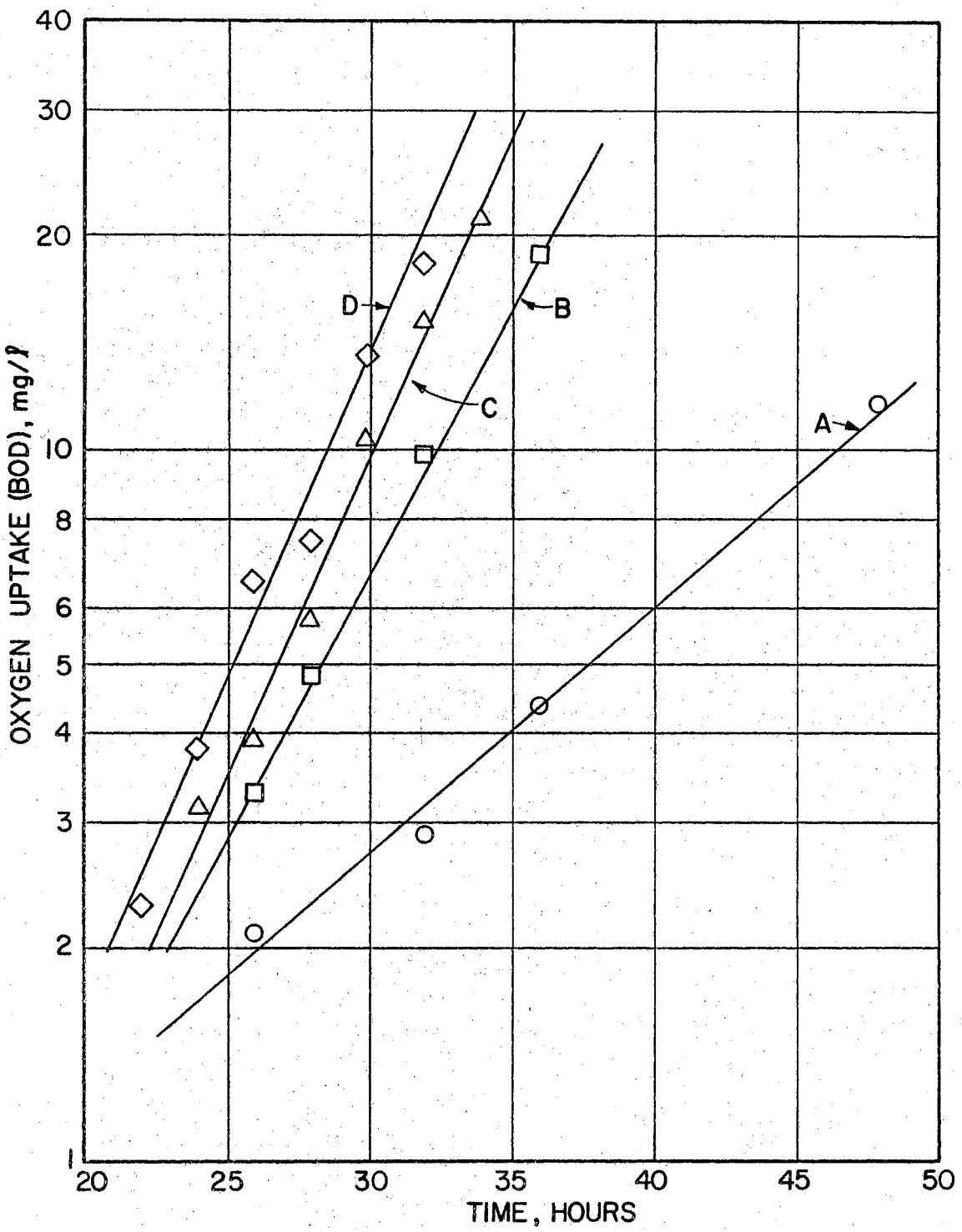


Figure 47 - Increasing oxygen uptake rates for indicated system (Experiment Q).

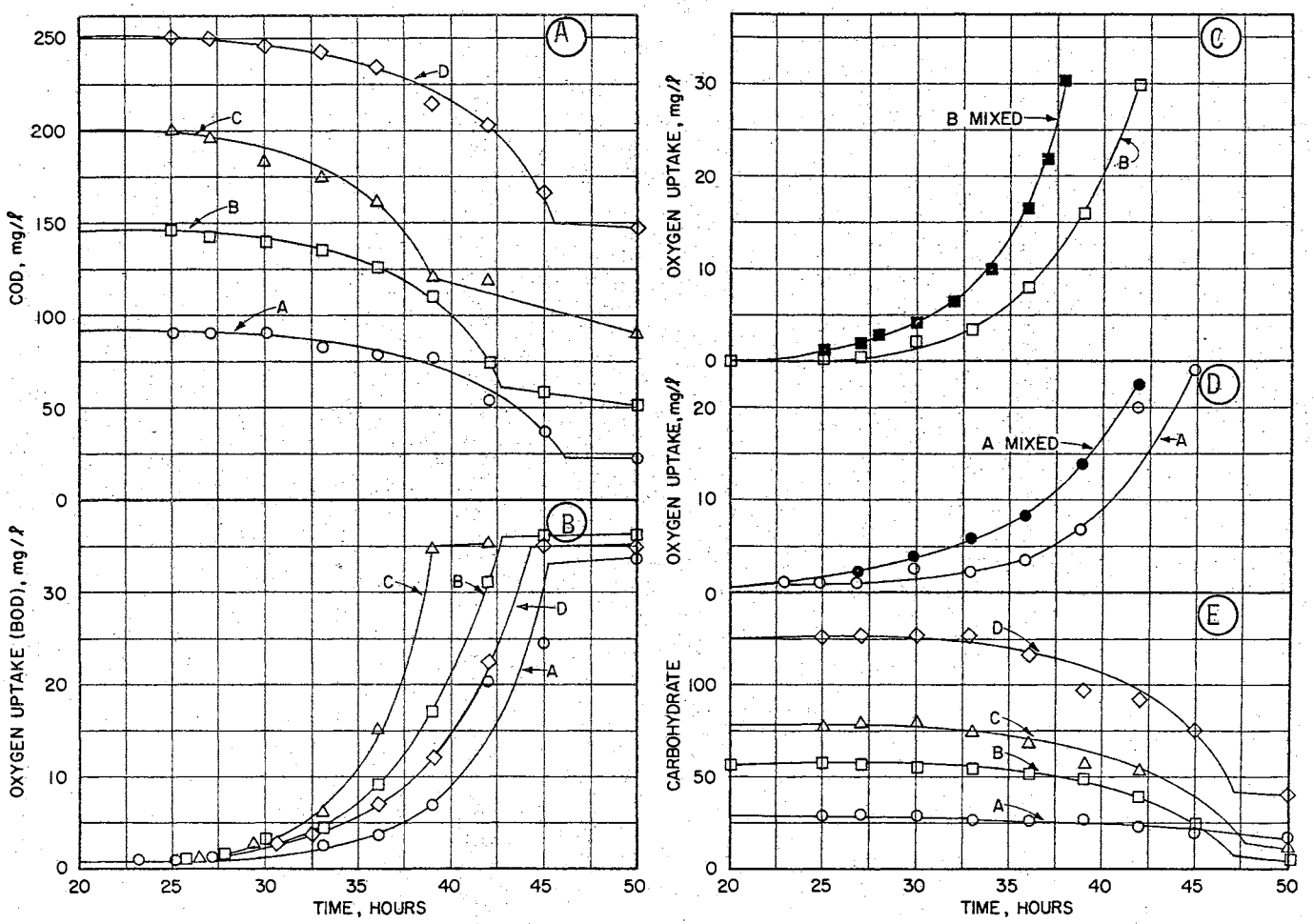


Figure 48 - Changes in parameters for bottle systems when employing glucose-glutamic acid substrate and sewage seed (Experiment R).

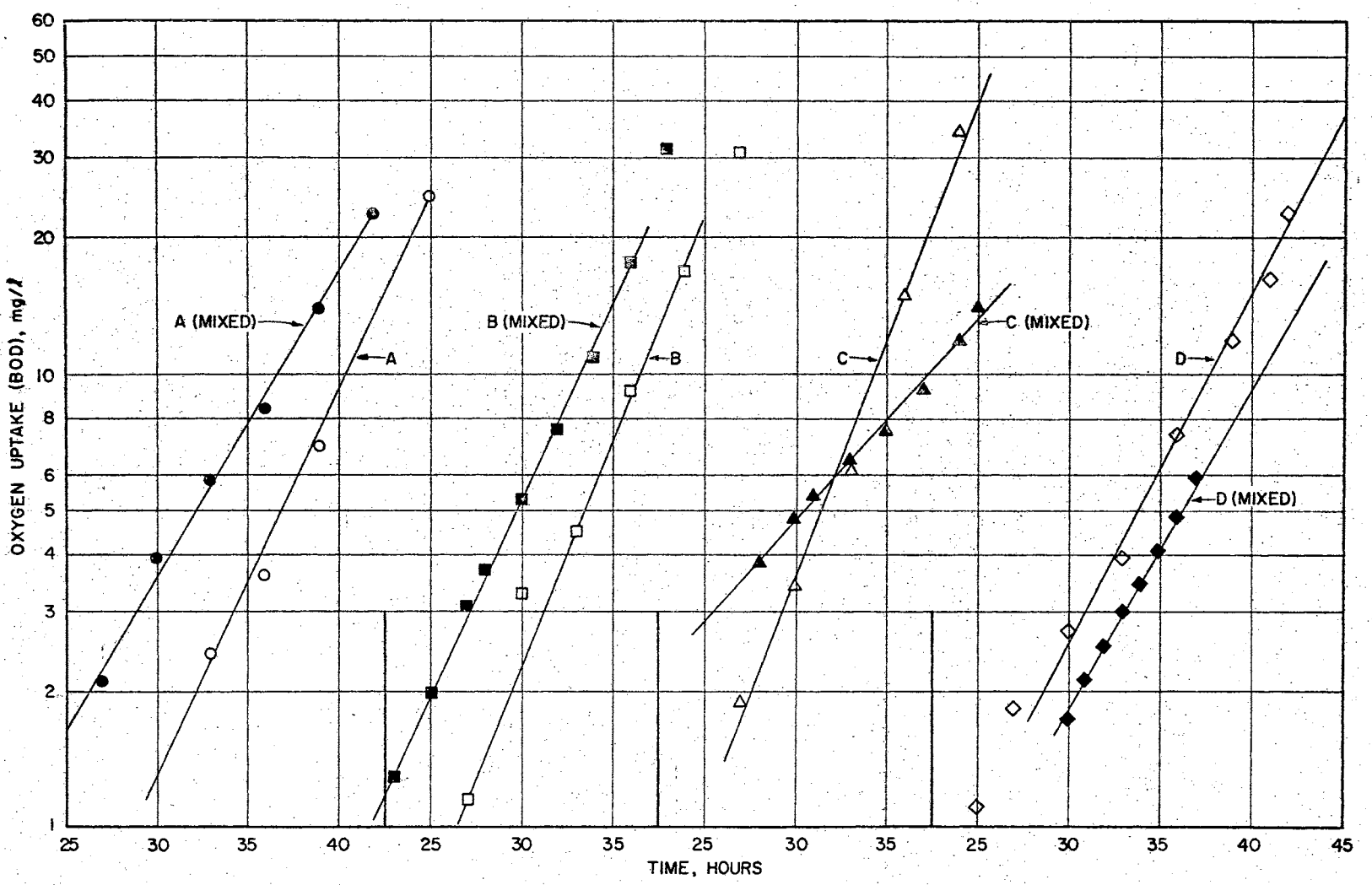


Figure 49 - Increasing oxygen uptake rates under both mixed and quiescent conditions for indicated system (Experiment R).

TABLE XI

OXYGEN UPTAKE RATE CONSTANT AND INITIAL COD VALUES FOR EXPERIMENTS Q AND R

Experiment	Bottle System	Initial COD, mg/l	k_j, day^{-1}
Q	A	30	0.83
Q	B	100	1.82
Q	C	124	2.15
Q	D	140	2.23
R	A	94	2.05
R	B	142	2.32
R	C	198	2.48
R	D	258	1.87

In order to obtain data over a wider range of substrate concentration, experiment R was conducted using four systems with initial COD concentrations varying from 94 to 258 mg/l. Sewage seed and glucose-glutamic acid were also used in this experiment. The results of this experiment are given in Figures 48 and 49.

The lag period was about one day, with the same growth pattern being exhibited during the oxygen uptake period as was observed for all of the previous experiments. The increasing rate of oxygen uptake was found to be related to substrate concentration.

In order to measure the effect of mixing on oxygen uptake under the higher substrate loadings, one bottle from each system in experiment R was mixed with a magnetic stirrer, and the oxygen uptake was measured with an oxygen probe and a micro-ammeter. The mixed bottles were placed in a water bath which was isolated from the magnetic stirrer by an air space. The relative uptake rates are shown by the data given in Figures 48-C and 48-D and in Figure 49. The data as shown in Figures 48-C and 48-D indicate that the lag period was

shortened slightly by mixing. However, a semilog plot of the data as shown in Figure 49 shows that the increasing rate (line slope) for the mixed bottles was actually slightly lower than was observed for the bottles incubated under quiescent conditions. The indication of a shorter lag period as shown by Figures 48-C and 48-D was most probably caused by a decrease in sensitivity of the oxygen probe with time. Since the probe had to be left in the bottle at all times, it was not possible to run routine sensitivity checks as was done in previous experiments where the probes were used to monitor oxygen concentration in the open systems.

As may be observed by the relative slopes of the oxygen uptake curves for the mixed and quiescent bottles as shown in Figure 49, there was no increase in the oxygen uptake rate constant as a result of mixing. In fact, as previously noted, the line slopes indicate a slightly lower rate constant for the mixed systems, but here again this could be attributed to a decrease in sensitivity with time for the probes used in monitoring the dissolved oxygen concentration.

The only abnormality observed in this research was that found for system D in experiment R. The oxygen uptake rate for this system was lower than the rates observed for systems B and C, which had lower substrate concentrations.

The semilog plots of the oxygen uptake data as shown in Figures 47 and 49 indicate that the oxygen uptake rate was defined by a first order increasing function similar to the logarithmic phase of biological growth. These increasing oxygen uptake rate constants (k_i) for experiments Q and R were computed from these semilog plots, and are given in Table XI.

Figure 50-A is a plot of oxygen uptake rate constant (k_i) versus initial COD. It is seen that this plot is of the same form as proposed by Monod (72) for biological growth. Figure 50-B is a Lineweaver-Burk plot of the same data. The Lineweaver-Burk plot is a straight line form of the equation for growth rate as proposed by Monod (73). It is seen that the data approximate a straight line. The maximum oxygen uptake rate constant ($k_{i\ max}$) was found to be 3.79 day^{-1}, and the constant K_m was 103. The curve shown in Figure 50-A was plotted from the following equation:

$$k_i = 3.79\left[\frac{S}{S + 103}\right] \tag{69}$$

The increasing oxygen uptake rate constants for the channel, tank, and bottle systems for experiment B are also shown in Figure 50-A. These data were not used in computation of the constants in Equation 69, but were included to show that the relative substrate concentrations used in the three systems was reflected in the magnitude of k_i.

In summary, the results of the present research indicate that the biological response to a substrate is no different in a dilute flowing stream than is found in any batch experiment. The critical oxygen demand for the receiving stream occurred during the period of substrate removal, and the oxygen uptake rate during the increasing log growth period was related to the initial substrate concentration as shown by Equation 69.

It is seen from Figure 51 that there was a very rapid recovery in the oxygen content of the stream following the depletion of the exogenous substrate. The second phase demand occurring at about forty hours is seen to have had little effect on the oxygen content of the stream.

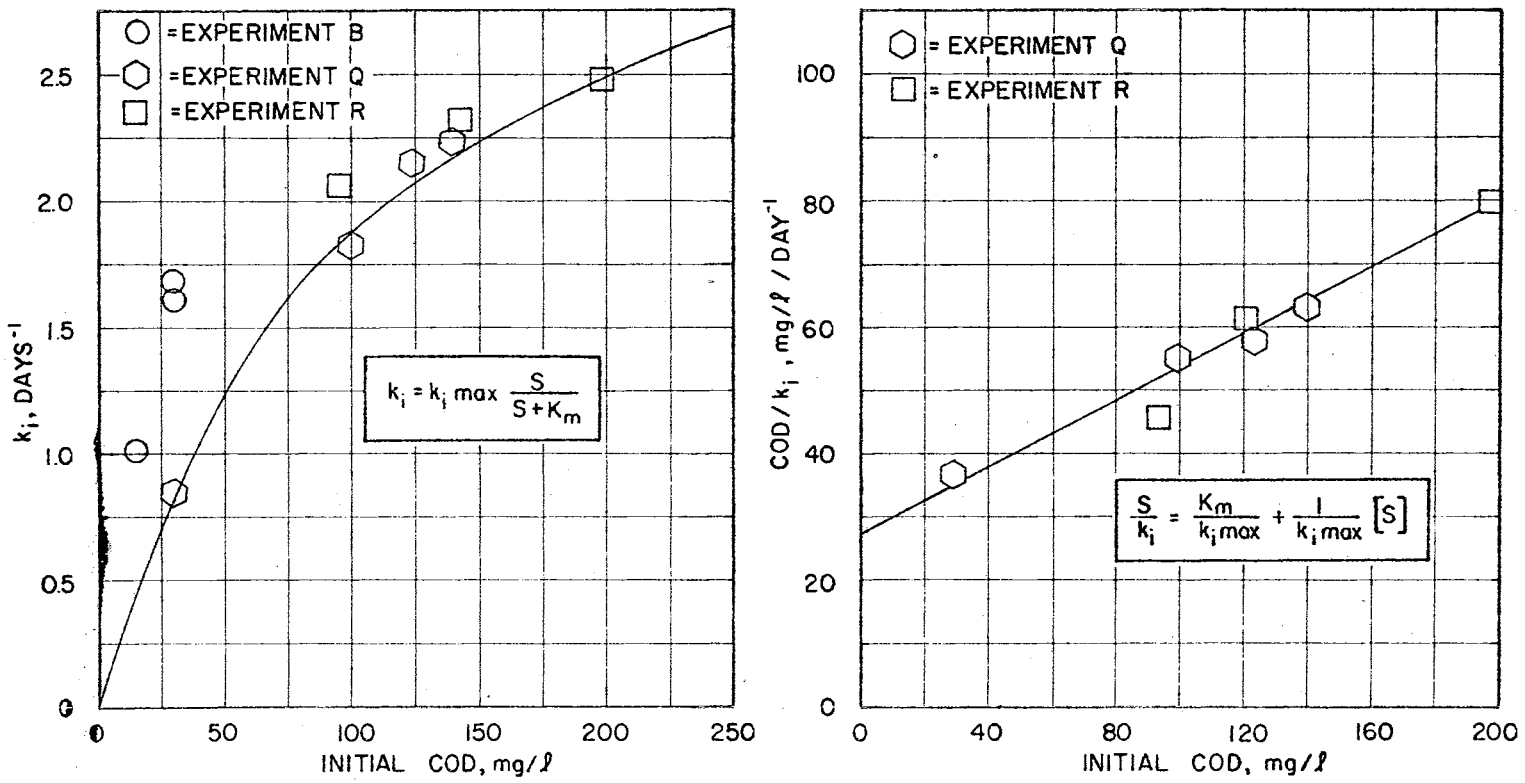


Figure 50 - Oxygen uptake-substrate concentration relationship.

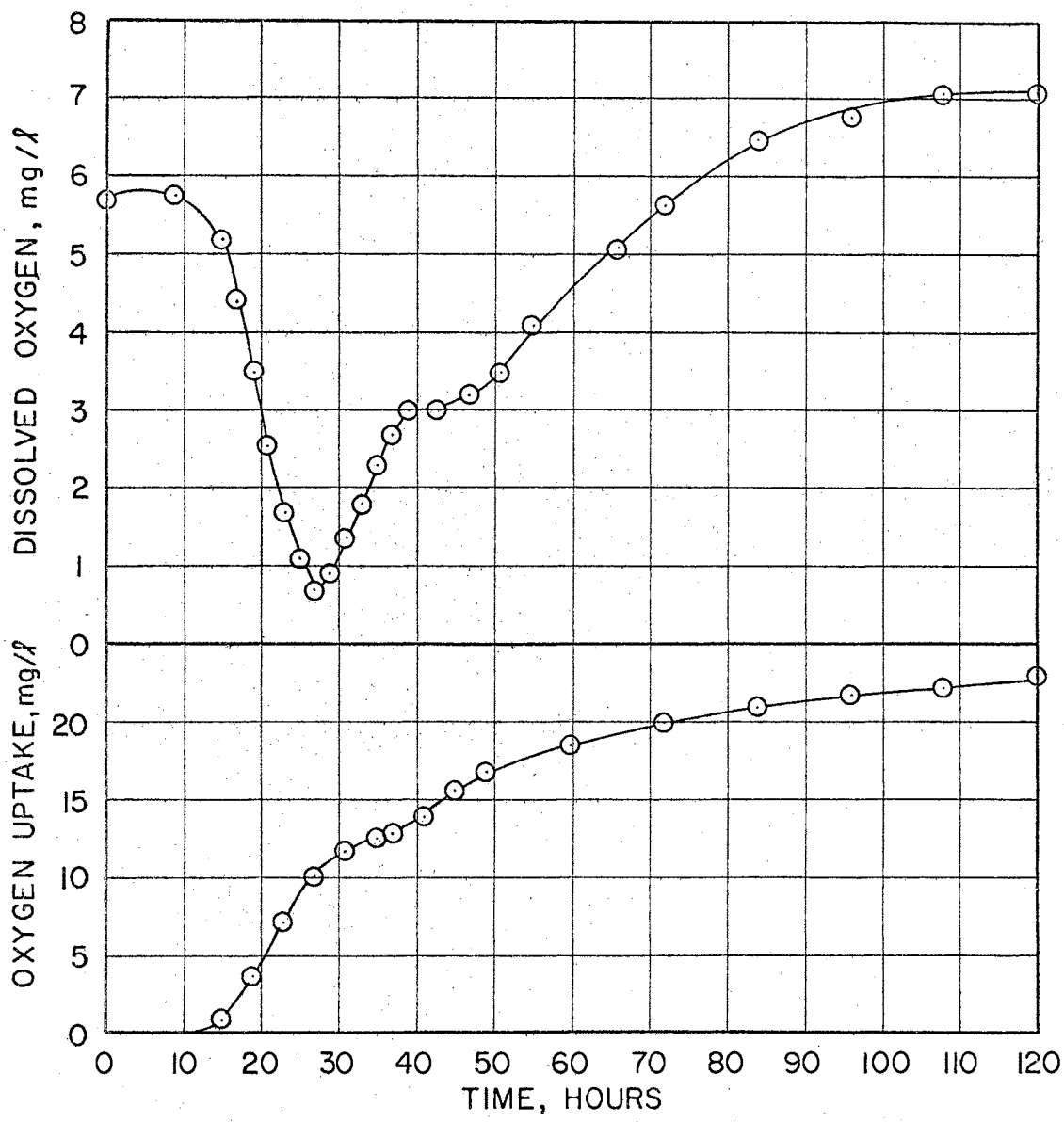


Figure 51 - Oxygen sag and oxygen uptake curves (Experiment A).

The plateau began at the low point in the O_2 curve (27 hours), and ended at the beginning of the second phase oxygen demand (39 hours), giving a 12-hour O_2 recovery period during the plateau. The oxygen uptake curve (BOD) from 39 hours to 120 hours was essentially defined by a decreasing monomolecular rate of 0.252 day^{-1}. This compares with an increasing rate (k_i) of 2.06 day^{-1} during the logarithmic growth phase.

CHAPTER VI

DISCUSSION OF RESULTS

A. Oxygen Solubility

There is no apparent explanation for the differences in the oxygen solubility data reported by Truesdale and his associates (4), and that reported by the Stream Pollution Control Section of the Tennessee Valley Authority (5). Both groups used the Winkler method of analysis for dissolved oxygen. Both laboratories used an amperometric endpoint by a back titration procedure following the addition of excess thiosulfate. The difference in the analytical procedure at this point was that the English group used potassium iodate as a primary standard in place of potassium bi-iodate. Hart (74) has proposed that the analytical procedures used by the English group may have resulted in the loss of iodine by volatilization as being a possible explanation for the differences in the data.

Knowles and Lowden (75) have shown that the amperometric procedure is the most sensitive means of detecting the iodine endpoint using thiosulfate. Their study indicated that 0.07 ml of 0.025 N iodine was required to give a detectable blue color with soluble starch. This indicates that the disappearance of the blue color when titrating to a visual endpoint precedes the amperometric endpoint by 0.07 ml when using 0.025 N thiosulfate. For the sample volume used in this research,

this difference was 0.07 mg/l .

The solubility of oxygen determined in the present investigation was 0.05 mg/l lower at 30°C, and 0.14 mg/l lower at 20°C than the values reported by the TVA group. Hence it appears that there was no genuine difference in the results of the present research and the oxygen solubility data presented by the Stream Pollution Control Section of TVA, but that the difference in the data was due to the method employed for detecting the endpoint.

As pointed out by Isaacs and Gaudy (2), a real test of the correctness of solubility data is a semilog plot of the oxygen deficits as shown in Figure 3. The solubility data from the present research were used in determining the reaeration rate for the one hundred and eleven reaeration experiments reported in Tables VIII and IX. The semilog plots obtained from the data indicate that the oxygen deficits obtained by using these saturation data were correct.

The saturation data from this research were also in good agreement with the values obtained by Isaacs (25) using the alpha method for determining the oxygen solubility.

While the barometric pressure depends on several factors, the most important factors affecting solubility are temperature and the barometric pressure correction for elevation. Oxygen solubility data are usually presented in tables for the temperature range found in natural waters, therefore the solubility for a desired temperature at 760 mm pressure is readily available. However, the correction for pressure is often neglected, even though it may be significant. In fact, records of barometric pressure are not ordinarily available in environmental engineering laboratories.

Twenty months of barometric pressure records obtained in connection with this research indicate that the average barometric pressure correction for elevation is approximately one inch mercury per 1000 ft elevation. A one-inch pressure correction gives a 3.4 per cent correction in the solubility of oxygen. At 20^{o}C this correction is 0.30 mg/l. Barometric pressure data from the Manual of Barometry (76) for several cities across the United States between about 36^{o} and 38^{o} latitude also indicate an average decrease in pressure of one inch mercury per 1000 ft elevation.

It may be more satisfactory for some laboratories to obtain barometric pressure data from other sources than to equip their laboratories for collecting it. Barometric pressure data for an area are available from local weather stations and from weather reports broadcast by local television stations. The pressure data given on television weather reports have been adjusted to a sea level datum, so they must be corrected to correspond with the local datum.

B. Reaeration Systems

Oxygen transfer in turbulent systems is a complex phenomenon which at present lacks complete definition and the principal deficiency in defining reaeration is the lack of a means of defining the rate of surface renewal. Higbie (14) has shown that mass transfer across the gas-water interface is defined by Fick's law (Equation 26), and the rate of mass transfer is related to surface age.

O'Connor and Dobbins (13), as well as Dobbins (18), have presented equations relating the reaeration rate constant to surface renewal. However, as so ably pointed out by others (16)(19)(20), it is doubtful if there is any substance to the assumptions made in the development of

Equations 13, 14, and 15.

The film theory is not consistent with what is known about turbulent flow. The penetration theory as applied to turbulent flow by Danckwerts (15) relates the reaeration rate to surface age. It is assumed that liquid eddies originate in the turbulent core of the water and migrate to the surface, where they are exposed to the atmosphere for a short period of time before being displaced by other eddies. The oxygen-enriched eddy is then returned to the bulk of the liquid, where the absorbed oxygen is distributed by turbulence. The problem lies in the fact that the surface renewal rate cannot be determined.

Tsivoglou, et al. (27) concluded from the laboratory experiments on gas transfer capacity that in turbulent systems reaeration takes place in at least two steps. These are the diffusion of gas across the liquid-gas interface, followed by the dispersion of the dissolved gas throughout the main body of water. It was concluded that the dispersion rate depends primarily on the kind and degree of turbulent mixing rather than on molecular gaseous diffusion.

The simulated channel, which was designed by Isaacs and Gaudy (2) of this laboratory and which was used in the present research, is the first apparatus to the writer's knowledge which provides a method for creating continuous streamflow conditions in the laboratory. This equipment appears to provide a very satisfactory method for studying the mass transfer phase of the oxygen balance without interference from the factors in the balance that cannot be eliminated in the natural stream.

The prediction equation (Equation 22) proposed by Isaacs and Gaudy (2) gives excellent correlation with the data from this research. The

additional parameters proposed by Isaacs and Maag (26) would appear to give wider application to the model.

As shown by Equation 37, the energy gradient as given by the Darcy-Weisbach equation is

$$S = \frac{f}{8} \frac{U^2}{Dg}$$

The term S is the volumetric rate of energy dissipation in ft-lbs of energy per pound of water per foot of flow. Webber (12) states that for turbulent flow the energy dissipation is due almost entirely to eddy viscous forces, with the dynamic viscous forces being negligible. Tsivoglou (27) has concluded that the dispersion of the gas throughout the liquid depends on the kind and degree of turbulence. Thus it seems evident that the rate of reaeration should be related to the volumetric rate of energy dissipation.

The hydraulic engineer has experienced the same problems which the bioenvironmental engineer presently faces in defining turbulence. After passage of nearly a century from the time of development of the Darcy-Weisbach equation for rate of energy loss, there are several prediction type of flow equations in general use. These are the Chezy, Hazen-Williams, and the Manning equations. This situation exists even though authors of various textbooks on hydraulics oppose the use of these equations because of their limited application (11)(12)(64). The equations are satisfactory for use in situations where the hydraulic parameters are similar to the conditions for which they were developed but, like the prediction equations for reaeration, the results are disappointing when they are applied to conditions outside their limited range.

The velocity gradient equation (Equation 40) as proposed by Camp and Stein (54) is not restricted in its application. The velocity gradient is expressed in terms of stream parameters which define the rate of energy dissipation. As shown by Equations 36 and 37, the parameters are f, U, and D. The analysis of the data from this research gave excellent correlation for the reaeration rate constant with the velocity gradient, and it appears on the basis of the above statements that the velocity gradient is not restricted in its application. The use of this relationship makes it possible to benefit from the contributions of the hydraulic engineer by relating the rate of energy dissipation to the dimensionless friction factor, f.

The kind and degree of turbulence are defined by the nature of the system. Thus it was not possible to relate a flowing system to a stirred baffled system in terms of a velocity gradient. This is apparent from the data in Tables VIII and IX, and from the regression equations for the simulated channel and the stirred tank (Equations 61 and 67). There is a linear relationship between k_2 and G for the channel, but the relationship is logarithmic for the stirred tank. A velocity gradient of 10^6 hr^{-1} gives a $K_{2\text{-}20^o}$ value of 0.124 hr^{-1} for the stirred tank, and 2.40 hr^{-1} for the channel with a one-foot water depth. Thus it seems apparent that the velocity gradient is affected by the geometric and kinematic relationships of the system, and a velocity gradient value for a flowing system is not applicable to a stirred system.

The stirred tank was found to be readily adaptable to laboratory and pilot plant use in reaeration and deoxygenation studies.

C. Deoxygenation Studies

It has been proposed that the "microbiology of waste waters could more properly be termed the microbiology of heterogeneous populations" (77). However, the bioenvironmental engineer has in general failed to apply the principles of biological growth to problems in waste treatment. This is particularly true in regard to the oxygen uptake in the BOD bottle and the application of bottle data to the events occurring in the receiving stream. The BOD test has probably been the subject of more research effort than any other facet of waste treatment, and yet Hoover proposes "no one considers it adequately understood or well-adapted to his own work" (35). In the opinion of the writer, the principal cause of this perplexing circumstance is that the objective of most of the research on the BOD test has been to seek refinements on the basis of decreasing first order rate kinetics and the objective has not been to elucidate the basic principles of the deoxygenation process and application of the results of the test.

While Phelps (10) partly developed the concept of first order decreasing rate kinetics for BOD rearation, he has also noted that there is no justification for the reaction being monomolecular. As far back as 1931, Butterfield (34) pointed out that the reaction most certainly had to be diphasic. In 1958, Busch (38) presented data showing that oxygen uptake during the BOD exertion consists of two phases separated by a plateau. Bhatla and Gaudy (45) have since published results of extensive laboratory studies which verify that the plateau does exist in the oxygen uptake curve. In view of the knowledge that is presently available relative to the response of a microbial population to a substrate it is somewhat surprising that bottle BOD data are so widely

employed. The substrate-growth relationships proposed by Monod (72) indicate that the growth rate and hence the oxygen uptake rates are related to substrate concentration. While the test has been widely criticized because of lack of adequate understanding and description of the reaction kinetics, it is universally employed in the assessment of wastes in the design and operational control of waste treatment facilities, in establishing effluent criteria for wastes before discharging to the receiving stream, and in analyses of stream data.

The oxygen utilization kinetics observed in the present research was very different from what is described by decreasing first order kinetics. The upper portion of Figure 52 shows a typical type of oxygen sag curve as defined by the "sag equation" proposed by Streeter and Phelps (1)(Equation 8), along with a sag curve as observed in the current research. While it is recognized that the entire recovery process is important in the overall use of the receiving stream, the critical stretch exists in the reach designated by the distance BD in Figure 52.

The results of the present research indicate that the biological kinetics for the substrate removal phase of waste degradation is defined by growth kinetics as given by a conventional S-shaped growth curve. As shown by data from all of the present research except the two experiments using sewage substrate, the oxygen uptake exhibited a lag period followed by a period of increasing rate of oxygen uptake corresponding to the period of substrate removal and bacterial growth. As substrate became limiting, there was an inflection point in the oxygen uptake curve where the curve goes from concave upward to concave downward. At the inflection point the rate of change in oxygen uptake went from an

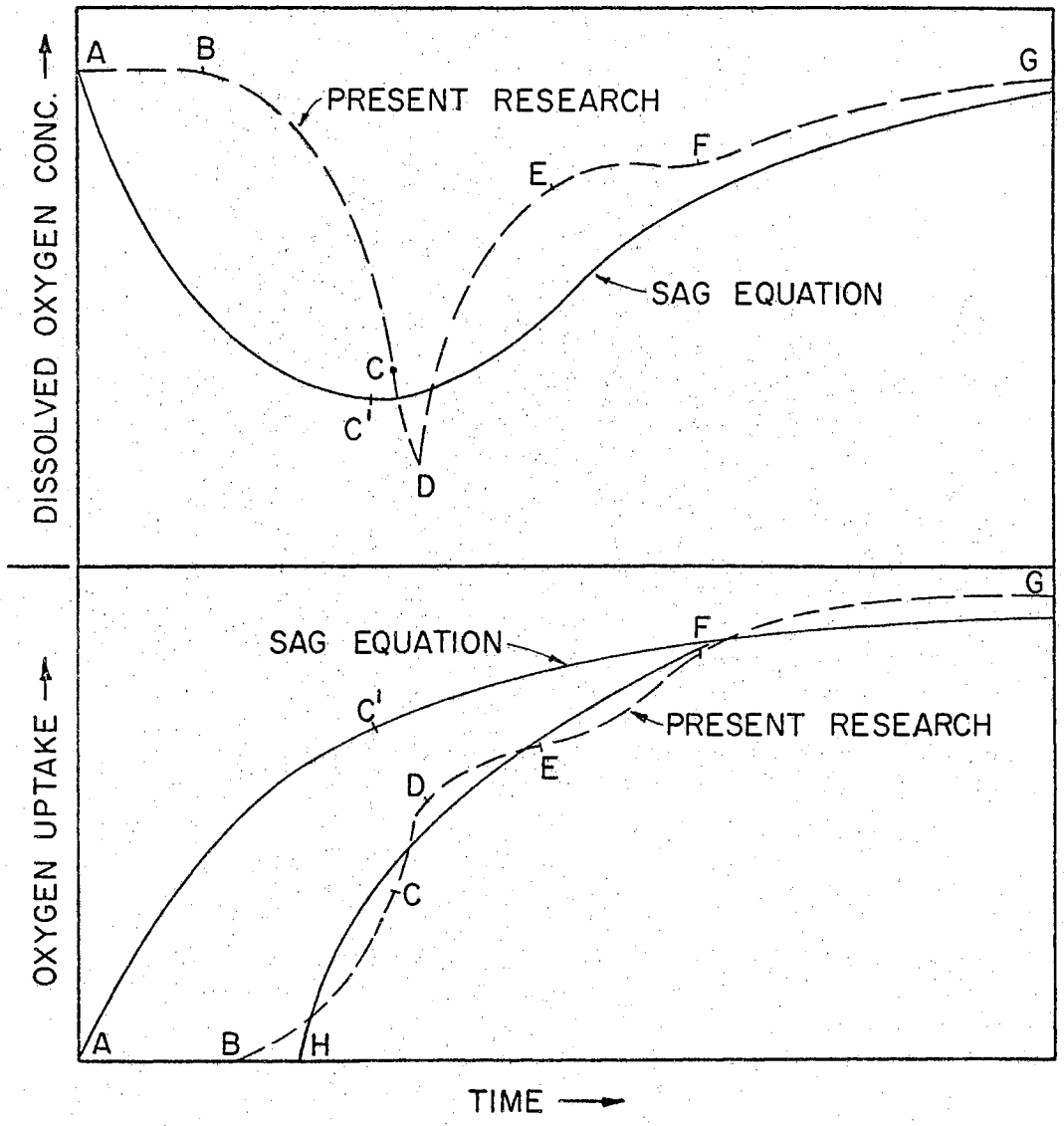


Figure 52 - Oxygen uptake as observed in this research and as given by Streeter-Phelps equation (Equation 8).

increasing function to a decreasing function, and the maximum rate of oxygen uptake occurred at this point. The oxygen uptake rate decreased to a very low value at the sag point, which was shown by the experimental data to be at the point of exogenous substrate removal and maximum bacterial population. The low point in the sag is shown as point D in Figure 52. The oxygen uptake continued at a very low rate for several hours following the point of exogenous substrate removal. The data for experiment B given in Table II shows an oxygen uptake of only 0.57 mg/l for a 4-hour period immediately following the depletion of the exogenous substrate. This period (D-E in Figure 52) is shown as a period of oxygen recovery in the dissolved oxygen curve and as a plateau in the oxygen uptake curve. At the time corresponding to the end of the plateau, the dissolved oxygen content had recovered from the critical point. The plateau was followed by a period of increasing oxygen uptake that was of low magnitude and short duration compared with the rate of uptake during the substrate utilization period. This period was followed by a low rate of oxygen uptake of extended duration that was essentially defined by decreasing rate kinetics.

Present practice is to force an oxygen uptake curve for bottle data to fit monomolecular decreasing rate kinetics by the construction of a line such as line H-F in Figure 52. This assumption provides solutions, but the validity of these solutions is questionable, and it certainly does not bring one any closer to the correct solution. As noted in the results of the present research, k_i day^{-1} was 9.5 times higher than k_1 for the same group of experiments. Gannon (78) reported river velocity constants 18.5 times greater than the rate constants found from BOD bottle data. Gunnerson (79) has noted that while the computation of oxygen

balances in streams requires a number of assumptions and approximations, probably the most troublesome of these is the assumption that the BOD rate coefficient, k_1, is a constant. Gannon (78) has also shown that because of the problem of fitting BOD data to a first order decreasing rate relationship, the k_1 value obtained can vary over a wide range depending on the method of evaluation. It was shown that the evaluation of the same set of data by various mathematical and graphical procedures that have been proposed for computing k_1 gave a range from -0.0002 to 0.0232 day^{-1}, and it was noted by the author that none of the procedures [see Gaudy, et al. (58) for procedures] gave satisfactory results when applied to a 2-stage curve.

Orford and Ingram (36) have noted that the monomolecular equation is a poor expression because of the variation of k_1 and L with time of observation, and because the parameters have very little physical or biological significance. Buswell, et al. (80) also have noted that the BOD reaction is not defined by the monomolecular law.

The course of the deoxygenation process observed in the open systems in the present research was the same as that found by Isaacs and Gaudy (2) using the simulated channel used in the present research, and by Gates, et al. (48), using a stirred tank reactor. Both Isaacs and Gaudy, and Gates, et al. noted a lag followed by a period of rapid oxygen uptake that was defined by increasing, and not decreasing, kinetics. The curves presented by Isaacs and Gaudy (2) also show a longer lag period for the bottle data than open systems, and in most of the experiments a lower oxygen demand during the first five days.

The lag periods experienced in the present research indicate that the period was related to initial seed concentration and to substrate

concentration. The average lag for the open systems in Group I experiments was 16.3 hours with a range from 12 to 30 hours. Similar lag periods were indicated by the data presented by Gates, et al (48). The data reported by Gates and his associates also showed a longer lag period for lactose than for the other substrates employed. Long lag periods were also observed in the present research when dry milk was used as a substrate. McWhorter and Heukelekian (40) reported that an increase in seed concentration reduced the lag period, but the initial seed concentration had little effect on the variation in the lag. Pipes, et al. (41) reported wide variation in lag periods observed for various substrates, and the data reported by Bhatla and Gaudy (45) also indicated variability in the lag period. Thus, it seems apparent that the summary opinion and experimental evidence is that the BOD reaction is subject to widely varying lag periods and is not adequately approximated by decreasing rate monomolecular kinetics. Also, the data from bottle experiments give widely varying results which are not suitable for applying to stream analyses.

As shown by the results of experiments Q and R, the increasing oxygen uptake rate was defined by the same type of kinetics as proposed by Monod (72) for biological growth. Thus the rate constant, k_i, is related to a measure of the biological generation time. Therefore, if oxygen uptake rates are related to substrate concentration, data from bottle experiments cannot be used to evaluate conditions in the receiving stream unless the substrate concentration is the same in both systems.

The oxygen uptake curve and sag curve for experiment B (channel) for the period from the end of the lag to the oxygen sag point are

shown in Figure 53. It is seen that the growth kinetics as proposed by Monod (72) defines the oxygen uptake to the inflection point of the curve. The slope of the oxygen uptake curve is the rate of oxygen uptake, $\frac{\Delta y}{\Delta t}$, and the inflection point is by definition the point where the rate of change of slope changes from an increasing rate to a decreasing rate. Thus the inflection point (point C) is the position of maximum oxygen uptake rate.

The inflection point was not the sag point, because the rate of oxygen uptake ($Y = 10^{k_i (t-t_o)}$) at this point was greater than the rate of reaeration (K_2D), and the oxygen content of the water continued to be depressed until the rate of deoxygenation was equal to the rate of reaeration. Thus, it is seen that the sag point did not correspond to the point of maximum oxygen uptake rate.

Although the rate of oxygen uptake was decreasing beyond the inflection point, it was still considerably greater than the reaeration rate (K_2D) to near the point of exogenous substrate depletion. Thus it appears from the results of the present research that since respiration requirements of a proliferating system were considerably greater than the endogenous respiration requirements, the oxygen sag point in the stream will generally occur at the point of substrate depletion. Hoover, et al. (35) reported that the respiration rates of growing organisms was ten to twenty times that of the endogenous rate.

Growth kinetics are not adequately defined beyond the inflection point. Kinetics as proposed by Monod (72) defines the oxygen uptake only to the point of inflection. The oxygen uptake curve beyond the inflection point was a decreasing function, but it was not a first order function. While there are mathematical relationships for defining

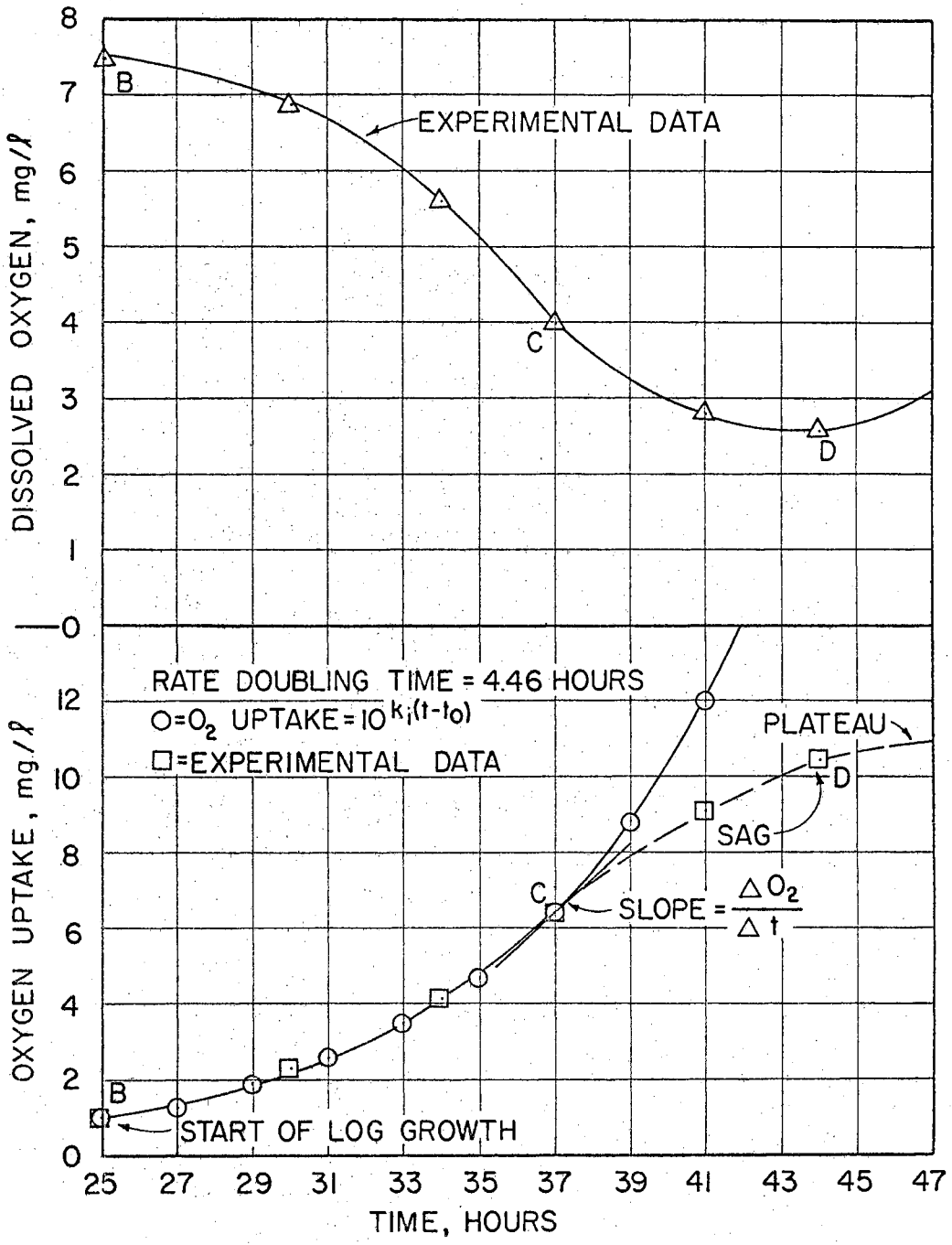


Figure 53 - Oxygen uptake pattern during period of exogenous substrate utilization (Experiment B).

an S-shaped curve similar to a growth curve, the constants in the resulting equation must be evaluated by curve-fitting procedures and would not be generally applicable since the curve must be related to the substrate concentration as shown by Equation 69. The growth-substrate relationship as given by this equation shows that higher initial substrate concentrations will give a greater k_i, and hence, a greater rate of oxygen uptake during the growth period. This information on the oxygen uptake rate is presented to show that the oxygen uptake in dilute systems was defined by kinetics similar to the growth relationships as proposed by Monod and to give additional evidence that the results of the present research indicate that oxygen uptake rates for dilute systems such as are found in receiving streams and BOD bottles are related to substrate concentration. Therefore, data from BOD bottles should not be used in stream analyses. This fact was also indicated by the reaction rates observed in the open and closed systems employed in the present research.

McWhorter and Heukelekian (40) have reported that the oxygen uptake rate was near maximum at the point of substrate exhaustion. However, this is contrary to the results observed in this research, as shown in Figure 53, and it is also contrary to present concepts of growth kinetics. Garrett and Sawyer (37) found that the oxygen uptake rate was directly proportional to substrate concentration at low concentrations of BOD. This concept would involve a two-phase growth-substrate relationship which is also contrary to commonly accepted growth concepts. Gaudy, Ramanathan, and Rao (81) have shown that growth rates are lower for systems operated at lower substrate concentrations, and that growth rates were defined by kinetics as proposed by Monod.

Experiments J and K of the present research employed settled sewage as substrate. It is seen from Figures 34 and 36 that the oxygen uptake rate for the open systems was reasonably defined by decreasing monomolecular kinetics. The data indicate that the carbohydrate and the exogenous soluble COD were depleted before the start of the experiment. The decrease in the total COD during the experiment could be caused by the utilization of particulate matter by the microbial population (there was no decrease in cell count), by cell respiration or oxidative assimilation, and by predator activity. Also, there was no bacteria log growth, and hence there could be no increasing oxygen uptake phase.

Hoover and his associates (35) proposed that the BOD test consists of two biochemical reactions, and that whenever a monomolecular reaction rate with a velocity constant of 0.1 day^{-1} is observed in a BOD test, the reaction is solely one of endogenous respiration.

Isaacs (25) has shown that settled sewage exerts an oxygen demand that is approximated by decreasing monomolecular kinetics. The data presented also show a lower 5-day BOD exertion in the bottles than in the open turbulent system. Komolrit, Goel, and Gaudy (71) have also shown that growing system solids subjected to endogenous conditions exhibit an oxygen uptake that is defined by decreasing kinetics. Thus it appears that systems employing high solids to substrate ratios or nonproliferating systems exhibit oxygen uptake rates that are essentially decreasing rate monomolecular in form. The results of the experiments employing sewage as substrate indicate that the biological growth in sewage a few hours old may be in an oxidative assimilation or endogenous phase. It most certainly was not in a growth phase, since the available soluble exogenous substrate had been depleted by this time

and the viable count has reached the stationary phase in the growth cycle.

A similar situation most surely existed in rivers below sewer outfalls in times when raw sewage was discharged to receiving streams. The sewage was not chlorinated, thus the conditions in the river may have been similar to what existed in the simulated channel and stirred tank in experiments J and K of the present research. That is, the time of flow in the sewers was sufficient for the biological growth to occur before or very soon after the sewage reached the river. Thus, investigations of polluted streams below the large cities as reported by Streeter and Phelps (1), Theriault (31), and Adeney (31) would be expected to give oxygen uptake curves that are defined by decreasing first order kinetics. The low value of 0.1 day^{-1} for the rate constant reported for the river water is a further indication that endogenous respiration was being measured. These conditions no longer exist below most of our major cities. Today, sewage is at least subjected to primary treatment followed by chlorination before being discharged to the receiving stream. Therefore, there are no extensive sludge deposits below outfalls, and the biological population is almost nil because of the chlorine residual. Hence a new biological population must develop in the receiving stream after the chlorine residual is exhausted.

The report by Gannon (78) on a survey of the Clinton River below the Pontiac, Michigan, sewer outfall, indicates that the chlorine residual persisted for 0.65 miles below the outfall. The dissolved oxygen profile shown for the stream indicates that a lag existed below the point where the chlorine residual was exhausted. This lag was followed by an increase in oxygen uptake manifested by an abrupt sag in

the oxygen content curve. The nature of the sag indicates a period of rapid oxygen uptake following the lag, which is in accord with the concepts proposed from the results of the present research. Also, it was reported that the bottle data for the river water did not agree with or correlate with stream measurements.

The oxygen uptake curves observed in the present research are also of the type as reported by Bhatla and Gaudy (45) for high energy systems using sewage seed and glucose substrate. The curves indicate the existence of a lag period varying from about fifteen hours to two days, depending on the seed composition. The experiments using a one per cent settled sewage seed indicate a lag of approximately eighteen hours. The lag period was followed by a rapid increase in oxygen uptake rate, corresponding to the period of substrate depletion. The plateau occurred at the point of maximum bacteria population and substrate depletion.

The oxygen uptake rates observed during the plateau in the present research show that the oxygen uptake rates are very low in the absence of an exogenous substrate. The second phase of oxygen uptake observed in the present research corresponded to predator growth as was observed by Bhatla and Gaudy (45) for both high and low energy systems. No evidence of a secondary growth as a result of protozoa activity as proposed by Butterfield (34) was indicated in this research. In fact, it was found that bacteria growth must precede predator growth. As noted in the results, there was an inactivation or die-off of the protozoa following inoculation of the systems with acclimated seed. Microscopic examination of samples indicated that the protozoa were completely inactive, and appeared to lyse. New predator growth was not observed

until bacterial growth was near a maximum. Thus the results of the present research indicate that predator activity was responsible for the second phase of oxygen uptake.

The present research also shows that the fraction of the theoretical oxygen uptake exhibited at the plateau was 39 per cent in the open systems and that the variation from this mean was not great. Gaudy, et al. (44) reported an average removal at the plateau of 34 per cent using glucose as substrate. Isaacs and Gaudy (49) reported an average removal of 35 per cent for four experiments using glucose-glutamic acid substrate. More extensive studies reported by Gaudy, et al. (67) covering forty-six experiments using a variety of substrates and seeds indicate the oxygen removal at the plateau is generally between 30 and 40 per cent of the theoretical. Busch (38) has reported that the plateau BOD value for glucose is 41.1 per cent of the theoretical oxygen demand. While there appears to be some variation in the oxygen uptake-BOD relationship at the plateau, it is emphasized that the variations are small compared with the variations found for the 5-day BOD values.

The experimental evidence from the present research indicates that mixing in the range found in natural streams, has no effect on the rate of oxygen uptake or on biological growth. Rickard and Gaudy (57) have shown that agitation does increase the oxygen uptake rate. Lordi and Heukelekian (69) have also reported higher oxygen uptake in stirred systems than in quiescent systems. However, the studies reported by Rickard and Gaudy employed continuous flow experiments at much higher substrate loadings and higher mixing rates than were used in the present experiments. Lordi and Heukelekian also reported that nitrification occurred two to three days earlier under stirred open conditions than

under closed conditions. While no nitrogen analyses were made, the general shape of the oxygen uptake curves do not give any indication of nitrification occurring in any of the experiments reported herein.

It is not thought that the high oxygen tensions employed in experiments Q and R had any effect on the biological response observed. Zobell and Stadler (82) found that the oxygen utilization per cell is independent of dissolved oxygen within the range employed in these experiments. However, they found that in concentrated nutrient solutions, rich in particulate matter and high bacterial concentrations, oxygen may become limiting in the vicinity of the respiring cells, expecially if the cells exist in clumps. Under these conditions the higher oxygen tensions would increase the oxygen gradient in the vicinity of the clumps of microbial floc. However, only dilute substrate concentrations and low biological solids were employed in the present research.

On the basis of the results from the present research and the findings of others as noted, it appears very evident that data obtained from BOD bottles in the laboratory are not applicable for predicting the course of deoxygenation in flowing streams. The open stirred reactor as employed in the present research is, in the writer's opinion, the most suitable means available for ascertaining the pollutional characteristics of a waste water. A reactor of sufficient volume can be used to permit sampling for several analyses, as was done in the present research. Not only was the stirred reactor found well-suited for use in laboratory studies, but also the capital investment and space requirements are no greater than what is required for the standard BOD procedure. The system selected should have a variable speed drive

so as to permit operation at a selected reaeration rate.

The use of an open stirred reactor would eliminate the inaccurate assumptions and approximations that are associated with the use of the BOD bottle in deoxygenation studies, and also provide an accurate assessment of the deoxygenation process occurring in the natural stream. This procedure also provides a means for determining reaeration rates in streams from the actual oxygen uptake data obtained from experiments in the stirred reactor.

CHAPTER VII

CONCLUSIONS

A. Oxygen Solubility

1. The results of the present research and those of the other recent studies (4)(5) indicate that the oxygen saturation data given in Standard Methods (3) are incorrect.

2. The results of this investigation support the data for oxygen solubility reported in the ASCE Progress Report (5) based on 0.07 ml of 0.025 N iodine being required to give a detectable color as reported by Knowles and Lowden as being correct. Since the data from this investigation indicate that the starch endpoint does give a lower oxygen solubility than the amperometric endpoint, studies involving the use of a visual starch endpoint in dissolved oxygen determinations should use saturation data based on a starch endpoint.

B. Reaeration Studies

1. The velocity gradient equation proposed in this research and the equation presented by Isaacs and Gaudy (2) correlate equally well with the reaeration rate coefficient for the data obtained in the present research.

2. The volumetric rate of energy dissipation depends on the nature of the system. The velocity gradient for the flowing system was developed from the Darcy equation for flow in turbulent systems, and

the velocity gradient equation for the stirred tank was developed for a baffled tank employing a marine impeller on a vertical shaft. Hence the velocity gradient for a flowing system is not related to one for a stirred tank.

The hydraulic parameters f, U, and D, are required to define the volumetric rate of energy dissipation and the vertical velocity distribution for a flowing stream.

C. Deoxygenation Studies

1. The deoxygenation response is not defined by decreasing monomolecular kinetics. This is true for both closed bottle systems and open turbulent systems. The results of the present research clearly indicate that the biological response to a substrate in dilute systems produces an autocatalytic growth curve and that biological growth is directly reflected in the oxygen uptake rates which are defined by increasing kinetics to the inflection point in the oxygen uptake curve. The increasing rate constants for this period are approximately ten times greater than the corresponding decreasing rate constants. A diphasic oxygen uptake occurs in a turbulent stream.

2. Mixing in the range employed in the present research appears to have no effect on the biological kinetics in systems employing low substrate concentrations such as exist in receiving streams and BOD bottles. Thus the biological response is independent of the reaeration rate or degree of turbulence of the system for the range of turbulence found in natural streams.

3. The oxygen uptake at the plateau is related to the initial substrate concentration. For both the open and closed systems employed in the present research, it was found that approximately 39 per cent of

the theoretical oxygen requirement had been exerted at the point of substrate depletion. Hence the percent oxygen uptake is independent of substrate concentration; however, the oxygen uptake rates were related to substrate concentration, and hence were different for the open and closed systems. Also, the lag periods were longer for the bottle systems and the 5-day BOD values were significantly different for the open and closed systems.

4. The critical reach of the receiving stream corresponds to the biological growth period which occurs during the removal of the exogenous substrate. Even for low substrate concentrations the oxygen uptake rates during this period will cause a significant decrease in the oxygen content of the stream. The actual magnitude of the decrease in oxygen concentration will depend on the substrate concentration and the reaeration rate. The oxygen uptake rates which are exhibited after the removal of the exogenous substrate are much less in magnitude, and in themselves do not have a significant effect on the oxygen balance of the stream.

5. Because of the variability and magnitude of the lag period in the BOD test, a short term test has no significance.

6. Oxygen uptake in dilute systems was defined by kinetics similar to the kinetics for biological growth, as proposed by Monod. Therefore, the oxygen uptake rate during the period of substrate utilization is related to substrate concentration, and BOD data from diluted bottle systems are not applicable to receiving streams. If one is to determine the actual oxygen uptake rate and the true effect of a waste on a receiving stream, the use of a system similar to the stirred tank employed in the current research is recommended. The open stirred

system can be operated to give the reaeration rate of the receiving stream and the true stream response to a waste can be ascertained. High oxygen tension bottle systems such as were employed in experiment P of the present research can be used. However, this procedure requires intensive sampling to obtain sufficient data for analyses.

CHAPTER VIII

SUGGESTIONS FOR FUTURE WORK

1. Since oxygen solubility is so important in the overall oxygen balance in receiving streams, additional research is needed to determine the difference in solubility when using an amperometric endpoint and a visual starch endpoint. Statistical data are needed on the individual's ability to detect the starch endpoint.

2. It appears that the velocity gradient, G, sufficiently defines turbulence to provide a means of correlating turbulence to the dimensionless friction factor, f. However, more data are needed where channel roughness is varied. Experiments could be designed to measure reaeration under various roughness conditions in the simulated channel employed in the present research.

3. Results of the present research indicate that oxygen uptake is related to substrate concentration. This relationship is defined to the inflection point in the growth curve by Monod kinetics. Additional research is warranted to elucidate the factors which influence the position of the inflection point in the oxygen uptake curve and to define the oxygen uptake curve beyond the inflection point.

4. The effects of chlorination on the oxygen uptake in the receiving stream have not been determined. It is evident that the chlorine residual greatly reduces the biological population, but it is

not known how this affects the new growth which must develop after the chlorine residual is exhausted. The nature of this new growth is what causes the oxygen depletion in the receiving stream, and at the present time the bioenvironmental engineer has not determined where this new growth will occur, and what substrate concentrations are involved in the oxygen uptake.

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