

STUDIES ON THE PREDICTION OF THE DISSOLVED
OXYGEN PROFILE IN RECEIVING STREAMS

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CHAPTER I

INTRODUCTION

Frankland believed that the slightest amount of sewage in water was injurious to health. In 1870, he said: "To remove it (sewage) from water would require the strongest of oxidizing agents. To think to get rid of organic matter by exposure to the air for a short period of time is absurd" (1). Frankland is usually credited with being the originator of the biochemical oxygen demand test, since he showed that the amount of oxygen consumed upon storage of a sample of water containing organic matter was dependent upon the time of storage. Since then, the BOD test has been used for many purposes; the original purpose, and the one of concern in this research, is the prediction or estimation of the amount of air (oxygen) required to stabilize organic matter in a receiving stream.

Waste waters (either treated or untreated) ultimately flow into a receiving stream. In the presence of sufficient nutrients such as nitrogen and phosphorus, which are usually present in ample amounts, the organic matter in the stream is used as a carbon source for aerobic heterotrophic microorganisms. The growth of these organisms lowers the dissolved oxygen (DO) content in the stream. The DO is replaced largely by surface reaeration, and if the oxygen supply is replaced rapidly enough in comparison to the rate of oxygen depletion due to microbial

growth, the dissolved oxygen will, after a period of decreasing concentration, recover to its former level. A mathematical description of this process was provided by Streeter and Phelps (2) in 1925. The Streeter-Phelps sag equation is based upon two opposing first order decreasing rate reactions, deoxygenation and reaeration. While the rate of physical reaeration of a body of water can be shown to follow such kinetics, factors such as depth, velocity, turbulence in the flow, stream geometry, and green plants and bottom deposits affect the kinetic constants for physical reaeration. The law stated by Streeter and Phelps also describes first order decreasing rate deoxygenation. However, in recent years, many studies have indicated that such a kinetic mode is not obtained in the stream or in the BOD bottle, which is usually used as the laboratory reactor in studies designed to determine the velocity constant, K , and the ultimate oxidizability of the organic matter present in the stream (2). It is difficult to believe that a "reaction" which involves complex substrates such as sewage and industrial wastes with complex microbial populations would follow laws of a monomolecular reaction.

A large portion of the work which has helped establish a clearer picture of the kinetics and mechanisms of BOD exertion in the BOD bottle and in dilute substrate systems in general has emanated from the bio-engineering laboratories at Oklahoma State University (3)(4)(5)(6)(7). Isaacs and Gaudy (8) found that the characteristics of BOD exertion in the BOD bottle did not compare to those in a simulated receiving stream. Later, Jennelle and Gaudy (9) showed that the dilution technique, which is the standard operating procedure in the BOD bottle analysis, could not be reliably employed because the concentration of organic substrate

affected the logarithmic velocity constant for oxygen uptake. Also, they found that the mixing rates used had no effect on the biological kinetics in systems employing low substrate concentrations. They devised a procedure for obtaining the oxygen uptake or BOD curve using an open stirred reactor for which the reaeration characteristics had been previously determined. Jennelle also found that the relation of oxygen uptake with substrate concentration was defined by an equation similar to Monod's equation for biological growth kinetics.

Since it has been generally concluded that the Streeter-Phelps sag equation is inadequate for the prediction of a stream's assimilative capacity, it is felt that efforts should be made to use the recent developments in BOD kinetics and mechanisms to propose a new method. A direct procedure which can be employed in the laboratory and related to the stream, has been proposed by Jennelle and Gaudy (9), and Gaudy (10). An open stirred reactor may be used, in which the reaeration rate may be determined for a particular temperature, volume, and stirring rate. The stirring rate is set to provide a reaeration constant (K_2) approximately equal to that of the stream, and the waste effluent can be added to the reactor at the same dilution as in the receiving stream. From the resulting DO profile and the known K_2 value, the O_2 uptake may be calculated. The BOD curve may then be combined with the K_2 value for the stream (or values for several reaches in the stream) to calculate the DO profile in the stream. In using this method, one employs the natural receiving stream water and the waste water concentrations which will exist in the stream, and generates actual O_2 uptake curves. The resulting curves may exhibit various types of kinetics; however, it is not necessary to describe the curve mathematically.

One phase of the present research involves investigation of the effects of the reaeration rate on the course of oxygen uptake in open stirred reactors. It was proposed to use values of K_2 which would not be much in excess of those normally observed in a receiving stream. Because of the changing geometry of streams, the amount of oxygen transferred varies in each reach; however, if O_2 uptake is the same for a range of K_2 values, a single O_2 uptake curve may be used for the calculation of the sag.

The major part of the investigation involved the employment of open stirred reactors to determine oxygen uptake curves for both synthetic and whole wastes. Using the simulated channel employed previously in the bioengineering laboratories of Oklahoma State University (8)(9), the oxygen uptake data developed in the open reactors could then be combined with the known reaeration rate for the simulated stream and, using a numerical computation technique, the course of the sag in dissolved oxygen could be calculated and compared to the observed oxygen depletion and recovery for the same amount of waste in the simulated stream.

CHAPTER II

LITERATURE REVIEW

The principal concern of the present research involves the biochemical oxygen demand concept in relation to the assimilative capacity of a receiving stream. The topic requires a review of the history and concept of the BOD test, the development of the test, its kinetics and mechanisms, and its use in predicting a stream's assimilative capacity, including the Streeter-Phelps sag equation and other methods.

Frankland (1) believed that "the oxidation of the organic matter in water is effected chiefly, if not exclusively, by the atmospheric oxygen dissolved in the water. If, therefore, water contaminated with organic matter be perfectly excluded from the air in a carefully stopped bottle, the gradual diminution in the amount of DO indicates exactly the progress in the oxidation of the organic matter." Since 1870, and Frankland's time, extensive work has been done concerning the BOD test and concept. Theriault (11) wrote a critical review of the work from 1870 through 1927. Also, O'Brien and Clark (12) published a review containing 816 references. Montgomery (13) in 1967, reviewed the dilution method of BOD determination and compared it to respirometer techniques. These three reviews cover the historical development of the BOD test and, therefore, only a brief review of the test and concept as they apply to stream purification will be presented in this report.

The BOD test has been applied to determine the strength of sewage or wastes, to measure treatment plant efficiency, to design sewage and waste treatment units, to establish stream and effluent standards, to set sewage charge rates, and to calculate the amount of pollution added to a stream. From its extensive use and varied applications, a great amount of controversy has arisen concerning both the BOD test and the concept.

Frankland (1) is credited by many as being the first to use a BOD test, and he believed the mechanisms to be strictly chemical (i.e., not biochemical) reactions. In 1884, Dupré (14) first suggested that the microphytes in water consumed dissolved oxygen for their own metabolic processes. Adeney and Becker (15) were the first to use the dilution technique, and established the 5-day period for the test. With a few modifications to the BOD analysis in the first half of this century, the test is essentially the same as it was 100 years ago.

In the early 1900s, some investigators tried open vessels in place of sealed bottles to make allowance for reaeration. However, Theriault (11) said "tests in open vessels are utterly inadequate for the purpose of supplying information concerning the balance which, under natural conditions, is obtained between the rate of reaeration and the rate of deoxygenation of a polluted water. It's more simple to consider them separately." Perhaps because of the "simplicity" factor, further work with the BOD test was continued using the standard dilution technique and sealed bottles.

Along with the standard BOD test, standard kinetics of the expression of oxygen utilization during the incubation period became "standardized" in the minds of many workers. In 1944, Phelps (16) stated that

"there is no real justification for holding that the rate of decrease of BOD is exactly monomolecular. In practical application, it appears on extensive study to be so nearly monomolecular as to justify the use of our present formulas. On the other hand, there are some facts suggesting that the monomolecular law does not exactly express the situation." Many investigators, including Theriault (11), before the above statement was made, had used and continued to employ the monomolecular interpretation of the BOD curve. This type of kinetic expression is still employed today.

The earliest notation of BOD kinetics other than first order was in 1926 by Greenfelder and Elder (17), who suggested that a second stage of BOD exertion could be due to the death of some organisms, thereby furnishing food for others. In 1959, Busch (18) reported two-stage oxygen uptake curves and defined the separation of the stages as the "plateau." He attributed the second stage to the metabolism of bacteria by protozoa.

McWhorter and Heukelekian (19) explained the phases of substrate utilization in four steps: (1) Exogenous substrate is used for oxidation, synthesis, and storage. The cell weight is at a maximum when substrate is removed. (2) Stored carbon is used and nitrogen content of the cells continues to rise, while oxygen uptake becomes slower. (3) Utilization of reserve cellular constituents ensues, and oxygen uptake proceeds at a still slower rate. (4) Metabolism continues very slowly. They observed a pause between the exogenous and endogenous phases, which was shorter for the higher substrate concentrations and did not appear above 1000 mg/l substrate. In the following discussion, Pipes stated that the oxygen uptake of a given mass of microorganisms is a

function of the metabolic activity of the bio-mass, and is therefore at the minimum during endogenous respiration and maximum during exponential growth.

Extensive work with the BOD concept has been completed at Oklahoma State University in the bioenvironmental laboratories. Gaudy, et al. (3) defined the BOD curve and proposed theories to explain the plateau. They found that the first phase of oxygen uptake corresponds to the period of substrate removal and includes periods of both exponential growth and declining growth rate. The plateau occurs at maximum viable count, and the last phase corresponds to a sharp decrease in numbers of viable bacteria. The plateau usually occurs during the first or second day of incubation. Also, 30 to 40 percent of the theoretical oxygen demand has usually been exerted at the beginning of the plateau. The plateau was found to occur with both heterogeneous and pure cultures.

The four theories proposed to explain the occurrence of a plateau in BOD exertion were, briefly: (1) for heterogeneous populations, a change may occur in predominance; either the species of bacteria predominating may change or protozoa may become predominant; (2) some of the cells which have reached maximum growth may lyse and release products which produce a secondary growth; (3) the same population of organisms which have used the exogenous substrate may continue to predominate but may need an acclimation period to synthesize new enzyme systems for metabolism of endogenous stores; and (4) an acclimation period may be required for the metabolism of byproducts released during the metabolism of the exogenous substrate. A fifth theory was also proposed from the work of Gaudy, Komolrit, and Bhatla (20), wherein diphasic oxygen uptake curves may be produced when sequential removal of two

exogenous substrate occurs. In summary, the plateau is considered to be caused by a change from metabolism of the original exogenous substrate to metabolism of a secondary substrate, which may be the bacterial cells produced during the first phase. The pause or plateau between the phases is thus due either to an acclimation period or to a lag between cessation of metabolism by one population and initiation of rapid metabolism by another population.

Later, Follett and Gaudy (5) used complex wastes, including some from wood pulp and paper mills and sewage. The plateau was evident, and correlated with the maximum cell population. It also appeared to be less pronounced at high substrate concentrations. It was concluded that the number of compounds in a waste has little effect on the occurrence of the plateau.

Bhatla and Gaudy (7) continued their work with heterogeneous populations and the role of protozoa in BOD exertion. They were eventually able to construct the following generalized sequence of occurrences in exertion of BOD during the incubation period: During the rapid phase of bacterial growth, the exogenous substrate is used for energy and synthesis. At the time of maximum bacterial population and exhaustion of exogenous substrate, the cells begin to use intracellular substances. Only a few protozoa may have been present initially, and since their major food source is bacteria, they have not been able to grow rapidly until this food source is plentiful; the protozoan population now begins to increase. If no protozoa were present, the bacterial endogenous phase would continue and, therefore, the plateau might extend on with no second stage of oxygen uptake. However, as the protozoa increase and consume the bio-mass, a second stage of oxygen uptake is exerted.

The destruction of the bio-mass or "self-clarification" may be observed directly in the reaction vessel as well as under the microscope.

Gates, Mancy, Shafie, and Pohland (21) have reported the results of studies using the open stirred reactors. They first investigated the sag equation at various reaeration rates and with various combinations of substrates and seeds including pure cultures. They found no agreement in their sag curves with the Streeter-Phelps sag equation. While comparing the oxygen uptake curve with the sag curve, they noted that the plateau and the maximum bacterial count corresponded to the minimum point in the sag. They also concluded that the influence of the bacteria continues approximately four hours beyond the low point in the sag, due to either oxidation of stored material or oxidation of released metabolic intermediates. The substrate had been removed by the time the minimum point of the sag occurred; however, with some multiple substrate systems--for example, glucose and lactose--the DO recovered after the glucose was removed. Then the lactose exerted a second lag.

In 1961, Lordi and Heukelekian (22) made investigations aimed at determining whether the rate of mixing had any influence upon the biological oxidation occurring in polluted waters. Using sewage and tap water, they compared open quiescent and closed systems, and open stirred reactors versus closed systems. At constant temperatures for all tests, they found no difference in oxygen uptake for the open quiescent and closed systems, but stirring increased the oxygen uptake in the open jug, with increased stirring velocities resulting in greater differences in oxygen uptake compared to the sealed bottles. Gannon (23) also compared the standard BOD bottle, open mixed jug, and sealed mixed bottle. He found mixing caused an increased rate of oxygen utilization.

Isaacs and Gaudy (24) compared BOD exertion in the standard BOD bottle to that in a simulated channel. A sag curve was computed using the Streeter-Phelps equation and the K_1 value from a BOD bottle, and then compared to the actual (observed) curve in the channel, and no similarity was found. One of the primary differences between the two oxygen uptakes was the presence of a more pronounced lag in the BOD bottle than in the turbulent system. This difference could have been attributed to the initial seed concentration of the two systems. If the seed in the BOD bottle was equal to that in the channel, the oxygen uptake curves were roughly the same. The authors found three distinct phases of O_2 uptake: (1) substrate utilization and increase in biological solids, (2) plateau, and (3) O_2 uptake increase due to growth of protozoa.

Recently, Ali and Bewtra (25) investigated the influence of turbulence on various parameters of BOD progression. They used two sets of BOD bottles for each experiment, with one set sealed and quiescent, and the other set sealed and stirred by a magnetic stirrer. The uptake rate was found to increase significantly with stirring when either sewage or glucose was used as substrate. The 5-day BOD was also found to be higher in all cases. They also agreed with Isaacs and Gaudy (24) in finding that the lag period was reduced with stirring.

Jennelle and Gaudy (9) compared oxygen uptake in four systems: (a) an open channel, (b) an open stirred reactor, (c) closed bottles quiescently incubated, and (d) closed bottles stirred during incubation. It was concluded that the agitation due to stirring in the bottles did not result in an increase in the rate of BOD exertion over that of the quiescent sealed bottles. However, the open stirred reactor and the

open channel resulted in a higher oxygen uptake, and were comparable. Studies were run to determine whether the lower substrate concentration, necessitated by the normal dilution technique, was the influential variable. The rate of O_2 utilization was found to be dependent upon initial concentration of substrate, i.e., lower rates at lower concentrations. The importance of this finding is evident in the fact that the rates of O_2 uptake control the downward leg of the sag curve, and determine the minimum DO in a receiving stream. Therefore, the direct use in the sag equation of a rate constant which has been obtained by employing the usual BOD dilution techniques cannot be expected to result in an accurate prediction of the minimum DO unless the dilution factors are the same in the BOD bottle and the stream. Several substrate concentrations were employed in these studies, and the logarithmic O_2 uptake rate constant, K_i , was determined. The Monod relationship appeared to describe the curve resulting from a plot of K_i vs. initial substrate concentration. Constants similar to Monod's μ_{max} and K_s were determined, $K_{i\ max}$ and K_m , and these values were found to lie within the same range as the microbial growth constants (26). These results also agree with similar ones reported by Gates, Marlar, and Westfield (27) for open systems. Because of the importance of determining such relationships in the prediction of oxygen depletion, further work, along the lines pursued by Jennelle and Gaudy, was carried out by Kelly (28).

With the early development of the general belief that the kinetics of BOD exertion followed a definite and mathematically describable course independent of mixing energy and concentration of carbon source, it seems natural that attempts would be made to incorporate such

concepts into formulations for estimating the course of DO depletion in natural waters. The most significant efforts in this regard led to development of the sag equation by Streeter and Phelps (2). Regarding exertion of BOD, they formulated the following law: "The rate of biochemical oxidation of organic matter is proportional to the remaining concentration of unoxidized substance, measured in terms of oxidizability." Streeter and Phelps noted: "This law happens to be similar to that which defines the course of monomolecular reaction...." Having concluded to their satisfaction that such definiteness was warranted, they were free to consider the whole process of self-purification in terms of two phenomena: (1) oxygen consumption by the biological decomposition of organic substances, the velocity of which is quantitatively in accordance with the velocity constant determined in the BOD test, and (2) reaeration, due to a DO deficit, by the absorption of atmospheric oxygen. The result of this simple balance was the following general equation for the dissolved oxygen deficit curve:

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

where D_a = initial DO saturation deficit of the water, D = saturation deficit after time (t), L_a = initial oxygen demand of the organic matter of the water, K_1 = deoxygenation coefficient, K_2 = reaeration coefficient. Their studies on the prediction of DO depletion in the Ohio River seemed to augur well for adoption of the sag equation as a useful method for estimating DO depletion due to entry of organic wastes to natural water courses.

This approach has been the subject of much criticism, however. For example, Leclerc (29) has described the events after a waste enters

the stream and nature reacts to it: Some material is held in suspension and deposited on the stream bed. Putrescent or oxidizable materials are diluted; some are converted into stable forms. The water is continuously reaerated while microbes and reducing reactions deoxygenate the water. Plants add oxygen during daylight hours, and remove it during dark periods. Temperature affects the amount of self-purification and the reaeration rate. This free and valuable self-purification varies with each stream. Leclerc and many other authors criticize the Streeter-Phelps equation because it does not include these important aspects of the oxygen balance. More will be said about improvements in the sag equation later in this chapter.

A further review of the reaeration aspects is warranted in order to help to understand the sag equation. The value for K_2 used in the Streeter-Phelps equation is often selected on the basis of whether the stream has a slow, medium, or fast velocity. However, the degree of turbulence in a stream varies with the geometry of the banks and stream bed. Different chemical and biological factors may influence the ease of reaeration. The three categories of stream velocity used by Streeter-Phelps are too broad to describe adequately the effect of reoxygenation on the assimilative capacity of a stream, and K_2 values should be determined for the particular reach of stream in question rather than be selected and inserted into the equation in accordance with such a "loose" definition.

Isaacs (30) reviewed the work of many investigators who have studied river reaeration and proposed methods to calculate the reaeration coefficient for any stream. The basic premise of all reaeration formulas has been that K_2 is proportional to some function of surface

renewal or turbulence and inversely proportional to some function of the depth. It is important to note that other factors can affect K_2 . For example, Kothandaraman (31) found that contaminants in river water decrease the reaeration rate by approximately 15 percent as compared to the rate for distilled water. Kehr (32) compared K_2 values in tap water to reaeration rate constants with sewage, sewage sludge, and constituents of sewage. He found that sewage concentrations of 0.5 to 10 percent or more decreased K_2 , especially at higher flow velocities (turbulence), and believed the decrease was due to surface tension effects.

While the two opposing forces of the Streeter-Phelps sag equation, reaeration and deoxygenation, are usually considered of prime importance for description of the assimilative capacity of a stream, many investigators feel more variables should be added to the equation to describe the various physical, chemical, and biological events in a stream. Kittrell and Kochtitzky (33) in 1947 stated that the greater assimilative capacity of a turbulent stream is due partially to its increased reaeration capacity. But they believed that the rapid reduction in BOD was possibly due to adsorption of organic matter to bottom deposits where anaerobic degradation occurred without depletion of DO or reaeration capacity.

Wuhrmann, Ruchti, and Eichenberger (34) described two processes of self-purification: (1) sedimentation and formation of benthic deposits, (2) entrance into the food chain of the free floating organisms. The simulated stream employed in their studies was a 546-meter channel, and the substrate consisted of sugar beet molasses, fortified with glutamic acid and phosphate, made up in "ground water." A heterogeneous population rapidly developed, and some organisms attached to

the bottom and sides of the channel in five days. The substrate was removed during the first 100-200 meters.

Owens, Knowles, and Clark (35) developed an equation to predict the distribution of DO in rivers; it included the following factors: light intensity, temperature, amount of aquatic weeds present, initial oxygen content, and photosynthetic and respiratory rates of aquatic plants and benthic deposits. Their equation is an attempt to balance the various parameters against the change in oxygen content per unit surface area of the reach.

Lee and Hwang (36) have made a statement which is probably an accurate generalization regarding many of the complicated models. "The mathematical models that must represent a complex blending of biological, chemical, and physical factors are not simple and must be represented by complex differential equations. For a fairly complex system, these equations cannot be solved analytically."

The foregoing review was intended to demonstrate the broad areas of research involved in making approaches to estimations of the course of DO depletion in receiving streams and in estimating assimilation capacity. In general, reaeration of the stream is due mainly to physical processes, and while the methods of estimating the physical reaeration constants could be subject to greater refinement, this mode of reaeration is probably so dominant over other complicating factors that the inclusion of other factors in models does not seem warranted.

The work of Isaacs and Gaudy and of Jennelle and Gaudy, as well as a report by Gates, provide some indication that work on the exertion of oxygen demand (rather than reaeration) offers a fruitful avenue of investigation which may lead to development of predictive techniques

involving laboratory simulation of O_2 utilization in receiving streams for practical estimation of the DO profile. The use of the BOD dilution technique does not seem adequate for this purpose, and the present work was initiated to gain insight into possible new laboratory and computational techniques for predicting DO profile.

CHAPTER III

EQUIPMENT, PROCEDURE, AND ANALYSIS

A. Laboratory Equipment

1. Stirred Reactor Systems

The mechanically-agitated reactor was a flat-bottomed cylindrical Pyrex vessel with a diameter of 8.125 inches and a depth of 18 inches. Mixing was provided by either a Teflon-coated magnet (Sargent Magnetic Stirrer) or a 2-inch propeller, located one inch from the bottom of the reactor, mounted on a vertical shaft and driven by a Bodine 1/50 hp motor. The bar magnet speed was regulated by the use of the settings on the Sargent stirrer. The impeller speed was regulated by a rheostat. Constant temperature was maintained in the reactor by a Precision Scientific Lo-Temptrol recirculating water bath. Three reactors could be placed in a rectangular plexiglass vessel which served as the water bath tank.

The oxygen monitoring equipment consisted of a Precision Scientific lead-silver oxygen probe and a microammeter. The probe was immersed in the liquid, the reading was made, and the probe was removed. The agitation in the reactor ensured adequate velocity across the probe membrane.

2. Simulated Channel System

The simulated channel used was the apparatus developed by Isaacs (30) at the Oklahoma State University bioengineering laboratories. The apparatus is constructed of fiberglass and consists of a flat-bottomed cylindrical channel with rotating inner and outer walls. The channel provides a rectangular cross-section of flow, having an inside diameter of 48 inches, and an outside diameter of 73 inches. The rotating walls are independently driven by variable speed 3 hp motors. The channel width is 12.5 inches, and a maximum operating water depth is 18 inches. More detailed description of the apparatus and a discussion of its operation can be found in recent literature (8)(9).

Since the reaeration rate was determined before each test run at a previously selected wall rotation, it was not necessary to take velocity measurements of the water. The rotational speeds of inner and outer walls were checked with a stopwatch, and they remained constant throughout the experimental period.

B. Experimental Procedures

1. Effect of Reaeration Constant on Oxygen Uptake

In these studies, three Pyrex vessels were used, and agitation was accomplished with magnetic stirrers and later with motor-driven impellers. Each vessel was filled with ten liters of tap water; stirring was initiated, and the system was allowed to equilibrate to the constant temperature selected for the experiment (20, 22, or 25°C). The stirrers were adjusted to three different speeds.

To check sensitivity of the DO probe, a 2-liter beaker was filled with tap water and stirred until DO saturation was approached. A

standard BOD bottle was filled from this source of water, and a probe reading was taken at the same time on the water in the beaker. The manganous sulfate and alkali-iodide-azide reagents were added to the BOD bottle, and DO was determined according to the Alsterberg azide modification of the Winkler Method described in Standard Methods (37). This dissolved oxygen value was used with the microammeter reading to determine the initial sensitivity in accordance with the manufacturer's recommendation, and the same method was used throughout the experiments. The sensitivity of a recently renewed probe was usually high, and it decreased to a relatively stable range before sensitivity was lost. Several checks were required during each experiment, and the DO values were calculated by using an average sensitivity value between the standardization times. The probes were serviceable for various lengths of time; the average was two weeks.

The dissolved oxygen was removed from the reaction fluid by adding sufficient sodium sulfite to remove 8.0 mg/l of oxygen with approximately 0.02 mg/l cobalt chloride as a catalyst. The dissolved oxygen concentration was monitored at 15-minute intervals to establish a zero time. When the meter reading demonstrated an increase over the preceding value, that latter sample time was taken as zero time for the reaeration part of the experiment.

Each reaeration experiment was monitored from an initial low DO value (near zero) until the saturation level of dissolved oxygen was approached. The recorded values were used to define the saturation concentration of dissolved oxygen, C_s , and a reaeration rate constant, K_2 . The α method which has been described by Isaacs and Gaudy (8) was used in determining the reaeration constant. It should also be noted

that this method was modified to some extent in later experiments. This aspect will be discussed in Chapters IV and V.

The procedure outlined above was followed for many experiments at different stirrer settings, and many repetitive experiments at the same stirrer setting. In later reaeration experiments, the motor-driven impellers were used in place of the magnetic stirrers. In general, the magnetic stirrers were used for experiments run at low K_2 values, and the impellers for experiments at higher K_2 values.

Upon completion of the reaeration portion of the experiment, aliquots from stock solutions of mineral nutrients, buffer and substrate were added to the vessels to obtain the desired concentration of "pollutants." Table I shows the stock concentrations of mineral medium per 100 gm/l carbon source. The source of microbial seed population was either acclimated cells from a batch activated sludge reactor fed daily from the above stock solution (identified as old cells), or fresh sewage from the primary clarifier of the Stillwater, Oklahoma, waste treatment plant (i.e., unacclimated seed). The seed for the final experiment was prepared by acclimating a sewage sample for a period of one day. The concentration of seed employed in each experiment is listed on the figure or in the text of Chapter IV. The concentration is expressed in the standard units used in the BOD test; i.e., as the volume percent of microbial suspension added.

Zero time for the deoxygenation portion of each experiment was established with the completion of the seeding procedure, and a dissolved oxygen reading was taken at that time. The DO was monitored throughout the deoxygenation and recovery periods. Checks on the sensitivity of the probe were made at various times during the experiment.

Samples of the mixed liquor were subjected to microscopic examination at various times during the experiment. The reaeration constants, K_2 , and DO saturation values were determined using the DO values obtained prior to adding the carbon source. The accumulated O_2 uptake curve (BOD curve) was computed using these reaeration factors and the observed dissolved oxygen values during deoxygenation and recovery after adding the substrate. The computational procedure employed is outlined in the Appendix of this report, and sample calculations are provided therein.

TABLE I

COMPOSITION OF GROWTH MEDIUM STOCK SOLUTION PER 100 gm/l OF SUBSTRATE AS GROWTH-LIMITING NUTRIENT

Carbon Source ¹	
$(NH_4)_2SO_4$	50 gm/l
$MgSO_4 \cdot 7H_2O$	10 gm/l
$FeCl_3 \cdot 6H_2O$	0.05 gm/l
$MnSO_4 \cdot H_2O$	1.0 gm/l
$CaCl_2$	0.75 gm/l
KH_2PO_4	52.7 gm/l
K_2HPO_4	107 gm/l
Tap Water	To volume

¹Glucose, glucose-glutamic acid, slaughterhouse waste, Kraft liquor, or hardboard waste

2. Experiments on the Prediction of Dissolved Oxygen Sag Curves in the Simulated Channel From Oxygen Uptake Curves Developed in the Open Jar Reactors

The simulated channel and stirred open reactors were filled to the desired depth (18 inches for the channel, 670 liters; 10 liters for the stirred reactors) with tap water, and equilibrated to constant temperature. The water bath was set to keep the temperature of the stirred reactor equal to an average of the range of temperatures in the channel. The channel wall speed and the motor setting for the open jar were adjusted to predetermined speeds, and both were allowed to aerate for several hours before adding the sodium sulfite and cobalt chloride. These compounds were added to the channel in the same proportions mentioned in the preceding section for the stirred tank.

Monitoring of dissolved oxygen in the channel was accomplished by inserting the probe in the water, reading the value, and then placing the probe in a beaker of water for storage. The probe sensitivity was determined by the procedure previously described. After obtaining the data to determine reaeration characteristics of the vessels, the salts, buffer, substrate, and seed were added to each unit at the same time and in the same concentrations. When industrial components were used, the same ratio of total COD to supplemental nitrogen source was maintained. The systems were brought to volume, and the parameters monitored were temperature, speed, microscopic examination, probe sensitivity, and dissolved oxygen. Each experiment continued for approximately six days. The substrates employed were glucose and equal portions of glucose and glutamic acid; later, various natural waste components were employed. At the completion of each run, the accumulated oxygen uptake

was calculated according to a method previously described (sample calculations are in the Appendix), and plotted for the stirred tank. Calculations were made from these O_2 uptake curves, using the initial dissolved oxygen and the aeration rate in the channel to derive a sag curve in the simulated river channel. This DO profile could then be compared with the actual profile observed in the simulated stream. Sample calculations are presented in detail in the Appendix. The final experiments were conducted to check the procedure using actual wastes. One waste effluent was obtained from a nearby slaughterhouse and meat packing plant. A sample was collected from the plant effluent shortly after a killing period, and before any type of treatment. The waste consisted mainly of blood, and was deep red in color. A COD of 16,250 mg/l was registered for this waste. Two preliminary experiments were made on the waste in the open reactors to become familiar with the treatability characteristics of the waste at COD concentrations from 50 to 200 mg/l. A mixture of sewage and slaughterhouse waste was aerated for 24 hours to develop a seed. A third experiment was conducted to predict the effect of the waste on the artificial or simulated river. After storage in the cold, the waste retained its original COD of 16,250 mg/l, and was diluted to yield 50 mg/l in two open reactors and in the channel. The same procedures were followed with this substrate as with the synthetic wastes. In addition, COD samples were taken initially, at the low point of the sag, and at the end of the experiment. The second industrial waste consisted of wood pulp and digester liquor obtained from a hardboard manufacturer. The liquid was pale brown in color, and contained very little fiber. The pH was 4.5, and the COD of the stock liquor was 6,600 mg/l; the waste was deficient in

nitrogen. Preliminary experiments were run to establish optimum seed and substrate concentration for subsequent experiments in the open reactors and the simulated stream. Digester blowdown liquor from a kraft pulp mill was also employed. The black liquor had a COD of 150,000 mg/l, and a pH of approximately 10. The high sulphur content of this liquor was evident, and some sulphur (probably as H_2S) was stripped upon aeration of a dilute sample. The sulphur content caused a slight immediate chemical O_2 demand leading to an immediate increase in DO deficit of approximately one mg/l. This deficit was rapidly satisfied, i.e., within one hour.

An experiment was performed to compare the Streeter-Phelps sag prediction method with the procedure presented in this report. The procedure previously outlined for the open stirred reactors and simulated river were employed in this run, and BOD curves were also developed using standard dilution BOD bottle technique. The substrate was a combination of a fresh supply of slaughterhouse waste and the original supply of hardboard plant waste. The dilution water for the BOD bottles was the same as that used in the jars and in the simulated river, i.e., concentrations of the mineral salts and buffer were proportional to the nutrient concentration in the jars and the river. The two substrates were necessarily diluted in accordance with the requirements of the standard technique. The seed was obtained from sewage, and was acclimated to the waste for 24 hours, then added to the bottles (at final concentration of 0.5 percent). Prior to adding the above constituents to the BOD bottles, the tap water was aerated with compressed air to about 8.5 mg/l DO. Immediately after preparing the BOD bottles, the tap water was carefully added to the bottles by siphon. The bottles

were incubated in the same water bath used for controlling the temperature for the reactors; they were submerged to maintain a water seal. BOD bottles were periodically removed for dissolved oxygen analysis during the duration of the experiment (five days).

The predicted DO profile in the river calculated using the open jar technique was compared to the DO profile predicted by the Streeter-Phelps equation, using the standard BOD bottle technique.

C. Analytical Procedures

1. Dissolved Oxygen

Dissolved oxygen was monitored electrometrically using a Precision Scientific Company DO analyzer. The instrument was standardized frequently, using the Winkler Method as explained in Standard Methods (37).

2. Microscopic Examination

Wet mounted slides of random samples from the units were observed in order to gain some insight as to the type of microbial populations present. A Carl Zeiss phase contrast microscope was employed, and the samples were viewed at magnification of 970x.

3. Chemical Oxygen Demand

The COD procedure was that described in Standard Methods (37) for a 20-ml sample size, and the dilute procedure for concentrations less than 50 mg/l COD was used.

CHAPTER IV

RESULTS

In all, thirty-six experiments were conducted. For convenience in presenting the results, the experiments are referred to by number as well as descriptive name. The experiments were numbered chronologically, but are not necessarily presented in chronological order. (Some of the thirty-six experiments which were conducted are not included in this report.) The present chapter is divided into two major sections: Phase A, "Effect of Reaeration Constant on Oxygen Uptake," and Phase B, "Experiments on the Prediction of Dissolved Oxygen Sag Curves in the Simulated Channel From Oxygen Uptake Curves Developed in the Open Jar Reactors."

Experiment 11 was a reaeration run which was made to determine the consistency of K_2 values with the magnetic stirrers running at various speeds. In this experiment, the water was deaerated and allowed to aerate to approximately saturation level. DO was measured at frequent intervals during reaeration. Then without stopping or adjusting the stirring speed in any fashion, the water was again deaerated and the reaeration period again allowed to proceed. This procedure was followed for three serial reaeration periods. It was found that K_2 remained constant for any specific magnetic stirrer setting.

Experiments 12, 13, 14, and 15 were conducted to gain insight into

the effect of substrate concentration on rate and kinetic order of O_2 uptake. In general, these experiments verified the previous conclusions of Jennelle and Gaudy (9). However, more work on this aspect seemed warranted, and a decision was made to initiate a separate study along these lines. This study was made the subject of an MS thesis by a colleague in the bioenvironmental laboratories (28).

Experiments 16 and 17 were run to determine the best depth at which to locate the propeller. It was found that placement one inch from the bottom of the jar reactor was better than a location near the middle depths. Once obtained, these results were incorporated into the experimental procedures.

A. Effect of Reaeration Constant on Oxygen Uptake

Twelve preliminary experiments, which are not reported here, were conducted to develop technique and establish a relationship between the stirring speed and the reaeration rate. The α method used by Isaacs and Gaudy (8) was employed to calculate the saturation value, C_s , and the resulting deficit values were used to calculate the reaeration rate, K_2 . It was found that the calculated C_s value varied with the position on the reaeration curve for which the initial time values were chosen. Davis (38) states that the calculation points should be located at the extremities of the first order decreasing curve; however, many erratic values were found and some C_s values indicated supersaturation. Isaacs has made sample calculations (8) showing effects of assuming C_s values too high or too low; the resulting semi-logarithmic plot of deficit versus time will not be a straight line. Therefore, after these preliminary experiments, a trial and error method was developed in which

C_s values were selected to determine deficit values which plotted a straight line for K_2 calculation. This method of finding a C_s value required much less time than did computing the α method equation until a suitable or average value was found to fit the majority of data points. Thus, the method employed to calculate K_2 was, in the main, a graphical approach to the α method. After the reaeration portion of each experiment, the saturation value listed in Standard Methods (37) for the experimental temperature was used to calculate the deficits for the deoxygenation and recovery phases of the experiments.

From these preliminary runs, it was found that a relatively large range of K_2 values could be obtained using the magnetic stirrers 0.87 day^{-1} to 3.86 day^{-1} (calculated using natural logarithms). The magnetic stirrers were limited to this range because at very low speeds, fluctuations in power at times practically stopped the stirrer, while at fast speeds, the magnet would at times spin off center. However, the above range of values encompasses reaeration rates in a large number of natural streams. In later experiments, stirring motors with long shafts and propellers were used.

Fourteen experiments were conducted using the open stirred reactors to determine the relationship between reaeration rate and oxygen uptake. Various concentrations of glucose were used, but the K_2 was the only variable in an individual experiment. The temperature for runs one through 10 was 25°C , runs 18, 19, and 20 were at 20°C , and the final run, number 34, was made at 22°C . Results from two runs (numbers one and three) were discarded because of difficulties with the DO probe.

Figure 1 shows dissolved oxygen concentration during reaeration to

determine K_2 values and five days of the DO profile due to addition of a carbon source. This figure represents a set of sag curves typical of the remainder of the experiments in this section. Data points for the first 26 hours show the recovery of DO after its chemical removal by sulfite; the difference in reaeration rates in the jars stirred at different rates is quite apparent. When enough sampling points had been obtained to determine K_2 values, the synthetic waste was added (arrow on figure). The final concentration in the reactor was 75 mg/l glucose, with 0.25 percent acclimated cells added for "seed." The initial delay (lag) in the downward leg of the DO sag curve occurred in many of the runs. It was eliminated in other runs in which a higher seed concentration was used. For some runs, the downward and upward legs of the DO sag were not as smoothly curved as those shown in Figure 1, and they are termed "phasic" DO sag curves. This figure also illustrates three different types of sag bottoms. The curve for jar three is V-shaped, which was characteristic of units with higher reaeration values. The curve for jar one has a slightly rounded bottom; many of the curves had this appearance. Jar two had the lowest K_2 of all runs. Although the DO meter indicated the presence of a small amount of dissolved oxygen, the amount registered is most probably a result of lack of sensitivity in the DO probe. When this type of flat bottomed curve occurred, it was assumed that the DO actually attained zero. Under such conditions, the calculation of O_2 uptake using the DO profile data is not recommended. The recovery periods for these systems yielded smooth curves; however, some runs exhibited "phasic" recovery curves. This experiment was terminated after 183 hours, at which time the DO in the units was near saturation level.

Figure 1. Typical DO Profiles for Open Stirred Reactors, Including the Reaeration Phase Before Substrate Addition.

Experiment 20: 75 mg/l Glucose, 0.25 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.091 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.044 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.165 \text{ hr}^{-1}$

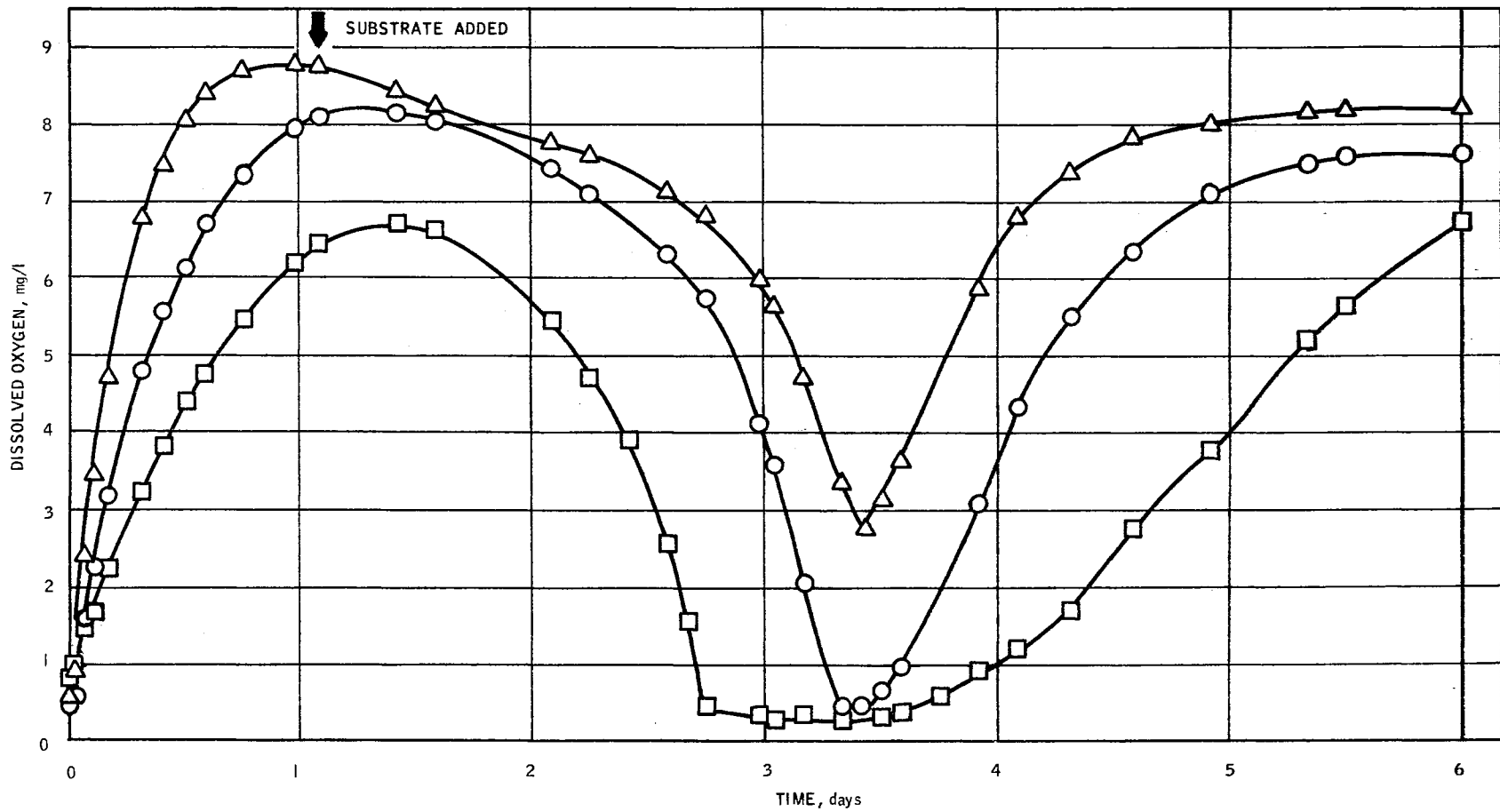


Figure 2 shows the accumulated O_2 uptake curves calculated from the sag curves of Figure 1. It can be seen that these curves do not follow "monomolecular" law; i.e., they do not follow a first order decreasing rate kinetic form. The shape of the curve for O_2 uptake varied somewhat with each run, but an autocatalytic S-shape was typically observed. A distinct "plateau" was not evident in this run, nor were plateaus found as typical features of all O_2 uptake curves. The early break in the curve for jar two at 40 hours was probably caused by DO deficiency. The difference in K_2 values, covering the rather broad range of 0.044 to 0.165 hr^{-1} , is seen to cause considerable differences in the O_2 uptake. The final values after 183 hours were 33.2 mg/l for the low K_2 , 40.3 mg/l for the intermediate K_2 , and 51.5 mg/l for the high K_2 .

In order to point out similarities as well as variations from the results shown above for other experiments of the same type, the remaining data are described briefly in the manuscript, and four additional O_2 uptake graphs are presented. Pertinent observations are also included in a summary table (Table II) at the end of this section of the chapter.

In experiment two, a glucose concentration of 50 mg/l was employed and the seed was 0.5 percent old cells. The K_2 values were 0.069 and 0.090 hr^{-1} . The bottom of the sag occurred about five hours earlier with the lower K_2 , and the minimum DO was maintained for eight hours. The higher K_2 value resulted in a sag curve in which the recovery phase began immediately after the minimum point was reached. The minimum dissolved oxygen concentration was 1.3 mg/l for the system with the higher K_2 , and 0.3 mg/l for the lower one. After three days, the DO

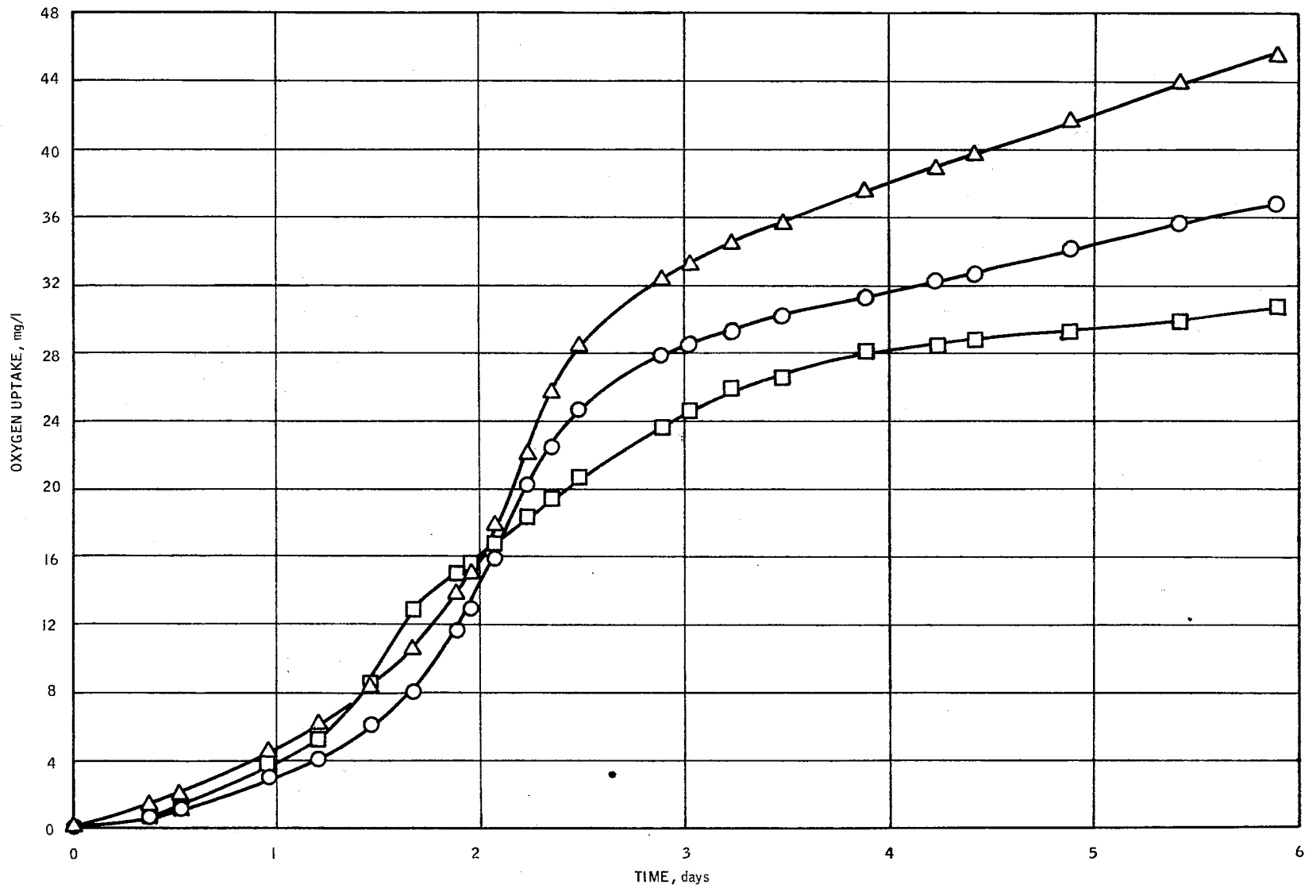
Figure 2. Typical Oxygen Uptake Curves for a Wide Range of Reaeration Rates.

Experiment 20: 75 mg/l Glucose, 0.25 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.091 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.044 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.165 \text{ hr}^{-1}$



had practically recovered to the initial values. The O_2 uptake curves were identical, and after 54 hours the total oxygen consumed for both units was 23 mg/l. This experiment was of rather short duration, and a second phase of O_2 uptake would not have been detected had conditions been such that a second phase would have occurred with longer aeration.

In experiment four, the glucose concentration was lowered to 30 mg/l, and the seed was decreased to 0.25 percent old cells. The minimum DO was 4.9 mg/l for the jar stirred to produce a K_2 of 0.112 hr^{-1} , and 4.7 mg/l for the jar with the lower K_2 (0.081 hr^{-1}). With the low substrate and seed concentrations, the sag curves had a characteristically slow decrease to the minimum DO and a slow recovery. Both O_2 uptake curves were S-shaped or autocatalytic in nature. At the end of the experiment (52 hours), 13.7 mg/l O_2 had been used for the system with the greater K_2 , and 11.9 mg/l O_2 in the jar with the lower K_2 value.

A substrate concentration of 10 mg/l in run five proved too low to yield a reliably calculated O_2 uptake curve. At the K_2 values employed, only a slight sag or none at all was exerted. Two O_2 uptake curves were calculated at this concentration, and they were very similar. Both appeared to follow first order decreasing kinetics to 48 hours, at which time the total oxygen uptake was 8.7 mg/l for the system with a K_2 of 0.090 hr^{-1} and 7.0 mg/l for a K_2 of 0.108 hr^{-1} .

In experiment six, a substrate concentration of 40 mg/l glucose and 0.25 percent old cells were used. The difference between the K_2 values was slight and, therefore, the sag curves and O_2 uptake curves were essentially the same. The minimum DO was 3.6 mg/l, and again the sag curves had gradually sloping sides. The O_2 uptake curves were S-shaped to 40 hours, when a sudden decrease in O_2 uptake rate occurred.

After 68 hours, the oxygen consumed was 15.3 mg/l for a K_2 of 0.069 hr^{-1} , and 16.7 mg/l for a K_2 of 0.076 hr^{-1} .

A concentration of 20 mg/l carbon source in run seven resulted in a much larger sag than was observed with the 10 mg/l employed in experiment five (K_2 values were only slightly lower in experiment seven). However, the minimum DO was 4.0 mg/l for the low K_2 value, and the legs of the sag curves flattened. The O_2 uptake curves were S-shaped and all increased at the same rate to 32 hours, at which time the O_2 uptake rate decreased sharply. The end of the autocatalytic O_2 uptake phase occurred earlier in the unit with the lowest K_2 than in the others, and the system with the highest K_2 exhibited the greatest total uptake.

In experiment eight, a wide range of K_2 values was employed. However, at the fast stirring rate, the stirring magnet would spin off center occasionally, and this set of data was of doubtful validity. The values for K_2 were 0.053, 0.091, and 0.20 hr^{-1} , and the glucose concentration was 50 mg/l with a 0.25 percent seed of old cells. The data for the system with a K_2 of 0.20 hr^{-1} were discarded. A large difference was noted in the sag curves for the two remaining jars. An 18-hour lag was observed in both units, after which the dissolved oxygen decreased in one jar from 6.6 mg/l to 0.70 mg/l, whereas in the system with a higher K_2 , the DO decreased from 7.0 mg/l to 4.2 mg/l. Again, both O_2 uptake curves were S-shaped. However, unlike many other experiments, the rate of O_2 uptake appeared to be greater for the system with the lower K_2 .

Experiment nine was the first run in which fresh sewage was used as the seed. Thirty mg/l glucose and 0.25 percent seed were added to reactors with reaeration rate constants of 0.060, 0.093, and 0.108 hr^{-1} .

All three responded with a 20-hour lag phase, a small sag, a slight recovery period, and another sag and recovery. The first sag occurred after 36 hours; the greatest depression in DO occurred in systems with lower K_2 values. Also, the rate of recovery was slower in the system with the lowest K_2 value. The second sag was much more pronounced for the lowest K_2 system. The minimum DO of the second sag occurred at 72 hours for the unit operated with a K_2 of 0.060 hr^{-1} , and at 90 hours for the others. The O_2 uptake curves for this experiment, shown in Figure 3, are slightly multiphasic and are essentially parallel lines for the systems with K_2 value of 0.093 and 0.108 hr^{-1} . It is noted that after almost six days, the total oxygen utilized for the unit with a K_2 of 0.108 hr^{-1} was 26 mg/l. It appears from these results that lower O_2 uptake can be expected in systems with lower K_2 values.

A variety of sag curves was obtained in experiment 10, in which the substrate concentration was 40 mg/l and a seed of 0.25 percent old cells was employed. All three units had an 8-hour lag. The sag curve of the unit with a K_2 of 0.058 hr^{-1} declined sharply to 0.6 mg/l DO, and the minimum level persisted for 10 hours. This flat bottom may have been caused by faulty probe response, because in another experiment (six) at this level of substrate with a comparable K_2 , the sag curve exhibited a rapid recovery of DO. The sag curve for the reactor with a K_2 of 0.085 hr^{-1} exhibited the latter type of curve. The higher K_2 of 0.105 hr^{-1} resulted in a sag curve with a slow declining leg and a rapid recovery leg. The O_2 uptake curves calculated from these sags are shown in Figure 4. At the low and medium K_2 values, the O_2 uptake curves were similar, while the higher value of K_2 resulted in a lower uptake rate during the second and part of the third day.

Figure 3. Phasic Oxygen Uptake for a Low Concentration of Substrate.

Experiment 9: 30 mg/l Glucose, 0.25 percent Sewage

○ = Jar 1, $K_2 = 0.108 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.093 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.060 \text{ hr}^{-1}$

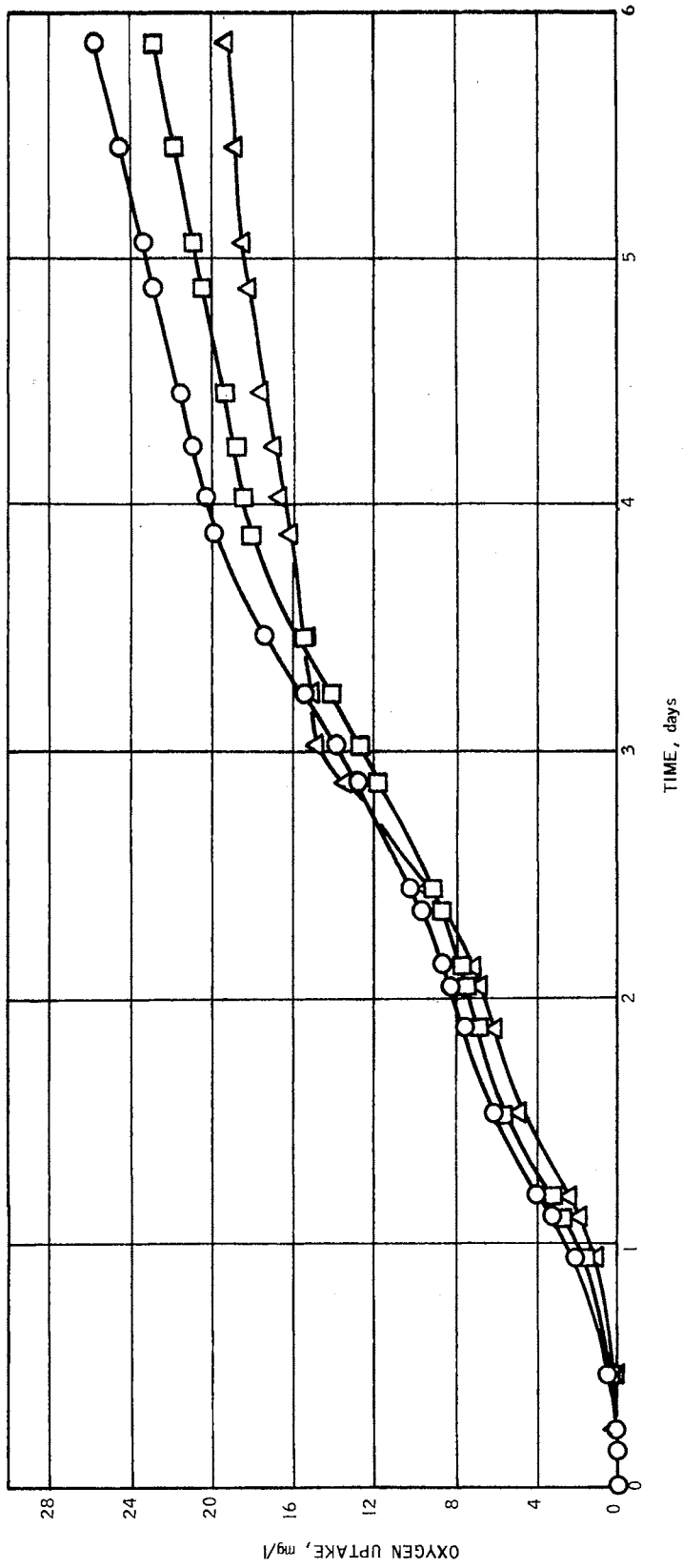


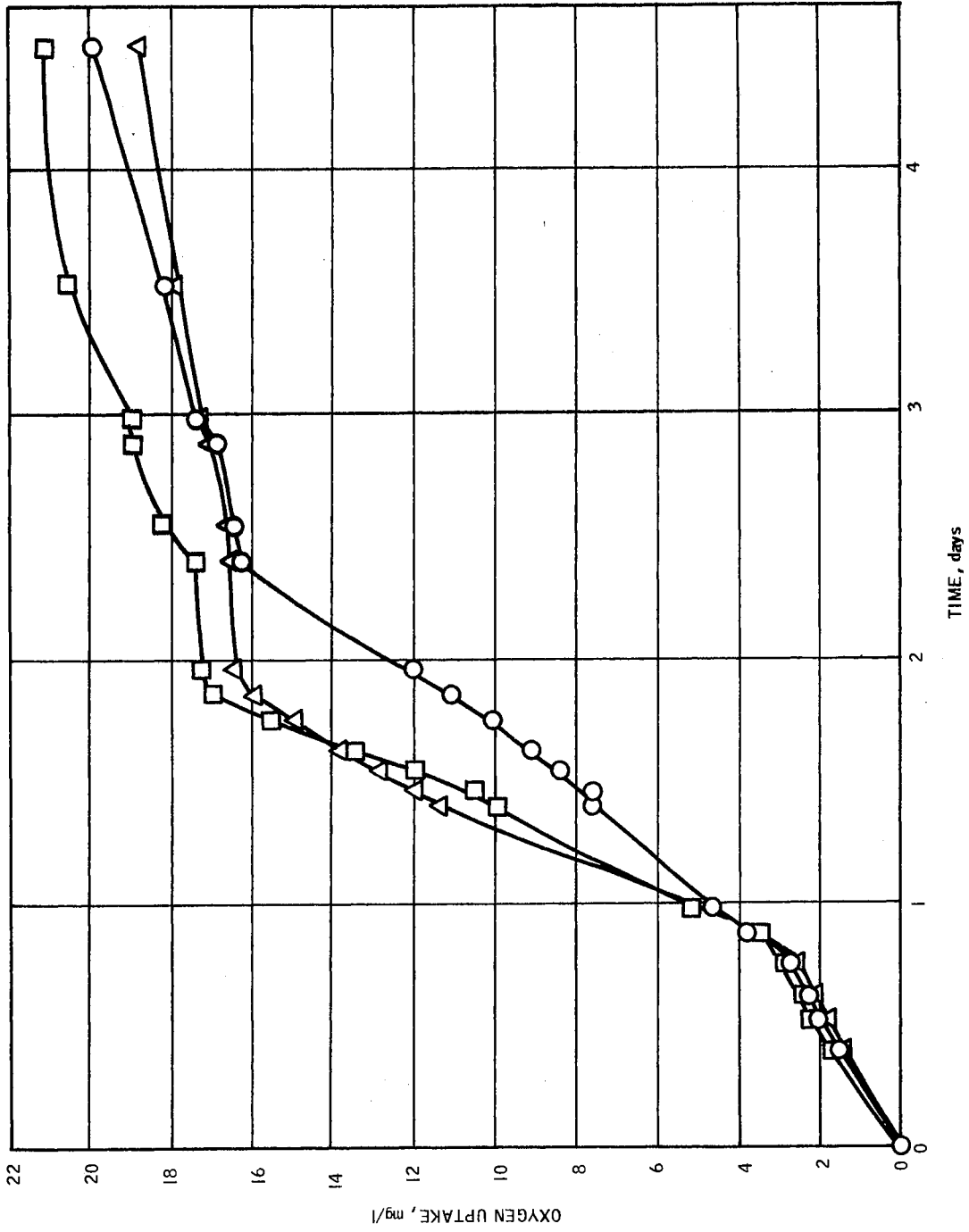
Figure 4. Oxygen Uptake Response due to Various Reaeration Rates.

Experiment 10: 40 mg/l Glucose, 0.25 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.105 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.085 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.058 \text{ hr}^{-1}$



In experiment 18, the effect of medium to high K_2 values on O_2 uptake was examined. The seed was 0.25 percent old cells, and 50 mg/l glucose was employed as a substrate. As would be expected, the lower K_2 values yielded the greater DO deficits at the low points in the sag curves. The dissolved oxygen depletion for a K_2 of 0.210 hr^{-1} was only 0.6 mg/l. Figure 5 is a plot of the O_2 uptake curves for this experiment. It is noted that for the higher K_2 values, the increasing leg of the S-shaped curve (approximate exponential phase) appeared to yield a slower rate of O_2 uptake. However, with a DO deficit of only 0.6 mg/l, the validity of the calculation procedure may be in doubt. In any event, it would appear that at a two-fold difference in K_2 value (0.09 versus 0.210 hr^{-1}), reaeration rate (agitation or turbulence) can affect O_2 uptake rate.

A wide range of K_2 values was used in run 19: 0.047, 0.089, and 0.154 hr^{-1} . Also, the feed was increased to 75 mg/l, while the seed was 0.25 percent old cells. A long lag of 24 to 36 hours and a double sag was observed for all three units. At the time, such a double sag was thought to represent an abnormal curve, and experiment 20 was run. This experiment was shown in Figures 1 and 2.

The final experiment to compare reaeration rate and O_2 uptake was conducted in the same fashion as all previous experiments. Four jars covering a large range of K_2 values were employed. Each was inoculated with 50 mg/l glucose and 0.5 percent of an acclimated seed developed from sewage. In all units, a slight initial sag occurred during the first day with partial recovery before the main sag developed. Figure 6 shows the resulting O_2 uptake curves. There is a definite indication that the degree of reaeration can affect O_2 uptake. Units one and four

Figure 5. Oxygen Uptake Curves for a High Range of Reaeration Rates.

Experiment 18: 50 mg/l Glucose, 0.25 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.128 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.090 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.210 \text{ hr}^{-1}$

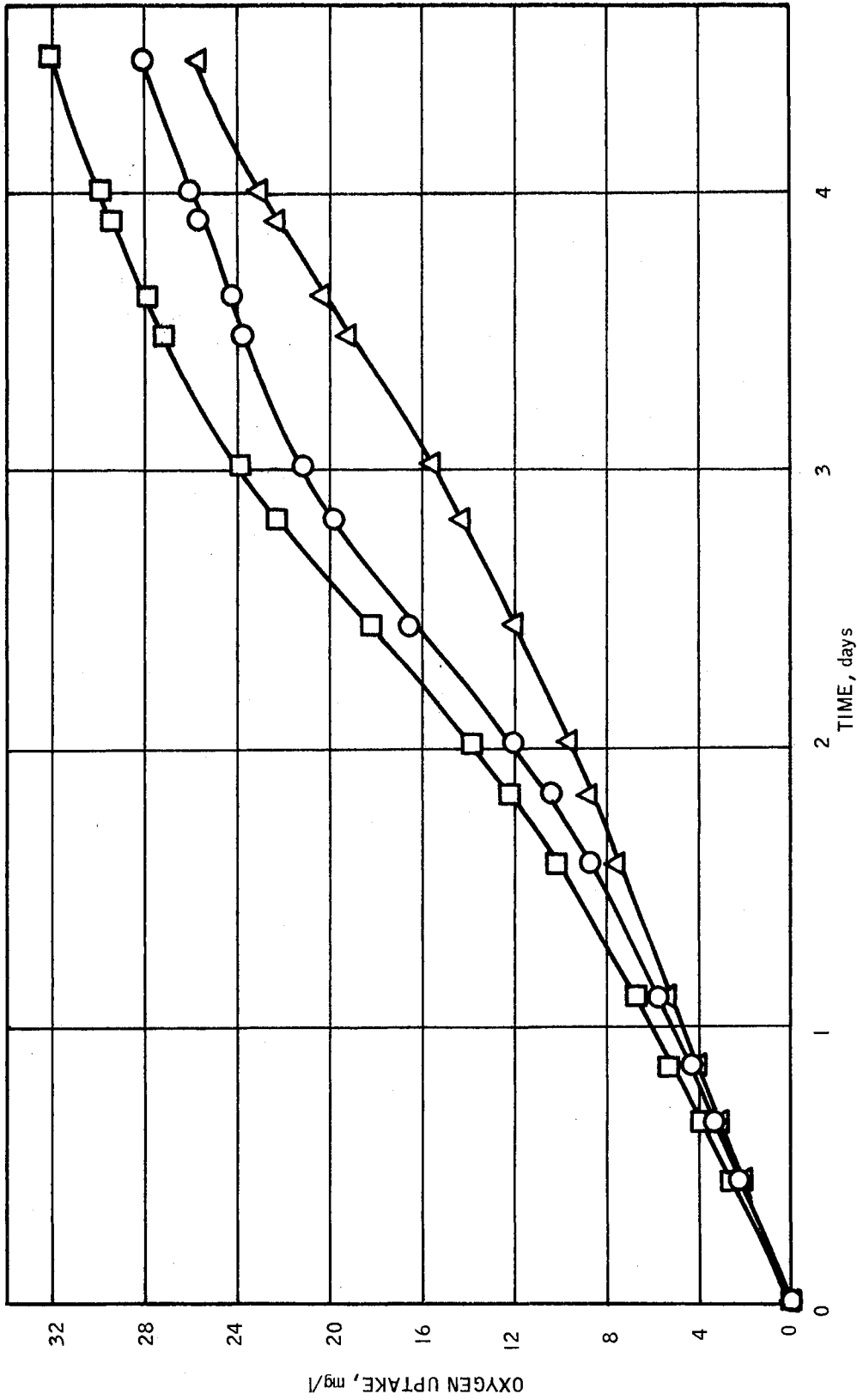


Figure 6. The Effect of Reaeration Rate on the Course of Oxygen Uptake.

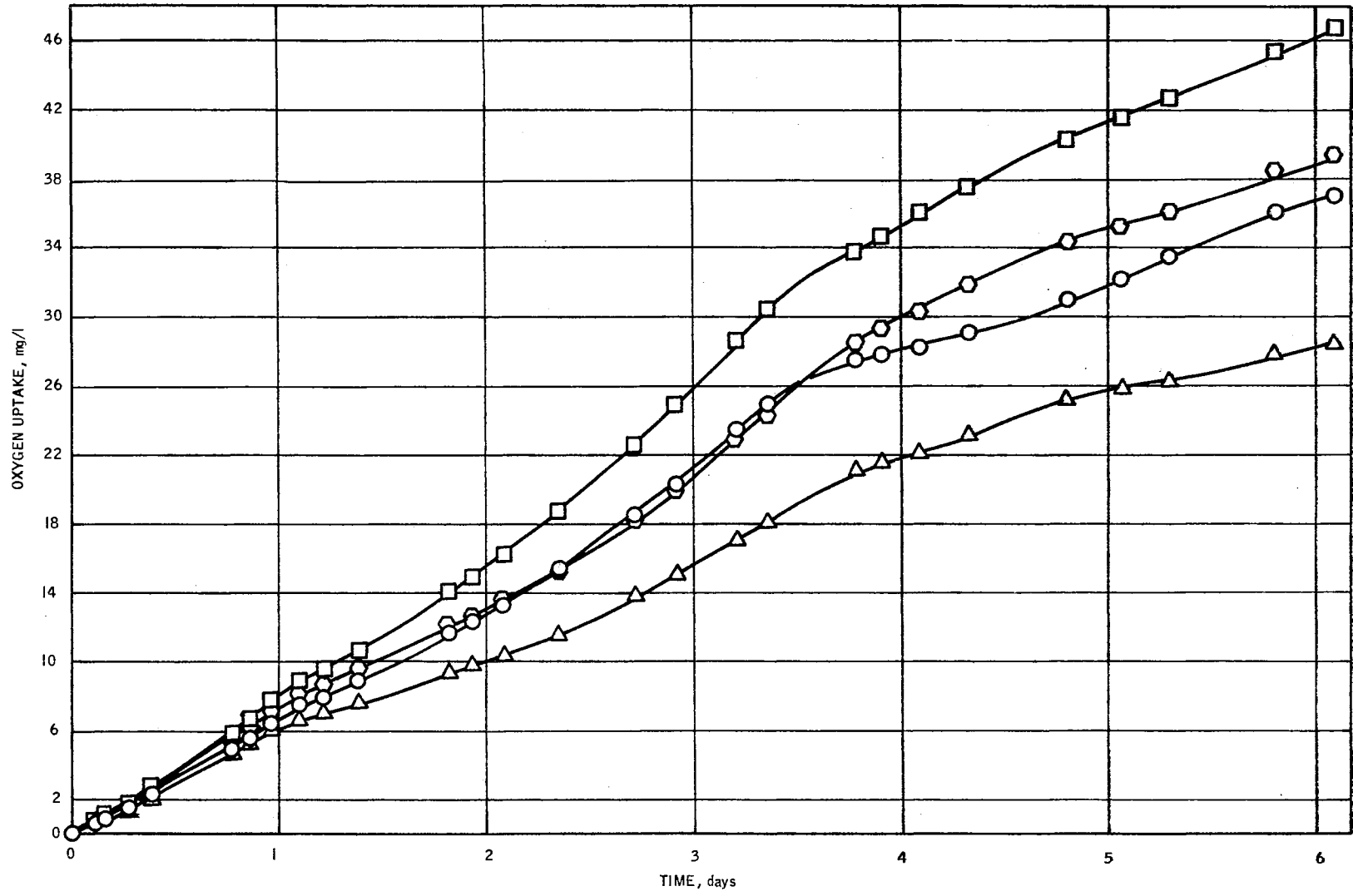
Experiment 34: 50 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.078 \text{ hr}^{-1}$

□ = Jar 2, $K_2 = 0.116 \text{ hr}^{-1}$

△ = Jar 3, $K_2 = 0.065 \text{ hr}^{-1}$

◇ = Jar 4, $K_2 = 0.095 \text{ hr}^{-1}$



with K_2 values of 0.078 and 0.095 hr^{-1} , respectively, yielded essentially the same O_2 uptake curve. However, the very large difference between O_2 uptake curves for jars two and three (highest and lowest values of K_2) indicates that greater O_2 uptake can be expected at higher K_2 values. An increase in O_2 uptake with increasing K_2 values was also shown for three systems in Figure 2. In Table II, key features of each of the experiments are summarized.

B. Experiments on the Prediction of Dissolved Oxygen Sag Curves in the Simulated Channel From Oxygen Uptake Curves Developed in the Open Jar Reactors

The next series of experiments was undertaken to determine whether O_2 uptake data could be employed to predict the DO profile of the simulated stream at known K_2 values. It was hypothesized that if this were possible, there would be some basis for formulating recommendation of a method to replace the usually employed BOD dilution technique. The numerical integration technique used in the present study to predict the DO profile does not require mathematical definition of the kinetic course of O_2 uptake (i.e., BOD exertion). Sample calculations demonstrating the computational technique are given in Table IV in the Appendix.

For this set of experiments, mixing in the open jar reactors was provided by motor-driven propellers rather than magnetic mixers. The stirring speeds were usually higher than those obtained with the magnetic stirrers, and the speed could be more reliably controlled. The operating temperature for the jars and river is noted in the legend of each figure. In order to make direct comparison of the course of

TABLE II
SUMMARY OF THE EFFECT OF REAERATION CONSTANT ON OXYGEN UPTAKE

1	2	3	4	5	6	7	8	9	10	11
Exper. #	Jar #	Glucose mg/l	K_2 hr ⁻¹	Type of Seed and %	Type of Sag Curve	Initial DO mg/l	Minimum DO mg/l	Type of O ₂ Uptake Curve	Total O ₂ Used, mg/l	Effect of K_2 on O ₂ Uptake
2	1	50	0.069	old cells 0.50%	smooth-flat bottom smooth-V-bottom	5.9	0.3	S-shaped	23 - 54 hr	Both curves identical for this period of time
	2		0.090			6.6	1.3	S-shaped		
4	1	30	0.081	old cells 0.25%	smooth smooth	6.1	4.7	S-shaped	12 - 52 hr 14 - 52 hr	Curves separate after 12 hrs
	2		0.112			7.0	4.9	S-shaped		
5	1	10	0.108	old cells 0.25%	flat flat	6.8	6.7	first order decreasing	7 - 48 hr 9 - 48 hr	Curves very similar during this time period
	2		0.090			6.2	6.0	first order decreasing		
6	1	40	0.069	old cells 0.25%	smooth smooth	6.1	3.7	S-shaped	15 - 68 hr 17 - 68 hr	Curves very similar
	2		0.076			6.2	3.6	S-shaped		
7	1	20	0.091	old cells 0.25%	smooth smooth smooth	7.2	4.5	S-shaped	16 - 76 hr 13 - 76 hr 10 - 76 hr	Curves diverged in accordance with K_2 values with lowest K_2 yielding lowest O ₂ uptake
	2		0.083			7.1	4.7	S-shaped		
	3		0.062			6.1	4.0	S-shaped		
8	1	50	0.091	old cells 0.25%	smooth smooth-flat bottom	7.0	4.2	S-shaped	21 - 93 hr 25 - 93 hr	Considerable difference in the O ₂ uptake curves, system with highest K_2 value yielded lowest O ₂ uptake
	2		0.053			6.6	0.7	S-shaped		
9	1	30	0.108	sewage 0.25%	smooth-double sag smooth-double sag smooth-double sag	7.7	5.5	S-shaped - plateau	26 -141 hr 23 -141 hr 19 -141 hr	Units 1 and 2 very similar. Difference between units 1 and 3 too great to consider as one curve
	2		0.093			7.8	5.6	S-shaped - plateau		
	3		0.060			7.2	3.1	S-shaped - plateau		
10	1	40	0.105	old cells 0.25%	phasic smooth smooth-flat bottom	6.7	4.5	S-shaped	20 -108 hr 21 -108 hr 19 -108 hr	O ₂ uptake in system with highest K_2 proceeded at slowest rate during the 36-hour period following the first day
	2		0.085			6.5	2.2	S-shaped - plateau		
	3		0.058			5.1	0.6	S-shaped		
18	1	50	0.128	old cells 0.25%	smooth smooth flat	7.5	5.8	S-shaped	28 -107 hr 32 -107 hr 26 -107 hr	System with highest K_2 yielded lower O ₂ uptake
	2		0.090			6.5	4.5	S-shaped		
	3		0.210			8.1	7.5	S-shaped		
19	1	75	0.089	old cells 0.25%	smooth-double sag double sag-flat bottom smooth-double sag	8.9	2.3	S-shaped - plateau	34 -150 hr 30 -150 hr 30 -150 hr	Three completely different O ₂ uptake curves
	2		0.047			9.3	0.6	S-shaped		
	3		0.154			7.6	5.6	S-shaped - plateau		
20	1	75	0.091	old cells 0.25%	smooth-V-bottom smooth-flat bottom smooth-V-bottom	8.2	0.5	S-shaped	40 -183 hr 33 -183 hr 52 -183 hr	Curves diverged in accordance with K_2 values with lowest K_2 yielding lowest O ₂ uptake
	2		0.044			6.7	0.3	S-shaped		
	3		0.165			8.7	2.8	S-shaped		
34	1	50	0.078	new acclimated cells 0.50%	phasic-double sag phasic-double sag phasic-double sag phasic-double sag	6.8	3.8	S-shaped - plateau	37 -146 hr 47 -146 hr 28 -146 hr 39 -146 hr	Units 1 and 4 very similar O ₂ uptake curves. K_2 values for units 2 and 3 too different to compare curves with units 1 and 4
	2		0.116			7.3	4.5	S-shaped - phasic		
	3		0.065			6.7	4.6	S-shaped - phasic		
	4		0.095			7.0	4.6	S-shaped - phasic		

exertion of BOD, the feeding and seeding methods for the reactors and artificial river were exactly the same, unless purposely made different, as was the case in some experiments.

After several experiments with glucose-glutamic acid and glucose alone, three actual wastes were used to test the method. The first was essentially animal blood from a slaughterhouse and meat packing company. The waste was collected from the plant outlet line before any type of treatment. The second waste was from a hardboard manufacturer and was also collected prior to treatment. The third substance was black liquor from a kraft pulping plant and was obtained before the material was recycled for reclamation of chemicals. One set of figures is shown for the glucose and glutamic acid runs, two for the glucose experiments, and all figures for the three wastes. Finally, the figures are shown for the concluding experiment which was designed to compare the Streeter-Phelps method with the new method reported here.

In experiment 21, a mistake in substrate concentration was discovered after the run was concluded. The river was fed a total concentration of 60 mg/l; however, the jars received only half this concentration. In experiment 22, the river was run with 30 mg/l total substrate (15 mg/l glucose plus 15 mg/l glutamic acid), while one jar had 30 mg/l and the other, 60 mg/l. Similar O_2 uptake curves were obtained in the open reactor and river, both of which contained 30 mg/l total substrate. Only slight depressions of DO (i.e., "sags") were observed at this concentration, and the lag phase in the jar was approximately 64 hours. These two preliminary runs provided experience with the river, the calculation procedure, and insight into concentrations of substrate and seed to be employed in subsequent experiments.

Figures 7, 8, and 9 show data for experiment 23 in which the substrate consisted of a mixture of glucose and glutamic acid (30 mg/l each), and sewage seed (0.5 percent) was employed. The remaining experiments with this substrate will be compared to these figures. The data for this experiment were also used in the sample calculations (presented in the Appendix) for O_2 uptake and the predicted sag curve. The K_2 values were all rather high, with that in the river (0.120 hr^{-1}) falling between the values for the two jars (0.099 and 0.136 hr^{-1}). The reactor with the highest K_2 (jar one) resulted in an abnormally high O_2 uptake rate, which may have been due to an error in substrate concentration, and the data could not be employed for predicting the DO profile in the river. It can be seen in Figure 7 that there was a delay or lag in initiation of the downward leg of the DO profile in the jar. This lag is evident in the O_2 uptake curves shown in Figure 8; it amounted to approximately 12 hours. However, if the 12-hour lag phase in the jar was eliminated from the calculation, the predicted sag curve corresponded well with the actual (observed) sag curve in the simulated river (Figure 9). The predicted low point of 1.90 mg/l DO occurred at the same time but was approximately one mg/l DO below the actual. Thus, the technique appeared to provide an acceptable approximation of the actual profile, albeit a conservative estimate of the minimum DO.

In a similar experiment (run 24), two jars were used. The fresh sewage seed produced an initial lag phase (20 hours) in the open reactors, but none in the river. Also, the decreasing leg of the sag curve was somewhat phasic in the jars, while the curve for the river was smooth. These two differences caused the low point of the sag for the jars to occur 32 hours after that for the river. Although there

Figure 7. Actual Sag Curves for Open Stirred Reactor and Artificial River.

Experiment 23: 60 mg/l Glucose-Glutamic Acid, 0.50 percent Sewage

□ = Jar 2, $K_2 = 0.099 \text{ hr}^{-1}$, 23°C

△ = River, $K_2 = 0.120 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$

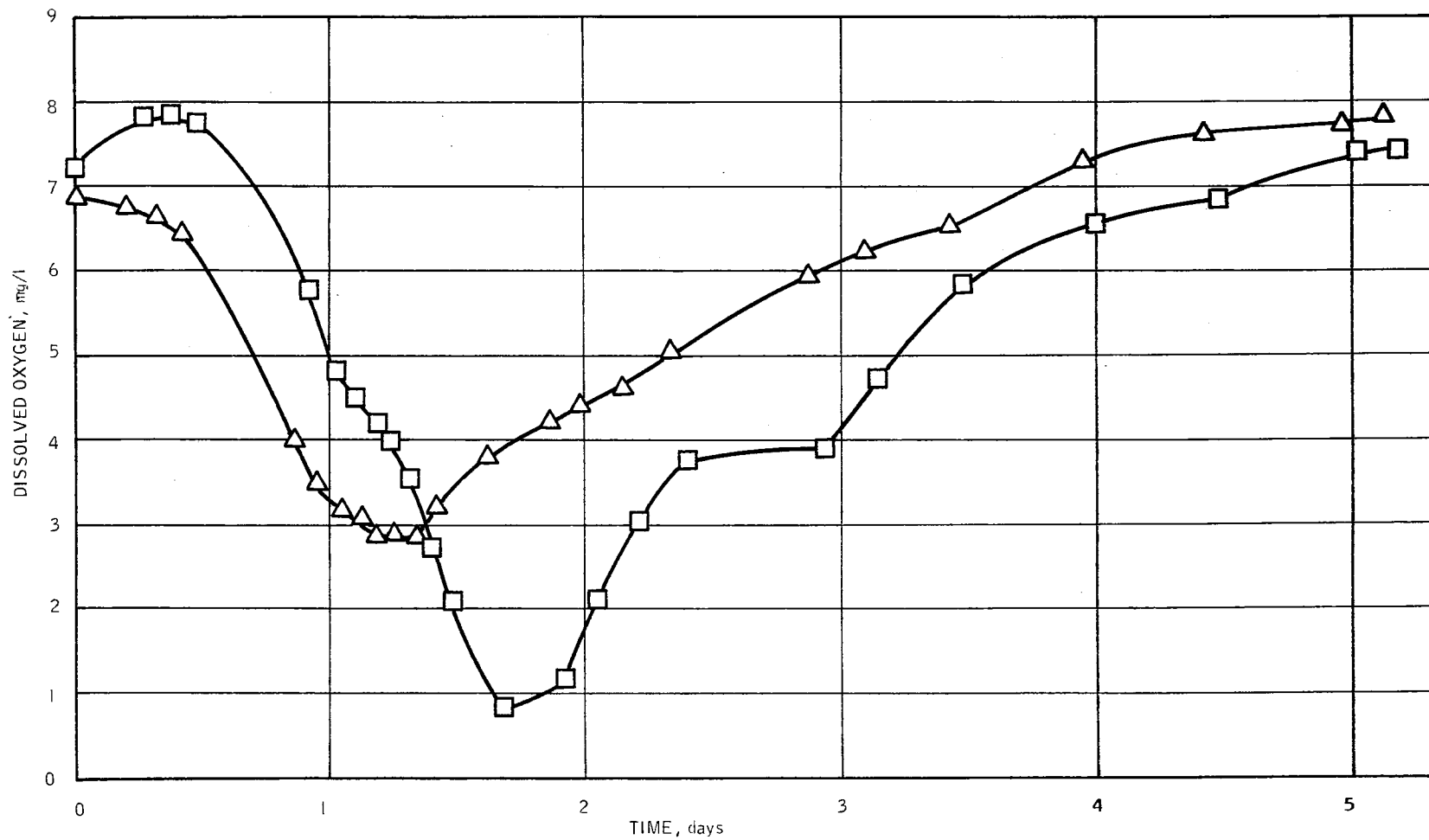


Figure 8. Oxygen Uptake Curves Calculated From Sag Curves in Figure 7.

Experiment 23: 60 mg/l Glucose-Glutamic Acid, 0.50 percent Sewage

□ = Jar 2, $K_2 = 0.099 \text{ hr}^{-1}$, 23°C .

△ = River, $K_2 = 0.120 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$.

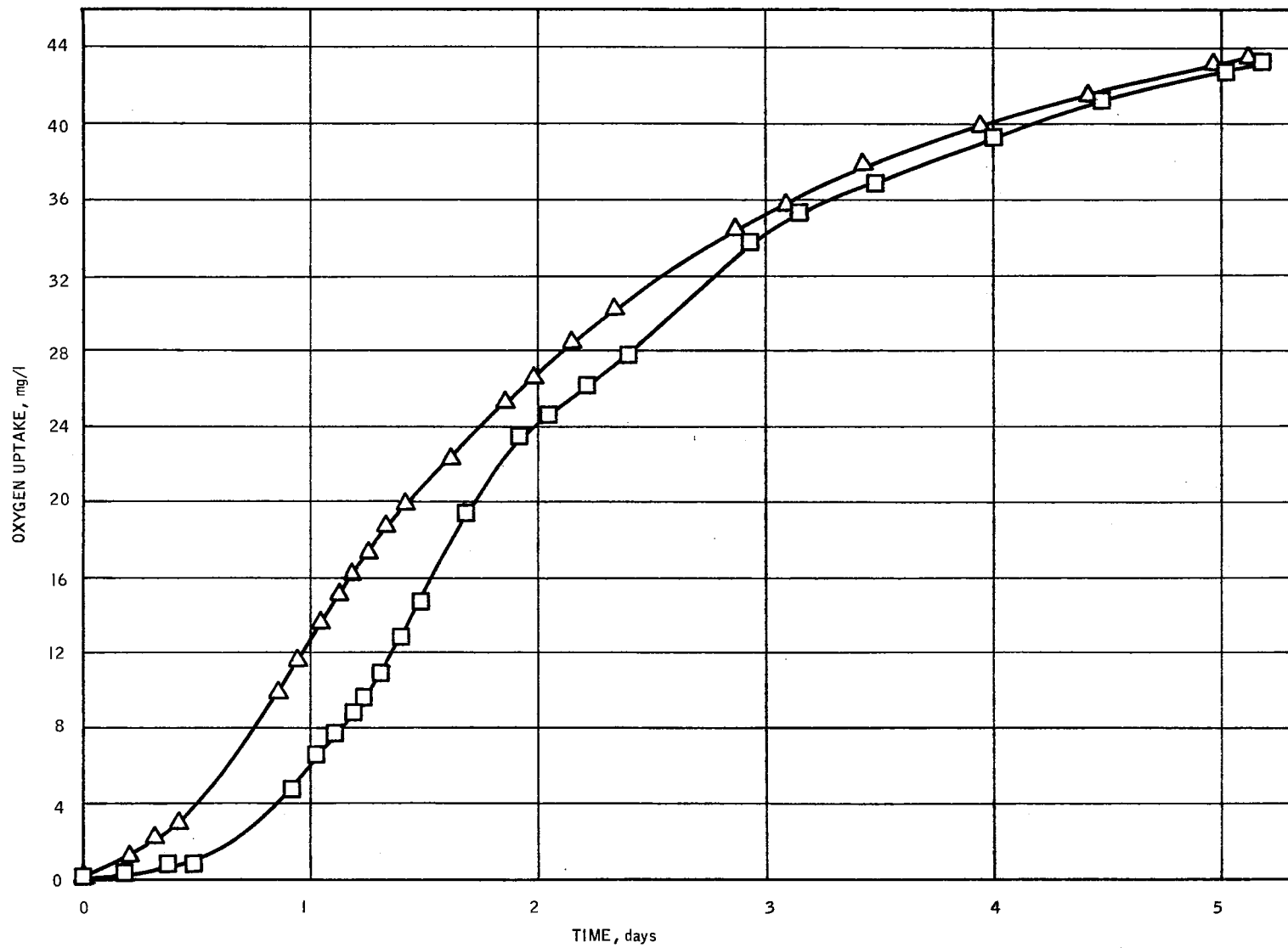
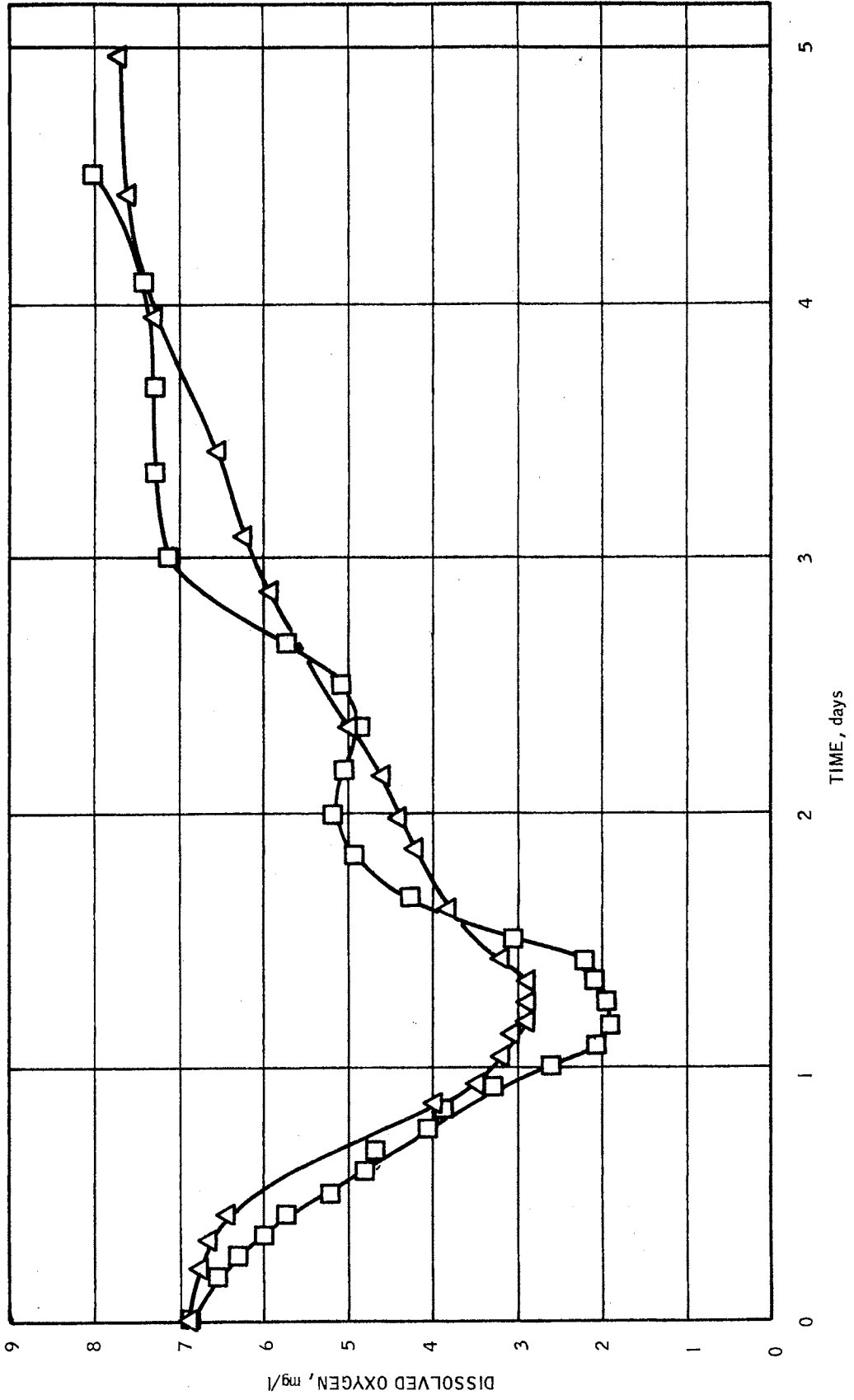


Figure 9. Sag Curve Predicted From O_2 Uptake Curve Compared to Actual River Sag Curve.

Experiment 23: 60 mg/l Glucose-Glutamic Acid, 0.50 percent Sewage

□ = Jar 2, $K_2 = 0.099 \text{ hr}^{-1}$, 23°C

△ = River, $K_2 = 0.120 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$



was only one mg/l difference in the minimum DO values, the O_2 uptake was greater for the jars than the river, and the difference appeared to be due to the two-phase decreasing leg of the sag curves in the jars. The greater O_2 uptake in the jars did not appear to be attributable to a difference in K_2 values, since there was only a small difference in these values: 0.102 in the river, compared to 0.114 and 0.134 hr^{-1} in the jars. The O_2 uptake curves were of the same general shape as those shown in Figure 8, except for the longer initial lag phase. One predicted sag curve fell below zero, and the other had a minimum point of 0.24 mg/l DO while the observed minimum DO in the river was 2.0 mg/l DO. Again, the jars predicted a conservative picturization of the DO profile in the river, but one which surely was not within acceptable limits. It was concluded from this experiment that unacclimated seed (fresh sewage) should not in any case be employed as seed material.

Starting with experiment 25, various acclimation procedures for seeds were tried in efforts to remove the lag phase in the open reactors. Fresh sewage was acclimated to glucose in minimal salts and buffer medium in order to begin an experiment with a pre-adapted microbial population. Effort was made to determine the percentage of seed necessary and the duration of the acclimation time for the seed. The substrate for experiment 25 was 60 mg/l glucose, and 0.5 percent seed was added to the jars and river. Results for this run are shown in Figures 10, 11, and 12. To develop a seed, a sample of fresh sewage was supplemented with glucose (approximately 1000 mg/l) and buffer salts. The system was aerated for 36 hours before use in experiment 25. The sag curve in the river started immediately, and reached a minimum DO of one mg/l approximately 40 hours before the reactors reached a low of 2.5 mg/l

Figure 10. Actual Sag Curves for Open Stirred Reactors and Artificial River.

Experiment 25: 60 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.108 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.134 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.080 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$

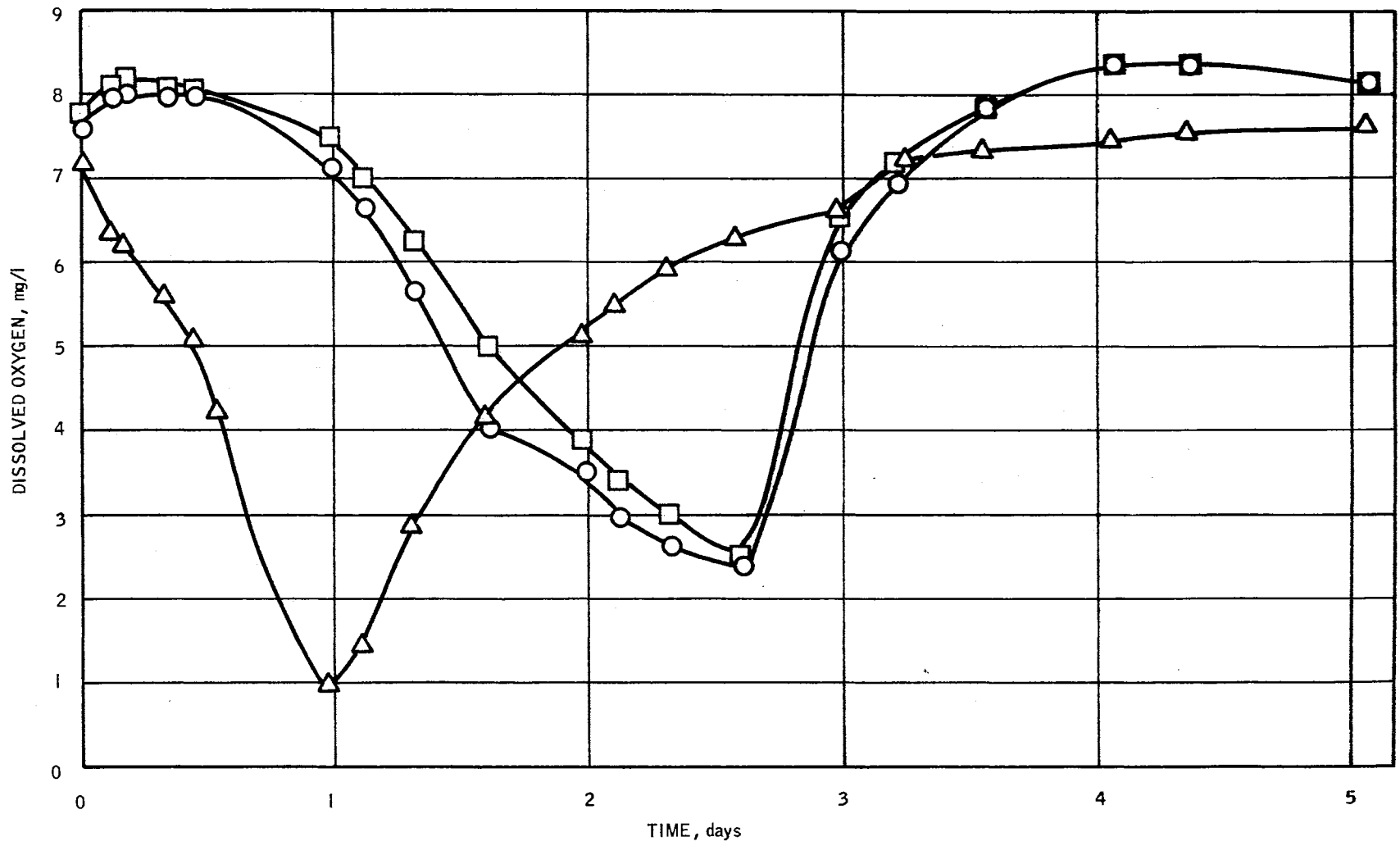


Figure 11. Oxygen Uptake Curves Calculated From Sag Curves in Figure 10.

Experiment 25: 60 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.108 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.134 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.080 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$

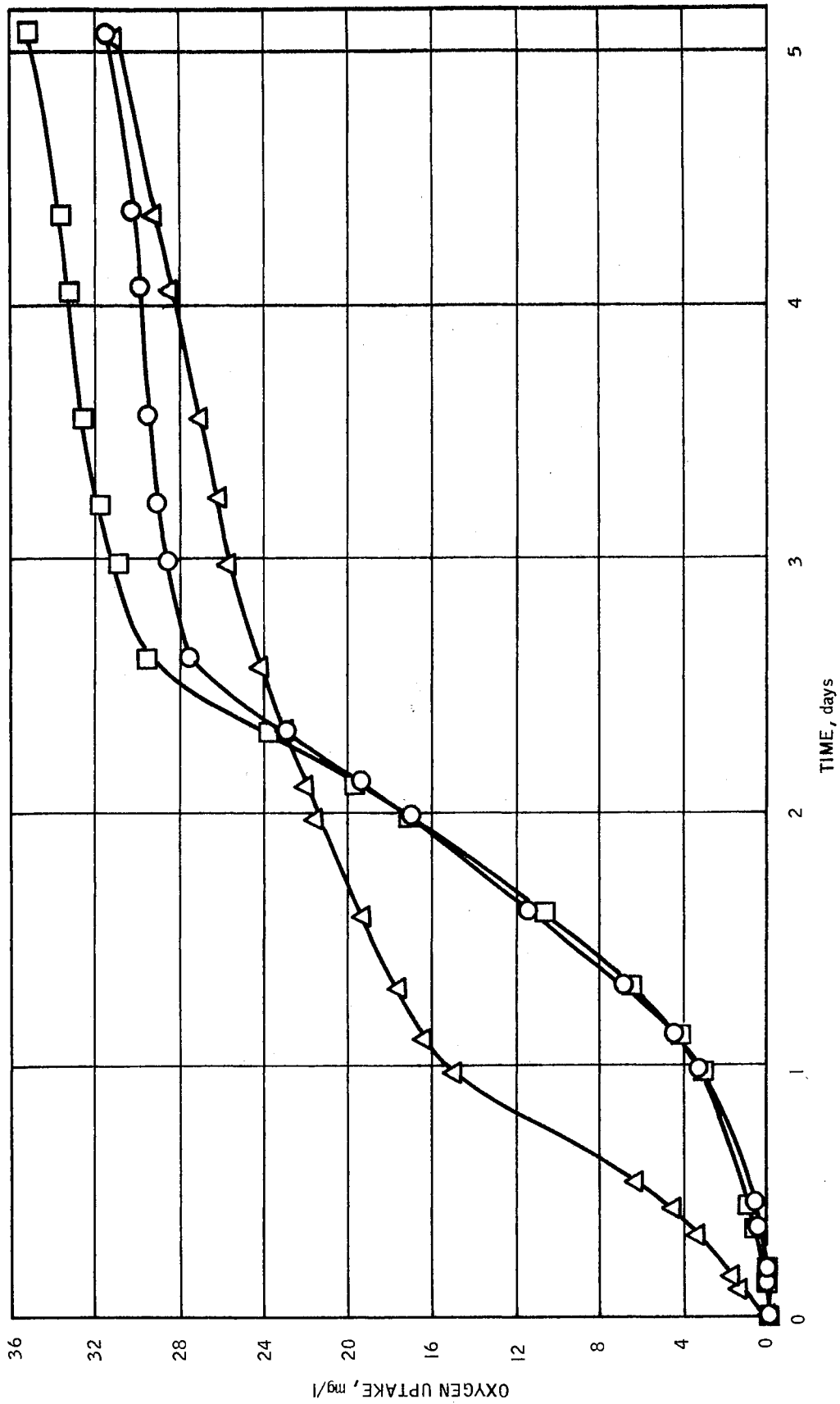


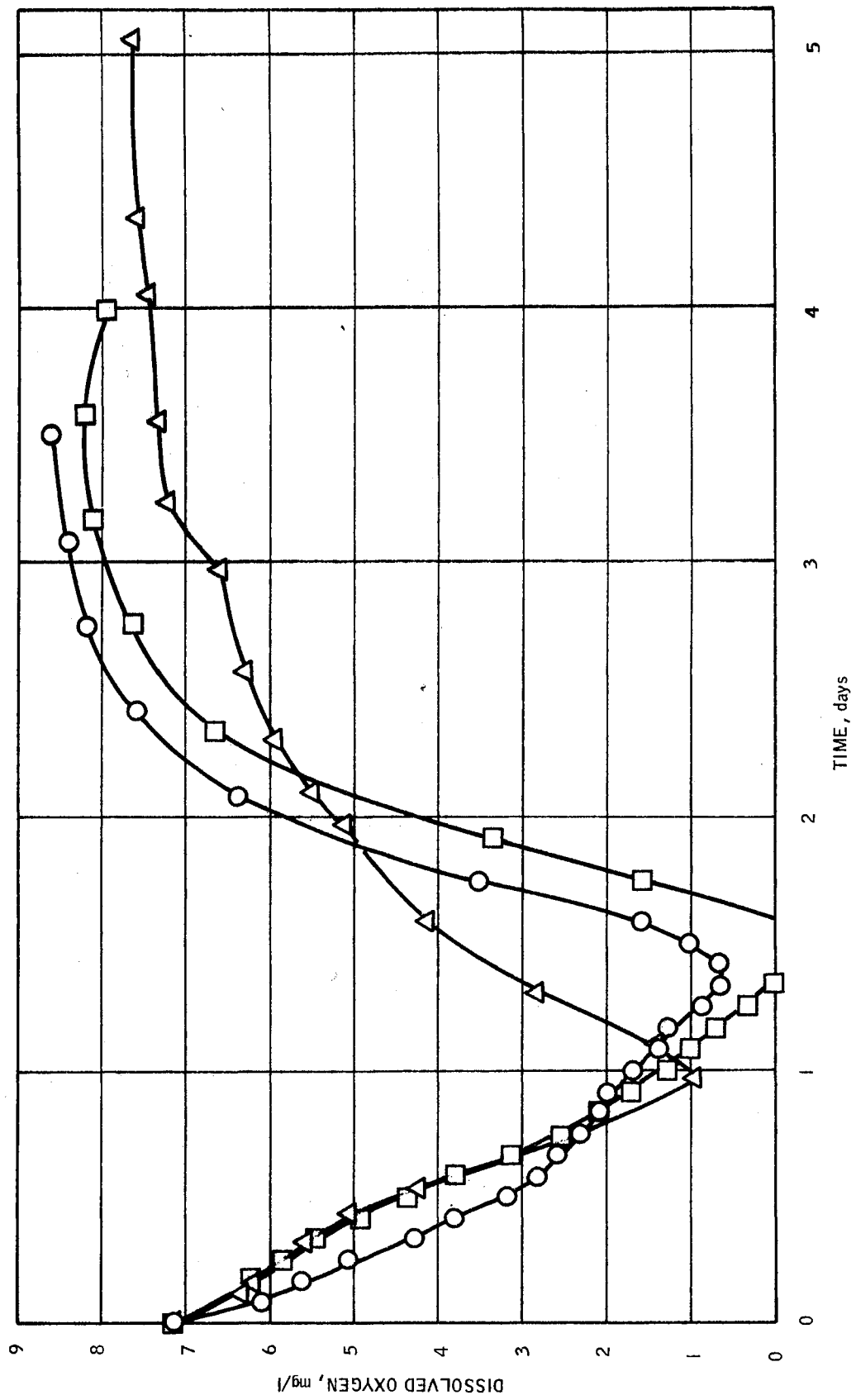
Figure 12. Sag Curves Predicted From O_2 Uptake Curves Compared to Actual River Sag Curve.

Experiment 25: 60 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.108 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.134 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.080 \text{ hr}^{-1}$, $21-22^\circ\text{C}$



(Figure 10). Oxygen uptake curves are shown in Figure 11; O_2 uptake in jar one ($K_2=0.108 \text{ hr}^{-1}$) was somewhat lower than in jar two ($K_2=0.134 \text{ hr}^{-1}$). From Figure 11 it can be estimated that O_2 uptake in the jars lagged that in the river by approximately 24 hours. In Figure 12, the actual river sag curve and the curves predicted from the jars are compared. These profiles do not coincide, and, in the main, the curve predicted using the data from jar one provides a more satisfactory estimate of the profile.

The glucose-glutamic acid combination was used as substrate in experiment 26. The seed was developed in the same manner as for experiment 25, but the sewage was aerated for 24 hours rather than 36 hours. A 1.5 percent seed was added to the jars in order to remove the lag. However, this amount of seed proved to be too high, and dissolved oxygen decreased to zero and did not recover for 12 hours. The usual 0.5 percent seed was added to the river, which reached a low point of 1.4 mg/l D_0 . It was impossible to evaluate any effect of time of pre-aeration of seed on lag time because the high amount of seed prevented any lag at all and caused the D_0 to fall to zero rather rapidly. In all three units there was a small second sag after partial recovery from the minimum D_0 . The higher O_2 uptake in the jars as compared to the river caused both predicted curves to fall below zero for several hours. Since the K_2 values in the jars and the river were essentially the same (0.090 and 0.115 versus 0.087 hr^{-1} , respectively), the greater O_2 uptake in the jars can be attributed to the greater amount of seed material. A check for substrate concentration (filtrate COD) carried over with the seed was not made in this experiment but previous determinations of carryover COD indicate that the higher O_2 uptake was not due

to extra substrate because of the greater amount of seed.

Experiment 27 was similar to experiment 25, except that 50 mg/l glucose was used instead of 60 mg/l. A 1.0 percent seed was used in the reactors, and 0.5 percent was employed in the river. This time, the seed was grown on glucose and preaerated for 20 hours before use. All three units showed a rather rapid decrease in DO, with essentially linear kinetics to the low point. Jar one, with a K_2 of 0.086 hr^{-1} , exhibited a low point of 0.80 mg/l DO, and jar two sagged to 1.40 mg/l DO (K_2 of 0.098 hr^{-1}). Sag curves for both jars had a rounded bottom, compared to the V-shaped bottom of the sag in the river. The K_2 of the river was 0.077 hr^{-1} , and the minimum DO was 0.50 mg/l. Oxygen uptake in both jars could be represented by a single line, and O_2 uptake for the river was similar to that in the jars. The predicted DO profiles were close to that observed in the river. The predicted curves yielded a minimum DO of zero, whereas 0.5 mg/l was recorded in the river.

Experiments 28 and 29 were conducted to compare effects of using 0.5 percent and 1.0 percent seed in the artificial river. In experiment 28, the jars received 0.5 and 1.0 percent seed, respectively, and the river, 1.0 percent. In experiment 29, the jars received 0.5 and 1.0 percent seed, whereas a 0.5 percent seed was employed in the river. The substrate was 50 mg/l glucose in both runs, and the K_2 values were practically the same for both the river and the jars for both runs (total range of $0.091 - 0.098 \text{ hr}^{-1}$). The seed was developed as in experiment 27. The 1.0 percent seed in the river caused a sag with a minimum DO of 0.15 mg/l. This concentration was recorded for five hours, which indicates that DO in all probability actually reached zero. When the river contained 0.5 percent seed, the minimum DO was

0.75 mg/l; however, the rate of depletion as well as the rate of O_2 uptake appeared to be slightly slower than when the 1.0 percent seed was used. This experiment was carried forward for only one day because the major aim was to determine whether the addition of a greater amount of seed to the river would greatly affect the course of O_2 depletion in the downward leg of the river profile. The results indicated that the additional seed did not have a very significant effect; however, in the jars, the difference in amount of seed did appear to make a difference in the rate of DO depletion. In fact, it appeared that the experiment was terminated before the low point of the DO sag was attained in the jar which received the 0.5 percent seed.

As a final experiment for a glucose system, run 30 is presented in Figures 13, 14, and 15. This experiment was essentially a repeat of experiment 29 (i.e., same K_2 values, seeding procedure, substrate, etc.). In jar two, which received the 1.0 percent seed, the DO approached zero and remained at this low level for nearly 16 hours, which negated its use for calculating an O_2 uptake curve. Consequently, the data for jar two are not shown. Figure 13 shows the observed DO profiles in the river and in jar one. Even though the seed concentration was the same in the jar and in the river, and even though the K_2 values were nearly the same, O_2 depletion in the river proceeded more rapidly.

The oxygen uptake curves are shown in Figure 14. In the simulated river there is evidence of a slight "plateau." However, the O_2 uptake curve calculated from the DO depletion in the jar shows no evidence of a "plateau." The O_2 uptake curves are rather similar; i.e., either could be considered as a rough approximation of the other, and, if an average curve were constructed, it might be usable within acceptable

Figure 13. Actual Sag Curves for Open Stirred Reactor and Artificial River.

Experiment 30: 50 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.098 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $19\text{-}21^\circ\text{C}$

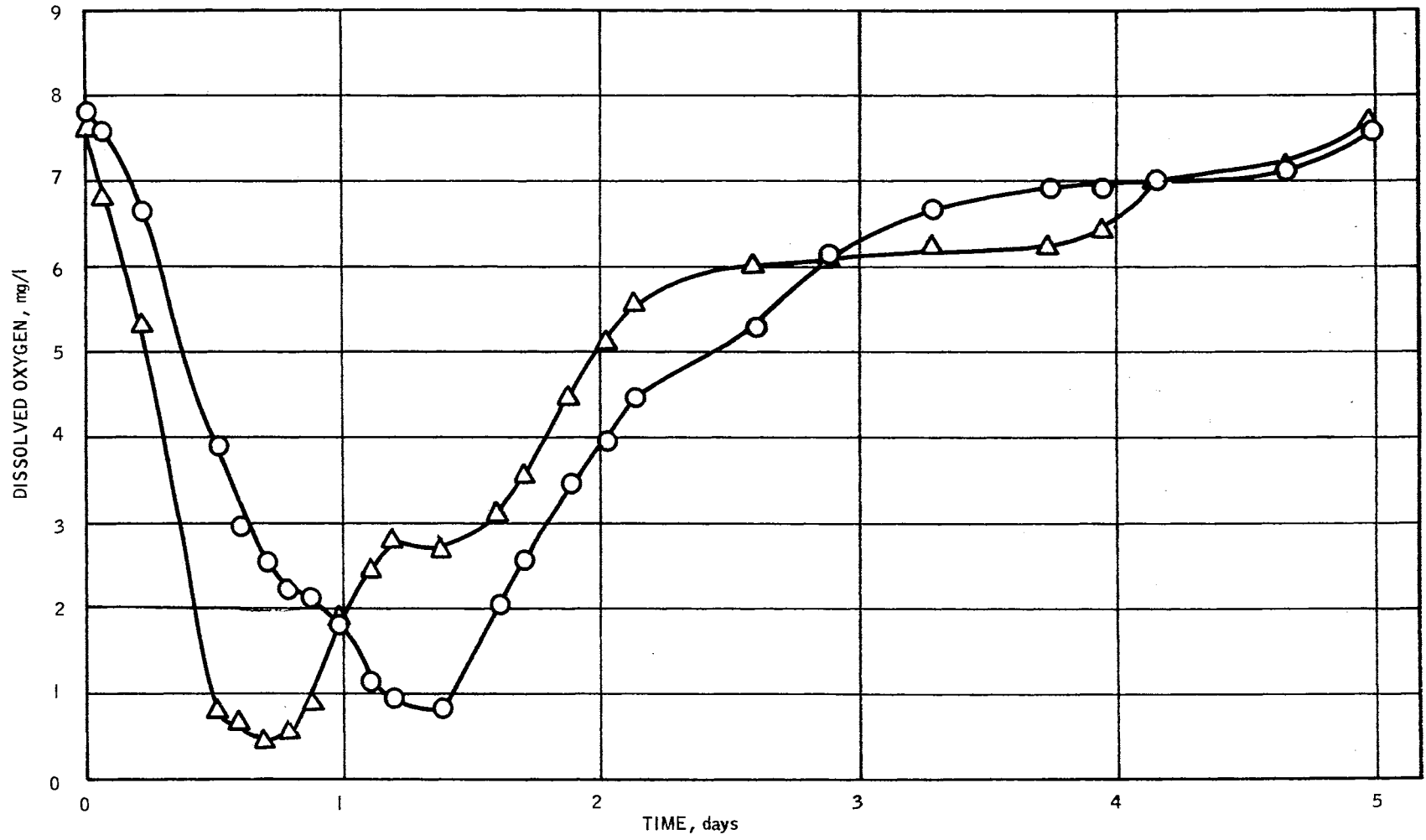


Figure 14. Oxygen Uptake Curves Calculated From Sag Curves in Figure 13.

Experiment 30: 50 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.098 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $19\text{-}21^\circ\text{C}$

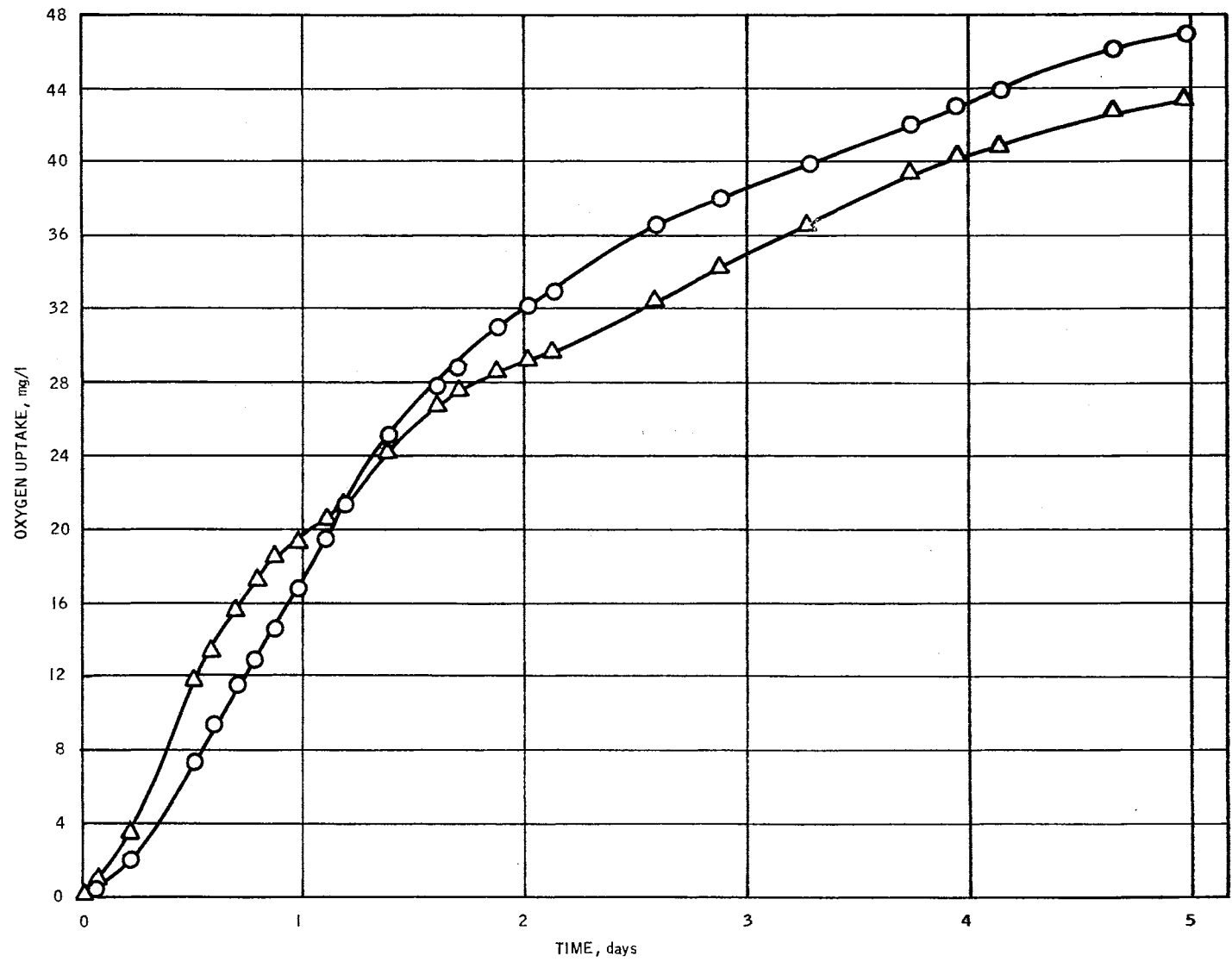
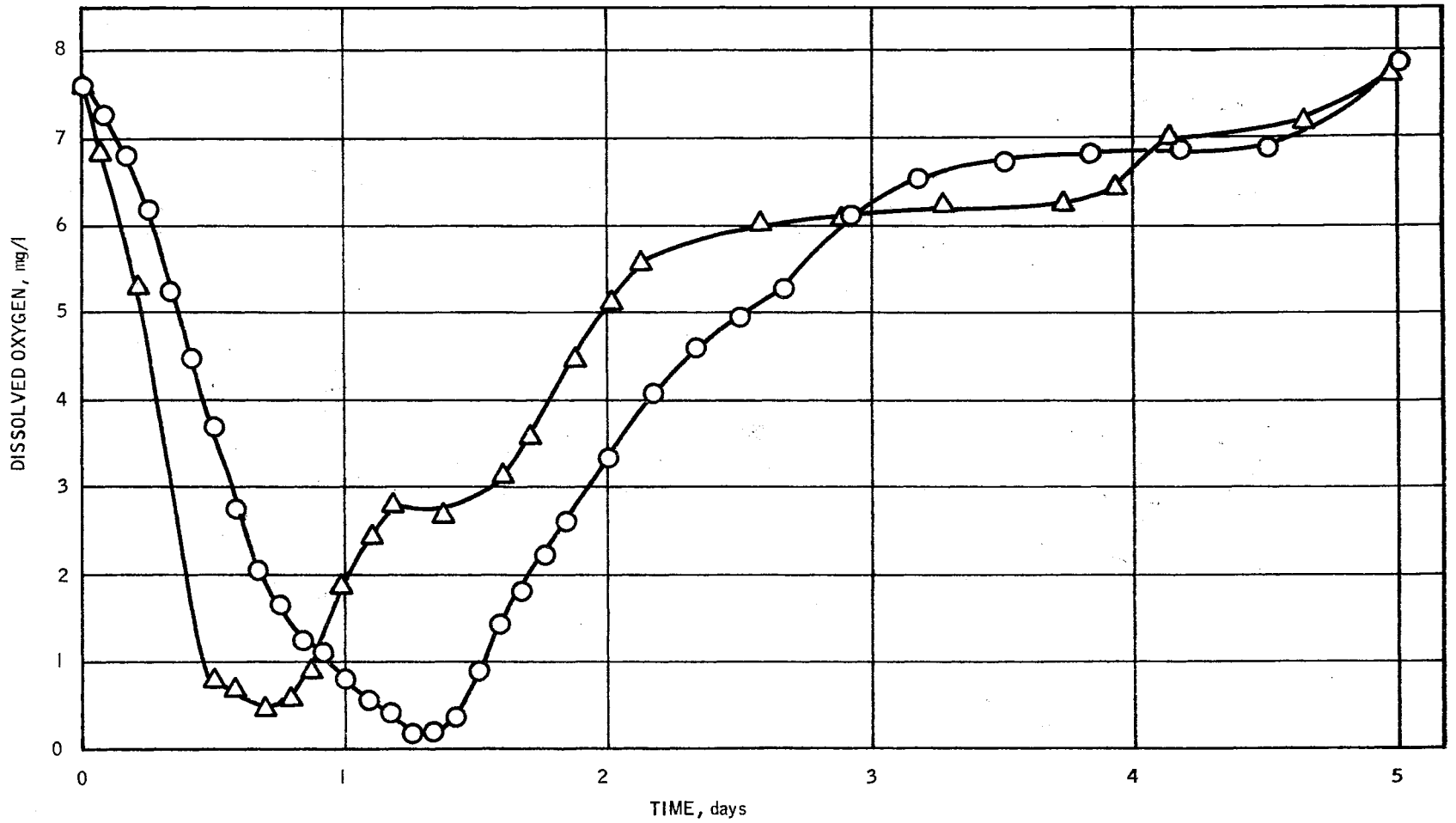


Figure 15. Sag Curve Predicted From O_2 Uptake Curve Compared to Actual River Sag Curve.

Experiment 30: 50 mg/l Glucose, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.098 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $19\text{-}21^\circ\text{C}$



limits for engineering prediction. It is noted that this O_2 uptake curve (jar one) is the one O_2 uptake curve obtained in all of the experimentations which approximates in any way the "monomolecular" form. However, even in this one case, there is some evidence of autocatalytic (S-shaped) O_2 uptake.

It is seen in Figure 15 that the DO profile predicted from the jar data yields approximately the same minimum DO as that observed in the river. The difference in "downstream" location of the low point of the sag is approximately 3/4 day, and in some instances this magnitude of difference could be an important factor. The major reason for displacement of the low point in the predicted sag is the slightly phasic nature of DO depletion in the downward leg of the sag in the jar (see Figure 13). Had this not occurred, the difference in location of the points of low DO would have been considerably smaller. The predicted curve shown in Figure 15 is much like the one for experiment 25 (see Figure 12) where the decreasing leg of the curve was phasic in the jar but not in the river.

Experiment 31 (Figures 16, 17, and 18) was the first in which an industrial waste was employed. Slaughterhouse waste was diluted to 45 mg/l COD in two open jar reactors and in the simulated stream. The seed population was obtained by inoculating fresh sewage into a sample of the waste plus mineral salts and aerating for 24 hours. Since previous experience indicated that there might be a lag period in the jars when the same seed concentration was employed in the jars and the simulated river, the seed concentration in the open jar reactors was increased. However, it can be seen from Figure 16 that the 1.0 percent seed for the jars was too high in comparison to the river, which had a

Figure 16. Actual Sag Curves for Open Stirred Reactors and Artificial River.

Experiment 3I: 45 mg/l Slaughterhouse Waste

○ = Jar 1, $K_2 = 0.081 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

□ = Jar 2, $K_2 = 0.102 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

△ = River, $K_2 = 0.059 \text{ hr}^{-1}$, 0.50 percent Acclimated Cells, $18-19^\circ\text{C}$

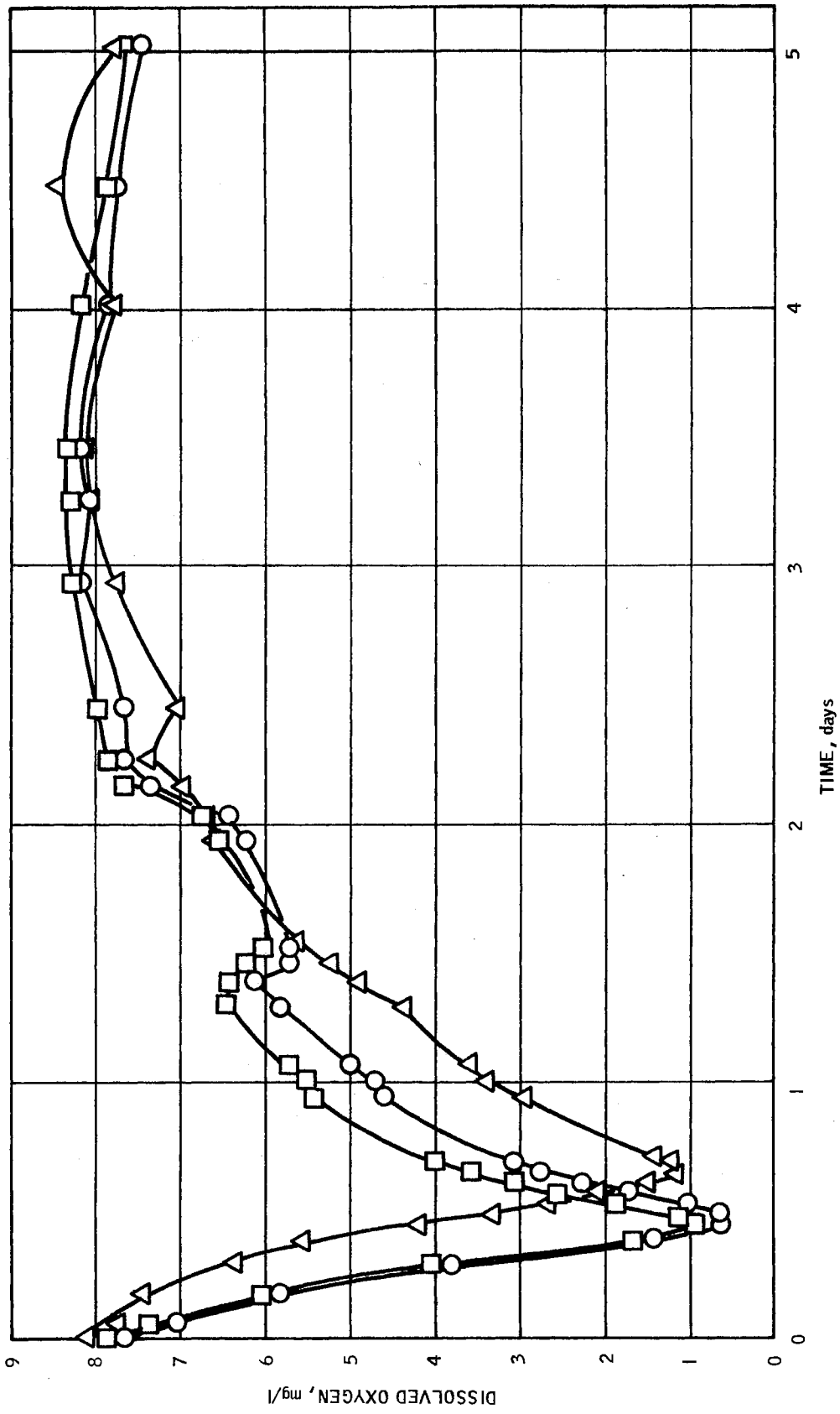


Figure 17. Oxygen Uptake Curves Calculated from Sag Curves in Figure 16.

Experiment 31: 45 mg/l Slaughterhouse Waste

○ = Jar 1, $K_2 = 0.081 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

□ = Jar 2, $K_2 = 0.102 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

△ = River, $K_2 = 0.059 \text{ hr}^{-2}$, 0.50 percent Acclimated Cells, $18-19^\circ\text{C}$

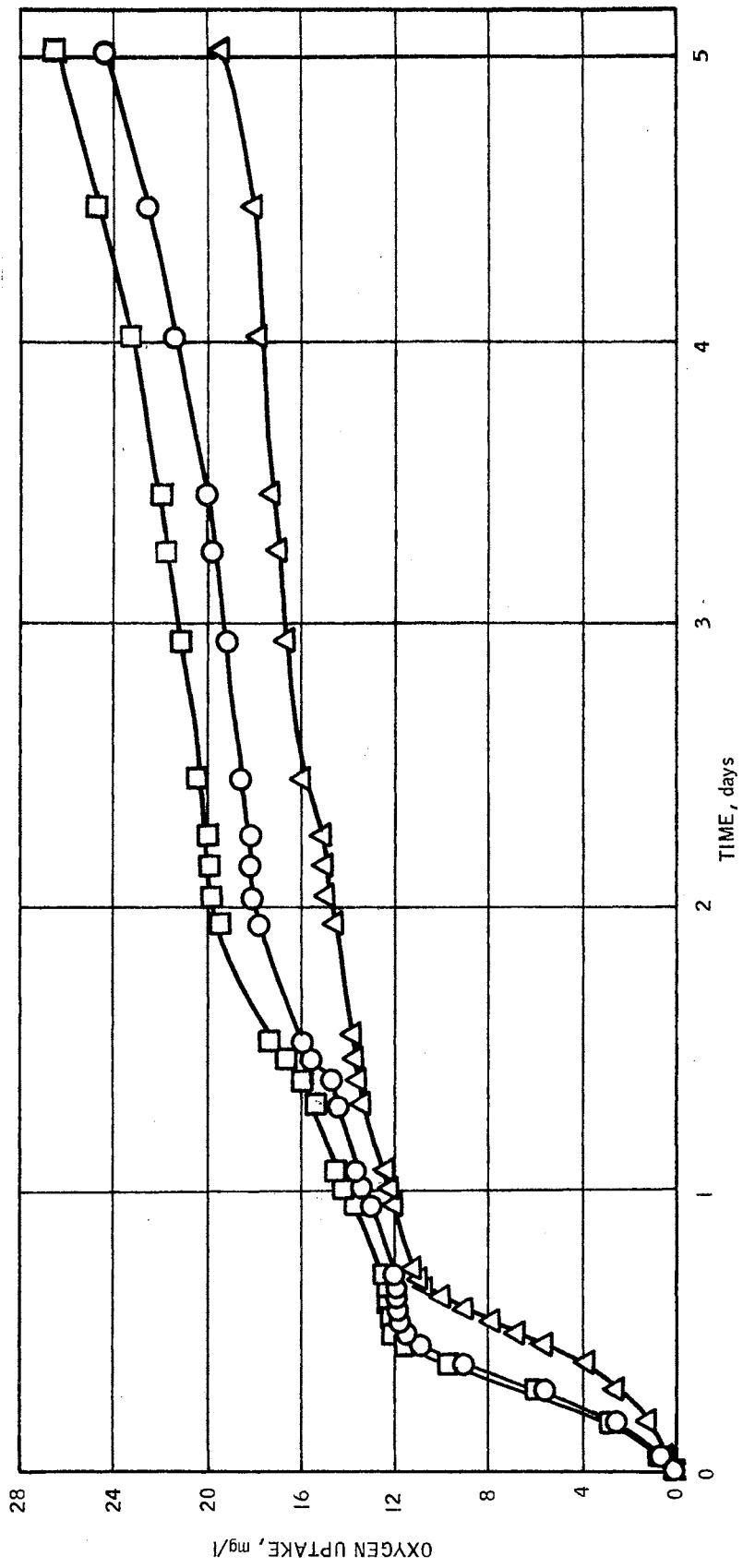


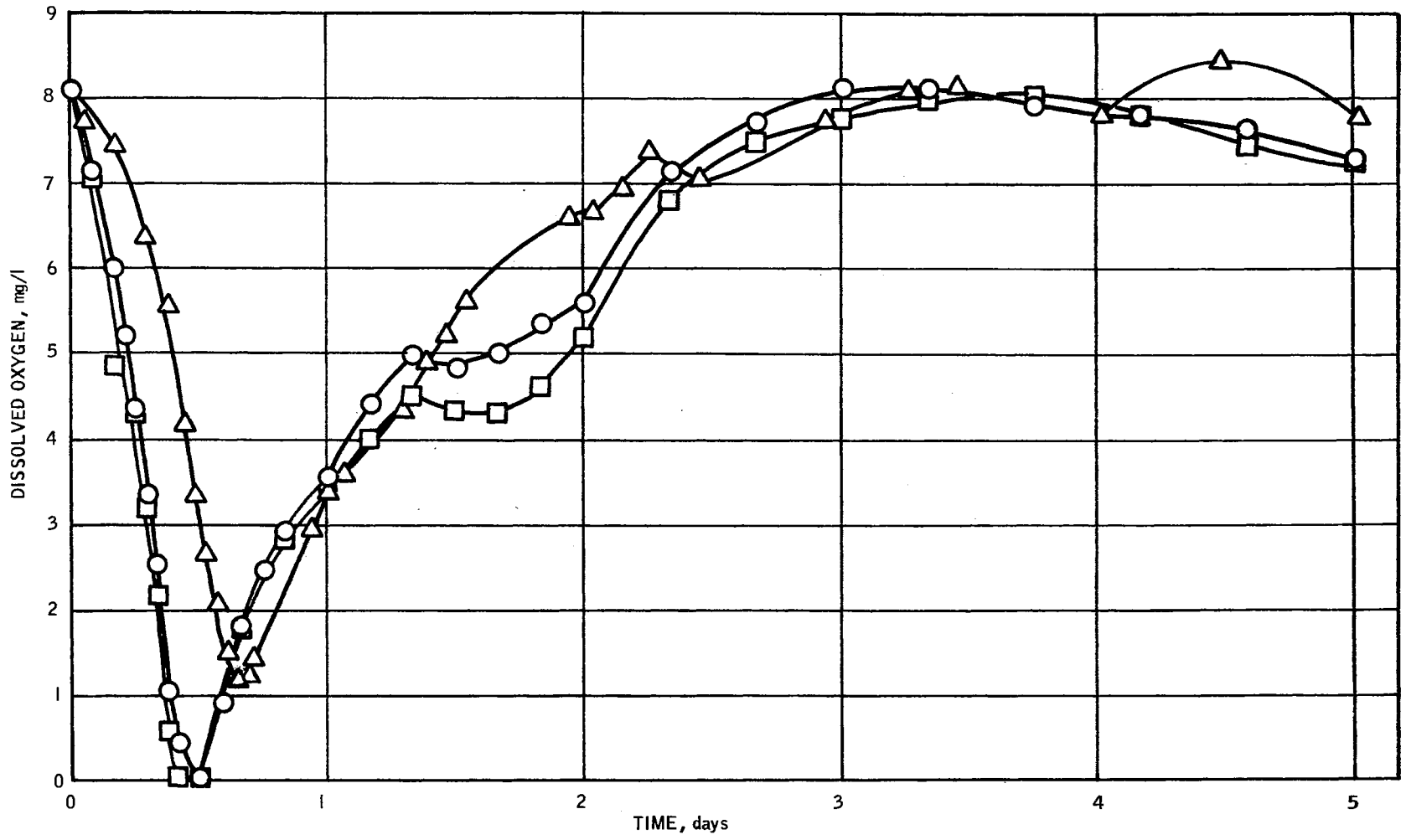
Figure 18. Sag Curves Predicted From O_2 Uptake Curves Compared to Actual River Sag Curve.

Experiment 31: 45 mg/l Slaughterhouse Waste

○ = Jar 1, $K_2 = 0.081 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

□ = Jar 2, $K_2 = 0.102 \text{ hr}^{-1}$, 1.0 percent Acclimated Cells, 21°C

△ = River, $K_2 = 0.059 \text{ hr}^{-1}$, 0.50 percent Acclimated Cells, $18-19^\circ\text{C}$



0.5 percent seed, and the DO depletion in the jars proceeded more rapidly than in the river, even though the reaeration rate in the river was considerably lower than in the jars. The calculated O_2 uptake curves are shown in Figure 17. Similar curves were obtained, and it can be seen that the O_2 uptake curve in the river proceeded somewhat more slowly to the "plateau" area and the overall or total O_2 uptake was lower than for the open jar reactors. The lower rate and total amount of O_2 utilization reflect the combined effects of lower seed population and lower reaeration rate. Integration of the O_2 uptake curves obtained in the jars with the reaeration coefficient of the river resulted in a conservative prediction of the DO profile in the river, as shown in Figure 18. In both predicted curves, the DO decreased to zero and recovered rapidly, and the bottom of the sag occurred four hours before the time actually observed in the simulated river.

During the experiment, COD samples were taken at the point of minimum DO in each unit. The average value for all three units was 17 mg/l COD (filtrate). Filtrate COD was also determined at the end of the 5-day experiment, and the same value was obtained. Thus it may be surmised that the available carbon source in the waste had been removed at the time of the "plateau."

Digester liquor from a hardboard manufacturing operation was used in experiment 32 (Figures 19, 20, 21). The initial COD in the two jars and the artificial channel was 48 mg/l. Fresh sewage was aerated with the waste (plus buffer salts medium) for 43 hours and added to the units to yield a concentration of 0.5 percent initial seed population.

In this experiment, similar values for reaeration constant in the open jars and the river were maintained by design and, as can be seen

Figure 19. Actual Sag Curves for Open Stirred Reactors and Artificial River.

Experiment 32: 48 mg/l Hardboard Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.087 \text{ hr}^{-1}$, 21°C

□ = Jar 2, $K_2 = 0.108 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $20\text{-}22^\circ\text{C}$

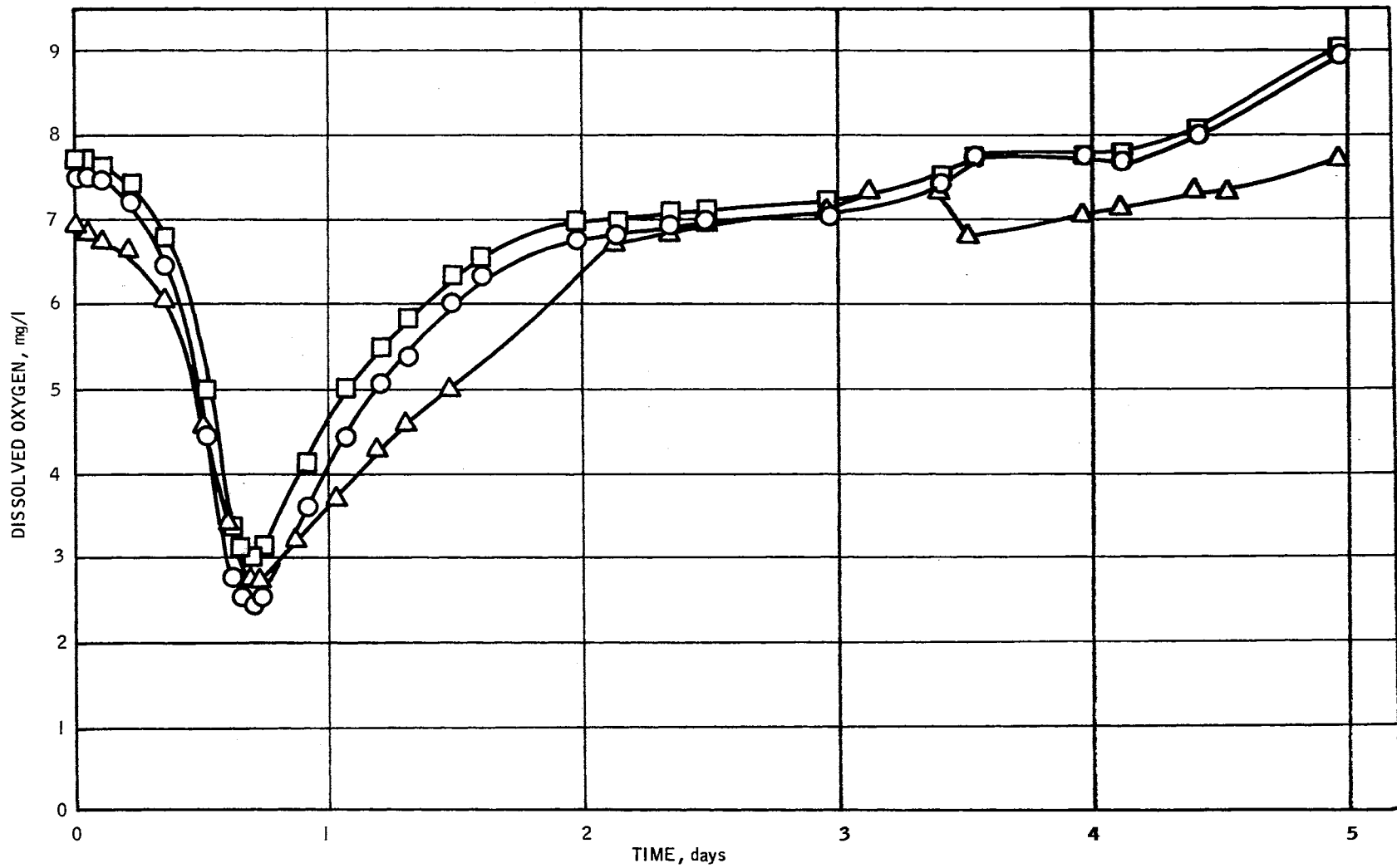


Figure 20. Oxygen Uptake Curves Calculated From Sag Curves in Figure 19.

Experiment 32: 48 mg/l Hardboard Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.087 \text{ hr}^{-1}$, 21°C

□ = Jar 2, $K_2 = 0.108 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $20\text{-}22^\circ\text{C}$

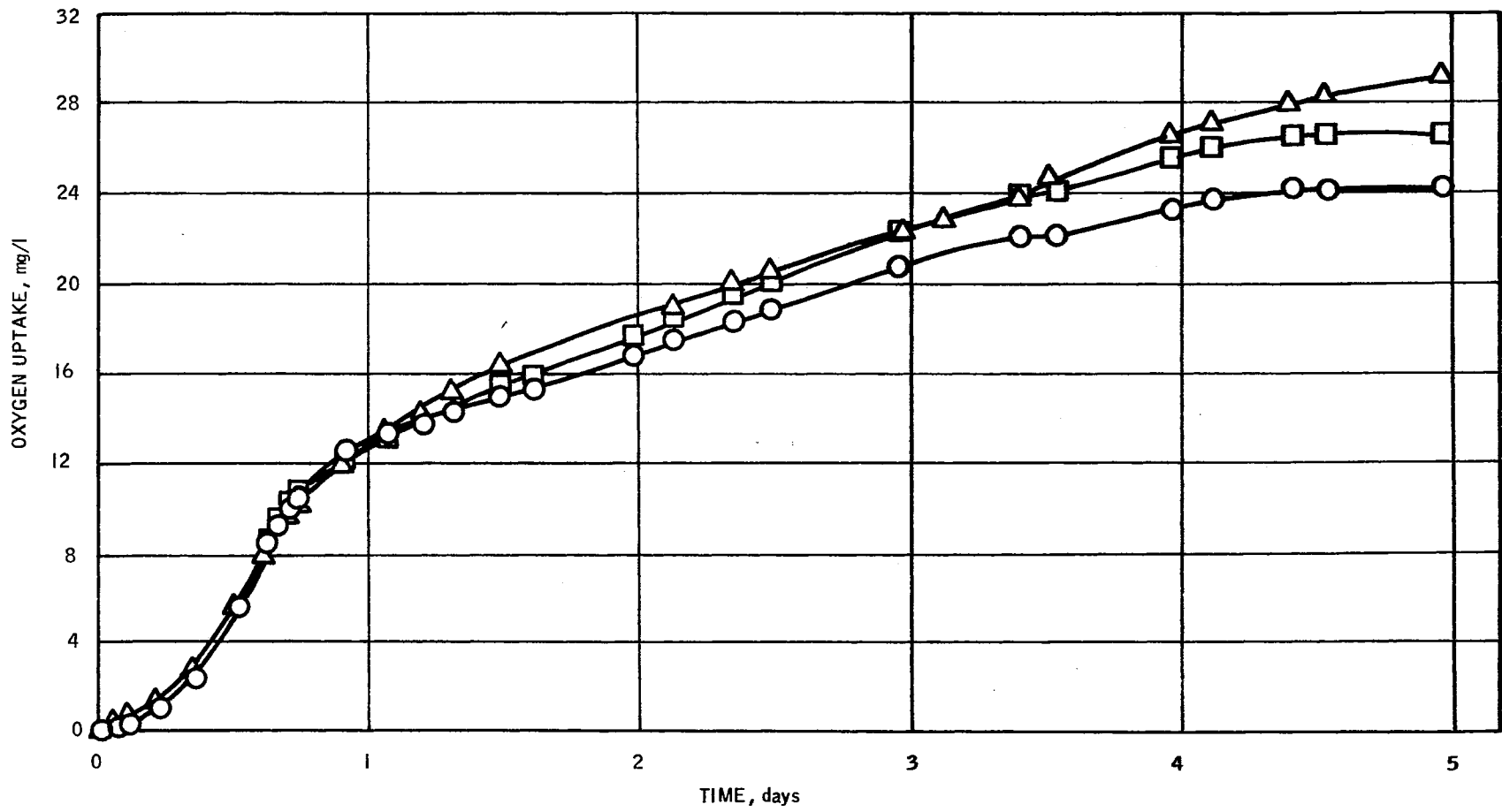


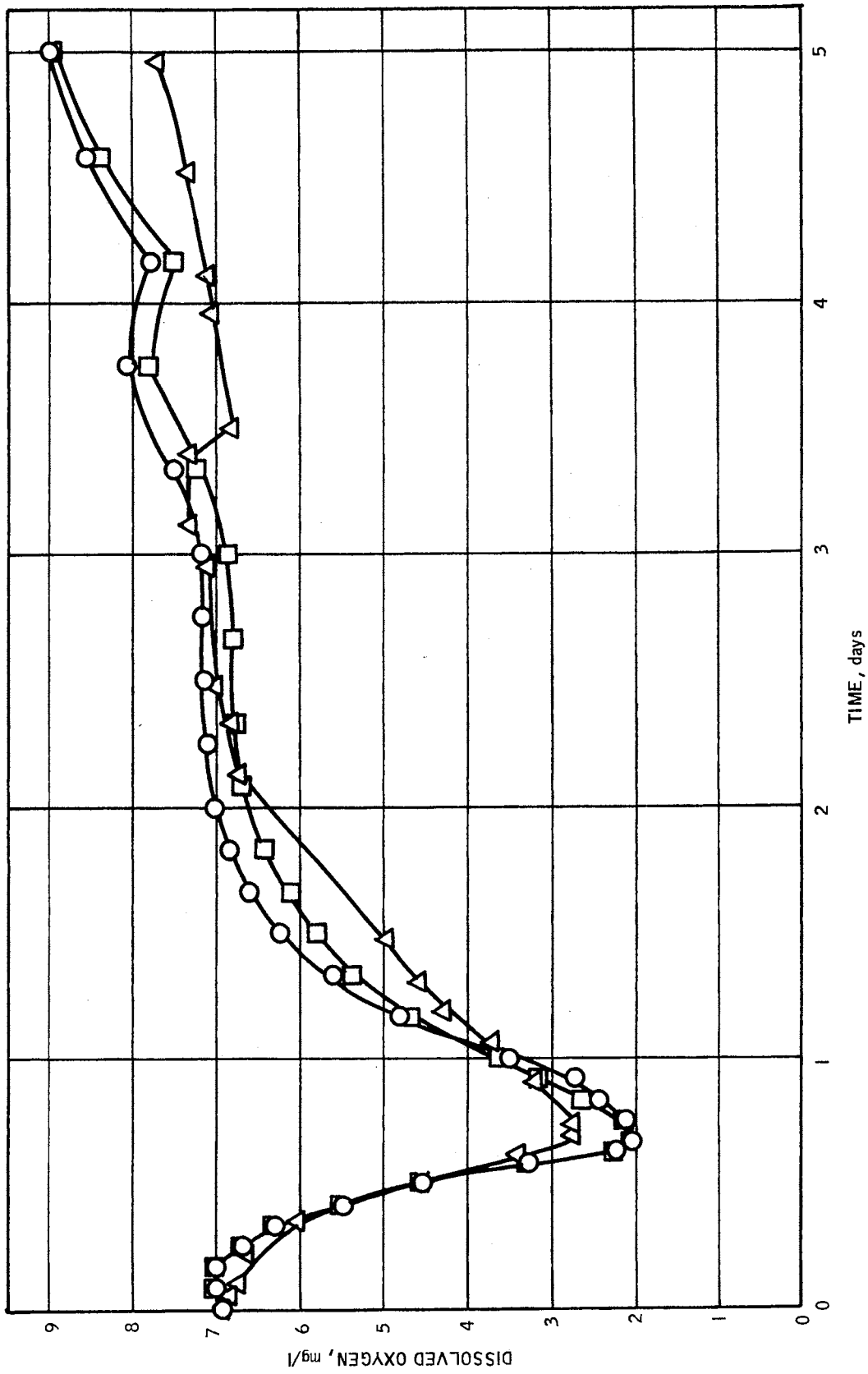
Figure 21. Sag Curves Predicted From O_2 Uptake Curves Compared to Actual River Sag Curve.

Experiment 32: 48 mg/l Hardboard Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.087 \text{ hr}^{-1}$, 21°C

□ = Jar 2, $K_2 = 0.108 \text{ hr}^{-1}$, 21°C

△ = River, $K_2 = 0.091 \text{ hr}^{-1}$, $20\text{-}22^\circ\text{C}$



from Figure 19, the DO profiles are very similar. The O_2 uptake curves calculated from these results are shown in Figure 20. They lie very close to each other, especially in the region of rapid O_2 utilization, which is the most significant portion of the curve from the standpoint of prediction of critical deficit. The curves did not exhibit a definite "plateau;" however, they were typical S-shaped curves characteristic of a system in which microbial growth is the dominant "reaction;" i.e., they could in no way be construed as following a "monomolecular" type kinetic order.

Figure 21 shows the plot of the two predicted curves compared to the actual curve observed for the river. COD analyses taken at the low point in the sag and at the end of the experiment indicated that the available substrate had been removed at the point of minimum DO.

Experiment 33 (Figures 22, 23, 24) was conducted using digester blow-down liquor from a kraft pulping operation as substrate. This liquor is extremely high in organic content and contains excess cooking chemicals, which are later subjected to recovery processes which also drastically reduce the organic content. An acclimated microbial population for use as seed was developed from an initial seed of municipal sewage. Cells were transferred daily or every other day for about two weeks into fresh medium containing the black liquor, and a well aerated sample was employed as source of acclimated seed for the experiment.

The initial COD in the jars and simulated river was 70 mg/l. However, a considerable portion of the COD of this waste is not metabolically available and the O_2 depletion was not large, as seen in Figure 22. The initial decrease in dissolved oxygen of approximately one mg/l is most probably due to an initial chemical demand of reduced sulfur

Figure 22. Actual Sag Curves of Open Stirred Reactors and Artificial River.

Experiment 33: 70 mg/l Kraft Liquor, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.094 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.122 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.069 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$

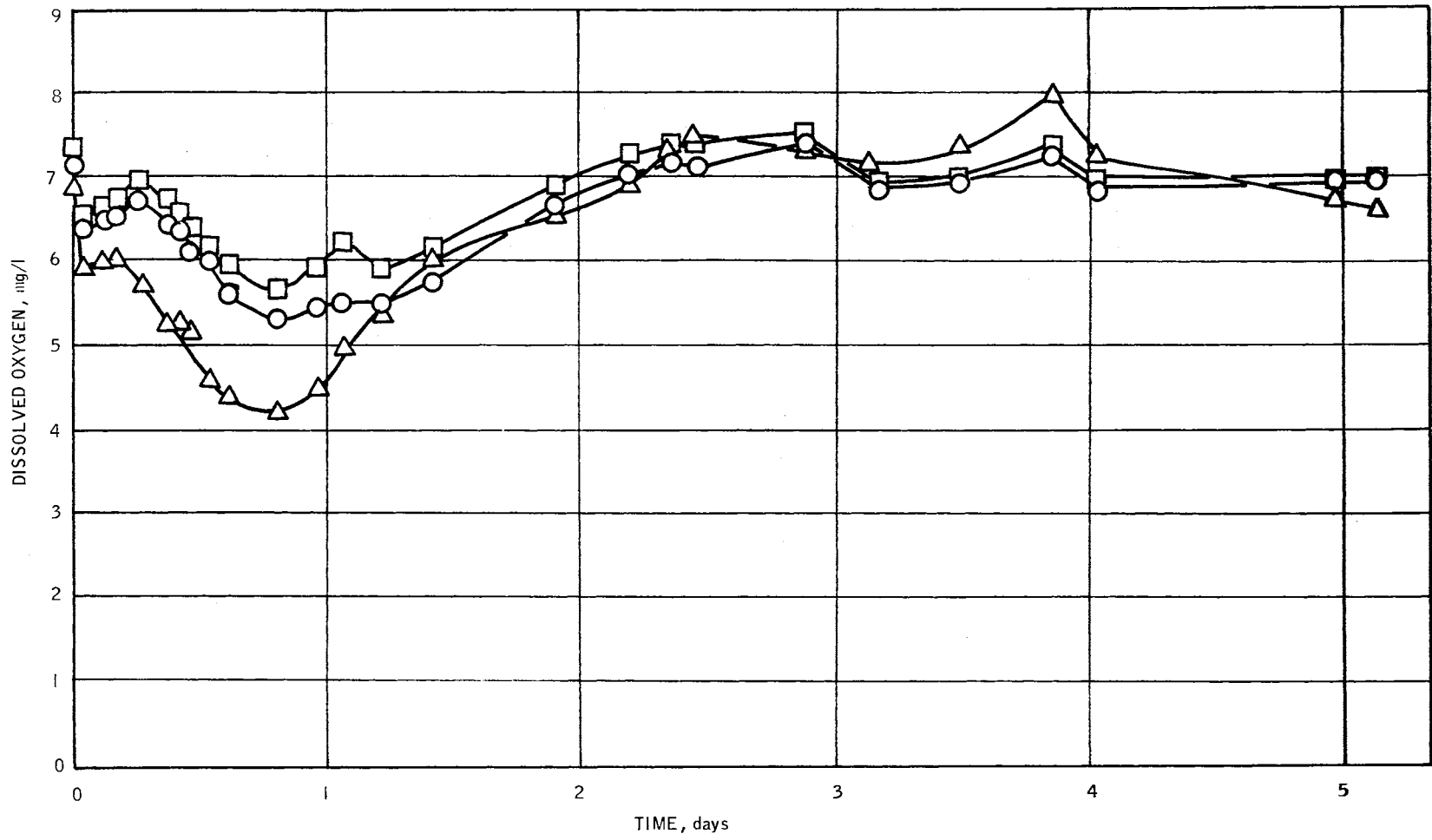


Figure 23. Oxygen Uptake Curves Calculated From Sag Curves in Figure 22.

Experiment 33: 70 mg/l Kraft Liquor, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.094 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.122 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.069 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$

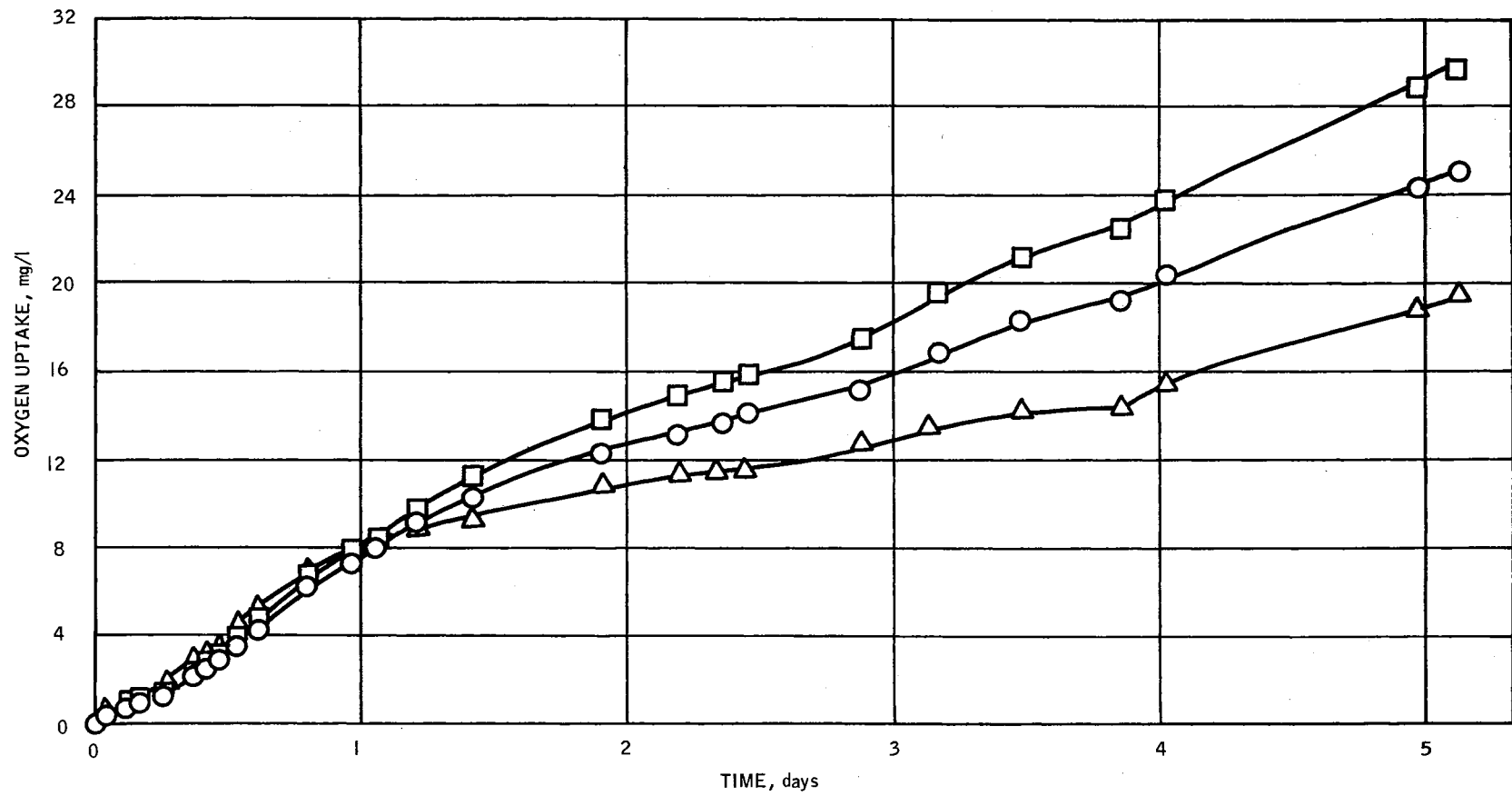


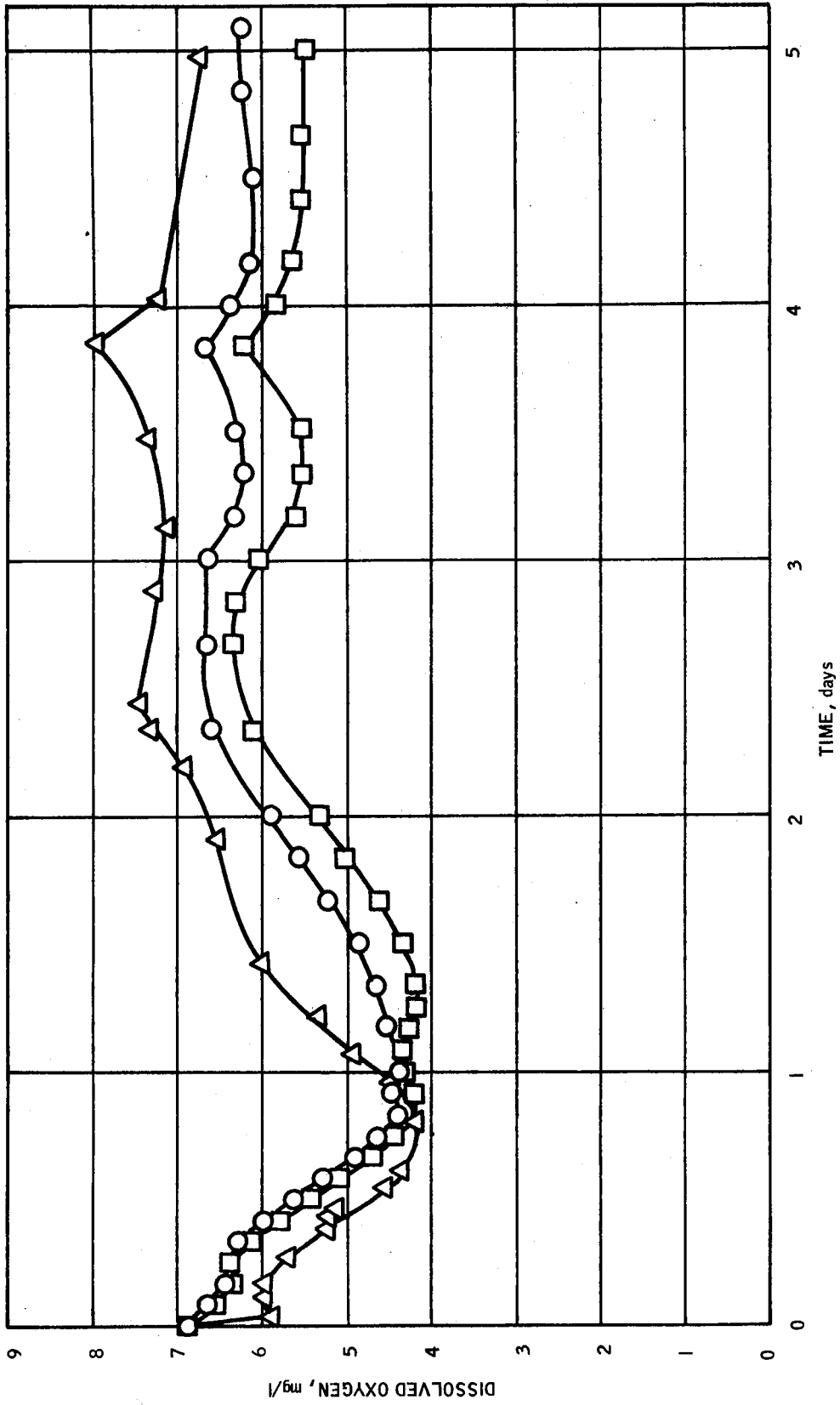
Figure 24. Sag Curves Predicted From O_2 Uptake Curves Compared to Actual River Sag Curve.

Experiment 33: 70 mg/l Kraft Liquor, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.094 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.122 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.069 \text{ hr}^{-1}$, $21\text{-}22^\circ\text{C}$



compounds in the black liquor. The resultant oxygen uptake curves are shown in Figure 23. During the first day (i.e., the time required to reach the low point in the sag curve), the O_2 uptake curves are practically the same. However, following this time, the rate of O_2 uptake in the river slowed down more rapidly than in the open jars. As has been noted in other experiments, lower K_2 values tend to give lower overall rates of O_2 uptake.

In Figure 24, the DO profiles predicted from the O_2 uptake curves in the jars are compared to the profile observed in the river. The predicted curves are rather close to the actual curve with respect to minimum DO and time to attain maximum deficit, but because of the greater O_2 uptake in the jars after the first day (Figure 23), the predicted recovery leg of the profile lags the actual profile.

Experiment 35 (Figures 25, 26, 27) employed a carbon source consisting of a combination of slaughterhouse and hardboard pulp wastes. The hardboard waste was from the same waste sample used in experiment 32, and it retained its previous characteristics during the 6-week cold storage period between experiments. A fresh sample of the slaughterhouse waste was obtained. The COD concentration of this sample was 38,000 mg/l (compared to 16,250 mg/l for the previous sample).

The general procedure for this run was the same as described for experiment 32. A seed was developed by acclimating an initial seed of fresh sewage to a mixture of slaughterhouse and hardboard wastes. After the reaeration stage of the experiment, the two jars and the river were polluted with 55 mg/l total COD of the two wastes (24 mg/l COD of slaughterhouse waste and 31 mg/l COD of hardboard waste) and 0.5 percent acclimated seed. Mineral buffer salts, including nitrogen source, were

Figure 25. Actual Sag Curves of Open Stirred Reactors and Artificial River.

Experiment 35: 24 mg/l Slaughterhouse Waste Plus 31 mg/l Hardboard Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.170 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.120 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.090 \text{ hr}^{-1}$, $20\text{-}23^\circ\text{C}$

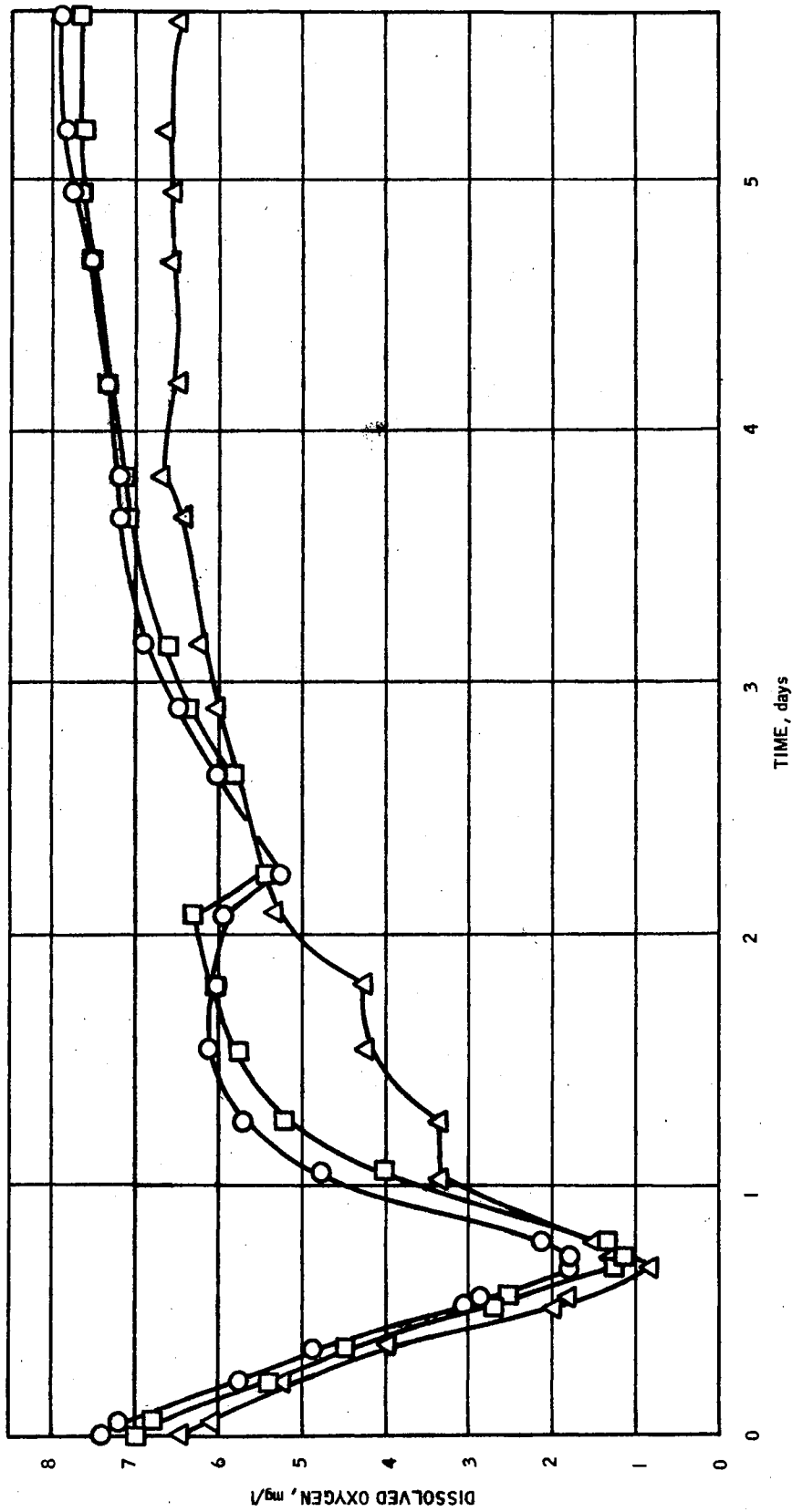


Figure 26. Oxygen Uptake Curves Calculated From Sag Curves in Figure 25.

Experiment 35: 24 mg/l Slaughterhouse Waste Plus 31 mg/l Hardboard
Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.170 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.120 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.090 \text{ hr}^{-1}$, $20\text{-}23^\circ\text{C}$

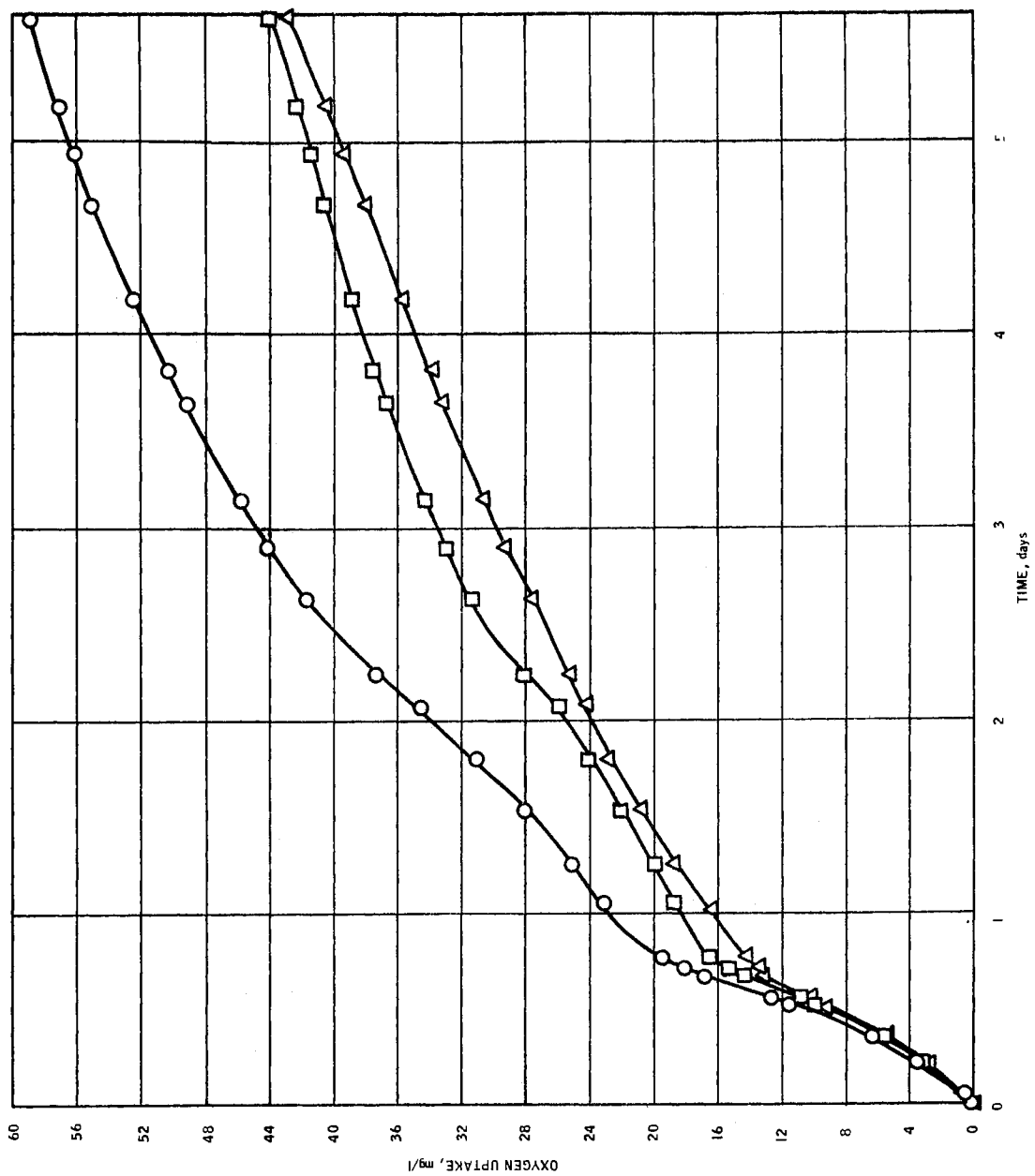


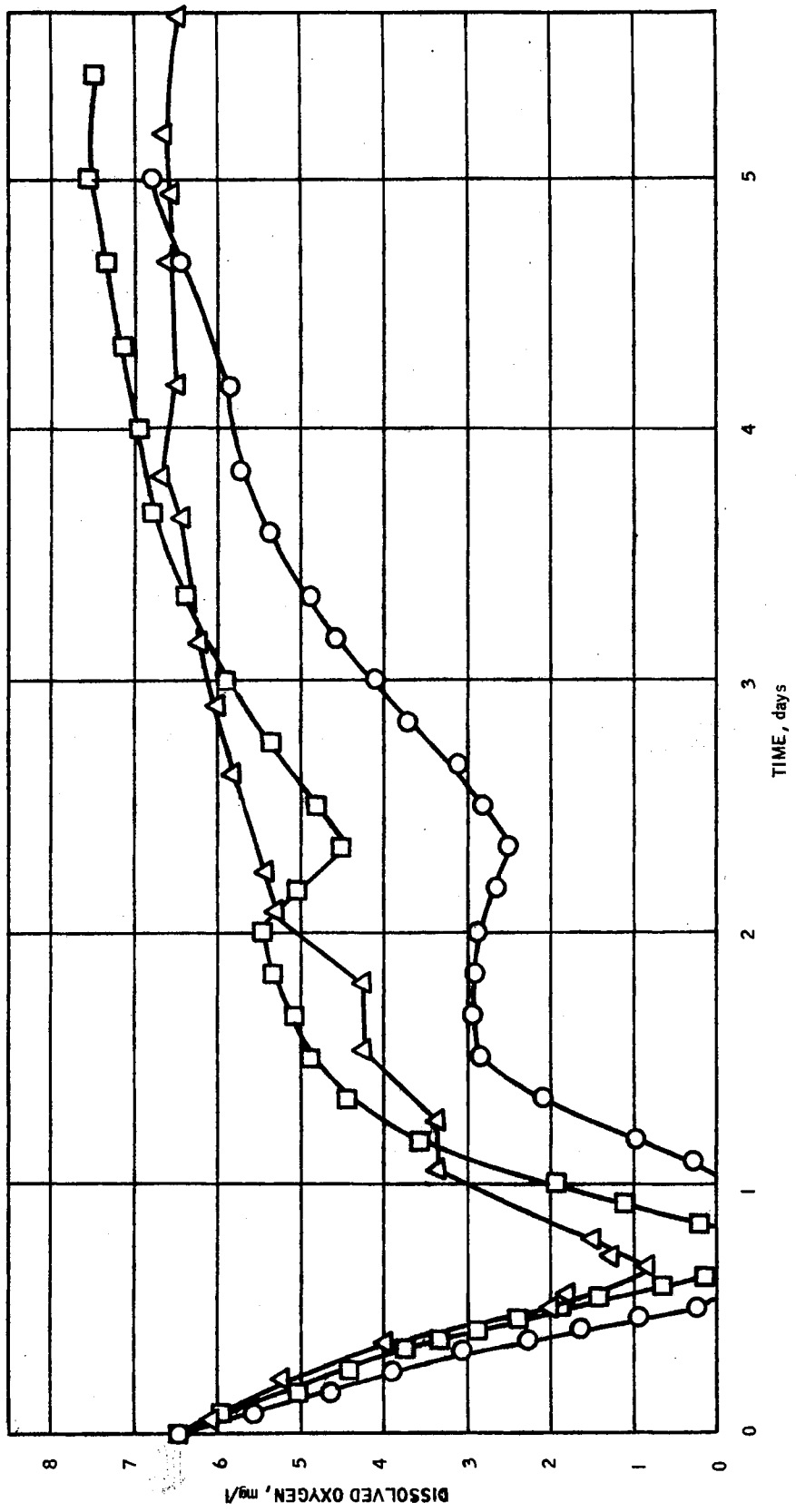
Figure 27. Sag Curves Predicted From O_2 Uptake Curves Compared to Actual River Sag Curve.

Experiment 35: 24 mg/l Slaughterhouse Waste Plus 31 mg/l Hardboard Waste, 0.50 percent Acclimated Cells

○ = Jar 1, $K_2 = 0.170 \text{ hr}^{-1}$, 22°C

□ = Jar 2, $K_2 = 0.120 \text{ hr}^{-1}$, 22°C

△ = River, $K_2 = 0.090 \text{ hr}^{-1}$, $20\text{-}23^\circ\text{C}$



added in proper proportion for a 50 mg/l total COD concentration (i.e., although the slaughterhouse waste contained organic nitrogen, inorganic nitrogen was added to ensure that nitrogen concentration was not a limiting factor).

The reaeration rate constants for jars one and two were 0.17 and 0.12 hr^{-1} , respectively, and in the river K_2 was 0.09 hr^{-1} . The observed sag curves are shown in Figure 25. All three curves were very much alike with the exception of the "step" recovery phase which occurred in the river.

The O_2 uptake in jar one ($K_2 = 0.17 \text{ hr}^{-1}$) was significantly greater than in either jar two or the river (Figure 26). The curve obtained in jar one could not be used to predict, with an acceptable degree of accuracy, the sag curve for the river. It is possible that somewhat more substrate than was intended was inadvertently added to jar one. The initial COD of the stock "pollutant" was 55 mg/l; however, it can be seen that 59 mg/l O_2 was utilized in jar one in 5 2/3 days. All units received waste from the same stock vessel; thus a pipeting error may have occurred when adding waste to jar one.

The predicted sag curves and the actual river sag are compared in Figure 27. The DO profile predicted from O_2 uptake in jar two "sagged" below zero DO. The DO could be calculated as minus 0.54 mg/l, or a total difference from the actual minimum DO of 1.34 mg/l. The decreasing leg, the time of minimum DO, and the general characteristics of the recovery phase were comparable for both profiles.

To compare the method of predicting a sag curve reported in this thesis with the standard Streeter-Phelps procedure, a BOD bottle experiment was conducted using the same combination of slaughterhouse and

hardboard wastes. The same stock quantities of waste were used, but in order that DO in the bottles not be exhausted, the combined waste was diluted five-fold. A 0.5 percent acclimated seed was added. The dilution water was made by adding minimal salts, nitrogen, and buffer (Table I) in proportional amounts for a total COD concentration of 10 mg/l. Initial COD determination was made on the contents of the BOD bottles, and a value of 18 mg/l was recorded. This value was considered as only an approximate check on the several dilutions from the concentrated stock.

The data points for the BOD bottle curve in Figure 28 were obtained by taking samples, titrating, and calculating the BOD in mg/l with a seed blank correction according to Standard Methods (37). The values recorded for each sample were multiplied by the dilution factor (i.e., $D_0 \times 5$) in order to compare the BOD curve from the bottle with that generated in the artificial river. The dotted line portion is treated as a lag phase when using the standard dilution technique and first order decreasing rate kinetics of BOD exertion assumed in the Streeter-Phelps equation; therefore, the "lag" was eliminated in making calculations. Also plotted is the O_2 uptake curve from jar two of experiment 35, which was used to predict the sag curve for the river in that run. It may be seen that the higher substrate concentration and possibly the degree of mixing was reflected in a more rapid rate of O_2 uptake during the first day.

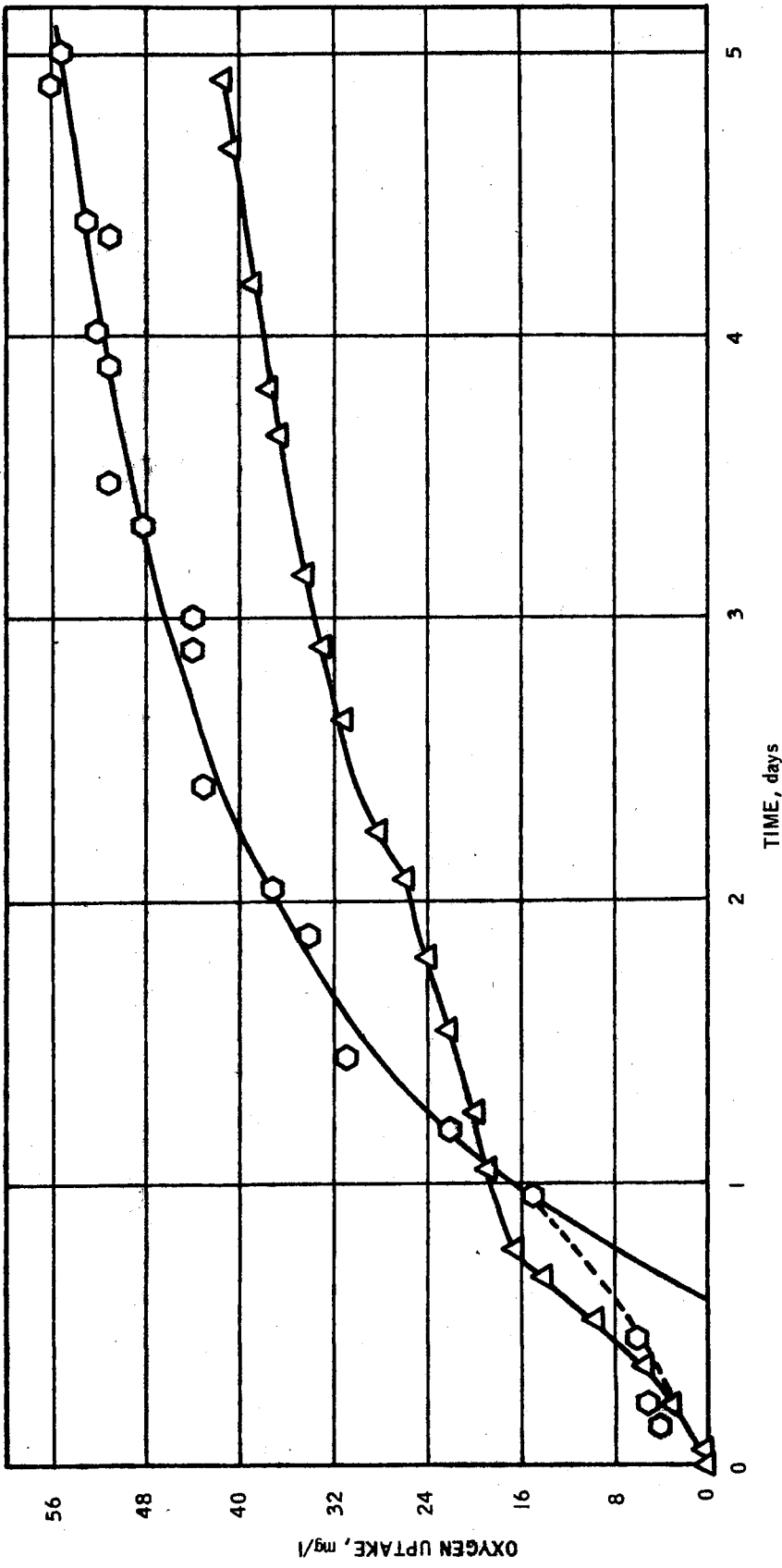
Calculation of the "BOD constants," k_1 and L_a , were made using the α method described by Gaudy, et al. (39). L_a was found to be 58.6 mg/l, and k_1 was 0.224 day^{-1} . These values, along with the k_2 of 0.938 day^{-1} for the river and 8.8 mg/l saturation DO in the river (from experiment

Figure 28. Oxygen Uptake Curve From BOD Bottle Compared With Curve From Figure 26.

Experiment 36: 18 mg/l Combined Slaughterhouse and Hardboard Waste,
0.50 percent Acclimated Cells

○ = Standard BOD Bottle Data, 22°C

△ = Jar 2 of Experiment 35, $K_2 = 0.120 \text{ hr}^{-1}$, 22°C



35) were employed to calculate the sag according to the Streeter-Phelps equation. Figure 29 shows the resulting DO profile (octagonal markers). The minimum DO was computed as minus 0.6 mg/l at 0.79 days.

For comparison, the same O_2 uptake curve was also employed to calculate a DO profile using the mathematical integration method employed in this thesis (triangles). The dotted line portion of the bottle curve was used in this case, i.e., there was no need to eliminate a "lag." The minimum DO was found to be minus 1.60 mg/l at 30 hours.

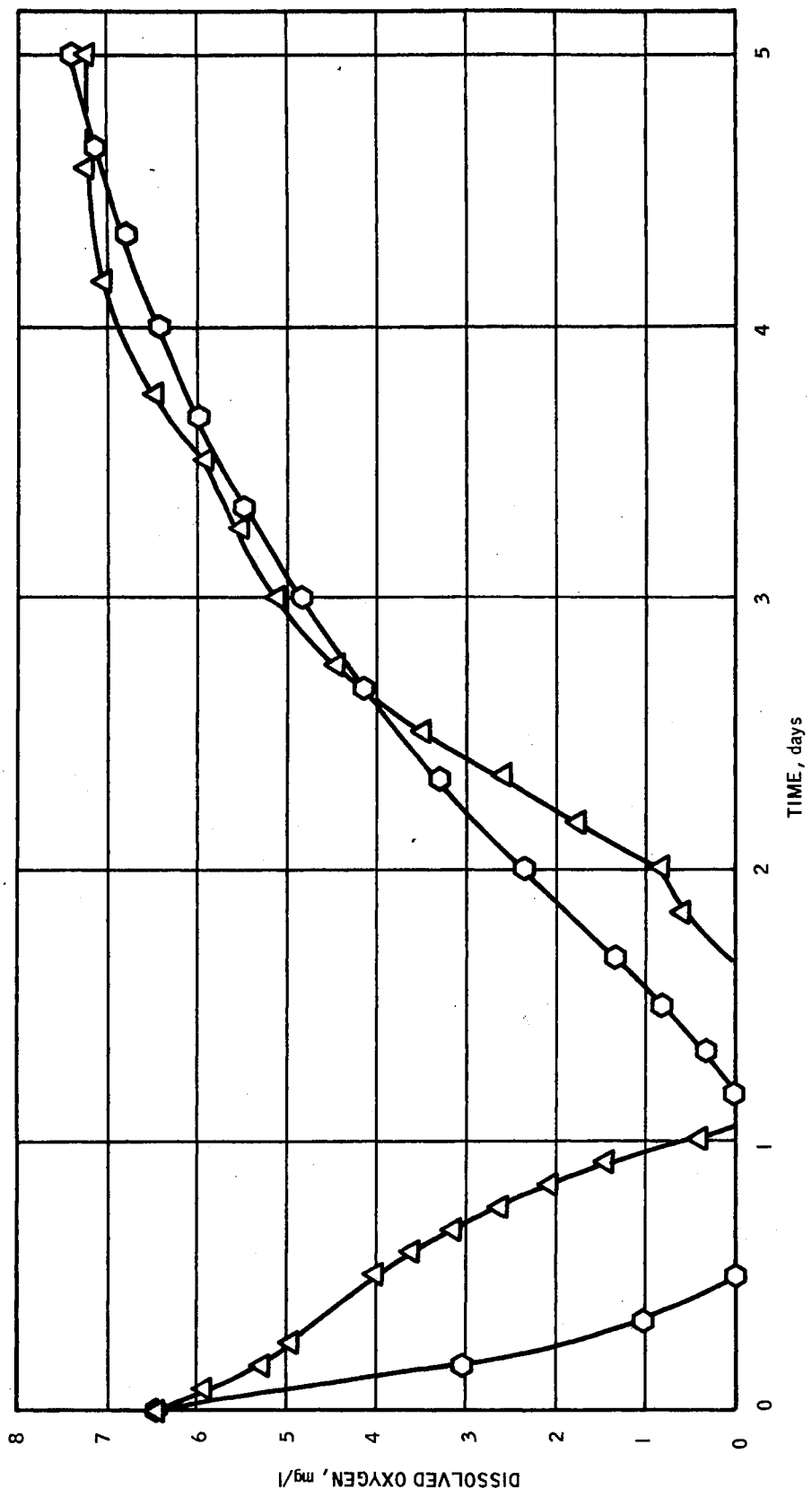
These two predicted curves may be compared to the DO profile predicted from the O_2 uptake curve of jar two in Figure 27. In the previous experiment, it is recalled that the dilution factor in the jar and the river were the same. The nature of the organic matter was the same in both experiments, and an acclimated seed was employed (although not identical seed samples). Thus, all three predicted profiles may be compared to the actual DO profile for the river shown in Figure 27. It can be seen that the open jar technique provides a predicted profile more in accord with the one observed in the river.

Figure 29. Two Predicted Sag Curves Calculated From Standard BOD Bottle Oxygen Uptake Curve in Figure 28.

Experiment 36: 18 mg/l Combined Slaughterhouse and Hardboard Waste,
0.50 percent Acclimated Cells

○ = Sag Curve Predicted by Streeter-Phelps Equation

△ = Sag Curve Predicted by Numerical Integration Method



CHAPTER V

DISCUSSION AND RECOMMENDATIONS

A. Effect of Reaeration Constant on Oxygen Uptake

The experiments conducted in this phase of the research were designed to evaluate the effect of reaeration rate on oxygen uptake. Lordi and Heukelekian (22) found no difference in BOD exertion when comparing open and closed quiescent reactors. However, stirring in the open reactor resulted in an increase in O_2 uptake over the closed quiescent jar, and the increase was magnified at greater mixing rates. Their K_2 values were 0.48, 0.82, and 1.06 days⁻¹ (\log_e). Gannon (23) used samples of river water to study the effect of mixing versus quiescent conditions on O_2 uptake in sealed BOD bottles. After five days the mixed bottle had utilized eight mg/l DO compared to six mg/l for the quiescent bottle with a slight increase in uptake rate for the mixed bottle. Jennelle and Gaudy (9) found stirring in sealed bottles to have no effect on oxygen uptake when compared to quiescent bottles. However, agitation in open systems did cause an increase in O_2 uptake. They also concluded that mixing, in the range employed in their research, appeared to have no effect on the biological kinetics when the systems employed low substrate concentrations such as exist in receiving streams and BOD bottles. Therefore, changes in reaeration rate in the range of those usually occurring in natural streams might

be expected to have little or no effect on oxygen uptake.

The results of the present research help clarify and, in certain respects, qualify, the tentative conclusion of Jennelle. The range of reaeration rate constants used in the present study was 0.04 to 0.21 hr^{-1} (base e). It was found that with increasing K_2 values the amount of oxygen uptake after the apparent logarithmic uptake phase was somewhat greater than that for lower K_2 values. In comparable systems, it was observed that after this phase the O_2 uptake curves in the slowly increasing rate phase(s) of uptake differed in increasing amount with increasing difference in K_2 . However, it was observed that O_2 uptake curves in the increasing rate phase of O_2 uptake (from zero to the point of inflection or until the plateau) were usually very similar unless one reaeration rate constant was approximately double the other. This first phase of O_2 uptake is of greatest importance in sag curve analysis because, in general, it describes the period of rapid DO depletion and the time of occurrence of the low point of the sag. In general, it would appear that one cannot totally disregard the K_2 value, i.e., O_2 uptake curves developed in the laboratory in open reactors should be obtained at K_2 values as close as possible to those expected in the receiving stream.

It should also be pointed out that the "sensitivity" of the DO probe presented some problems in analyzing results of various runs. As can be seen in Figure 1, the rapid decline in DO recorded for unit two and the extended flat bottom of the sag provide some indication that the DO actually went to zero even though zero DO was not recorded. In any event, there was in all probability a period of time, perhaps 3/4 day, when the system was operating under a period of tension which could have

been of sufficient magnitude to limit the system. This period of near zero DO also appeared as a distinct change in phase in the calculated oxygen uptake curve. When this extended period near zero occurred, it seems reasonable to assume that the organisms could have utilized more oxygen if it were supplied. The period of adjustment to the new environmental condition (oxygen-limited metabolism) makes it unwise to compare O_2 uptake during such periods with that in periods in which the system did not experience any deficiency in oxygen or to use these data in calculation. It is suggested that if an experimental unit exhibits such an extended flat curve near zero DO, the profile data should not be employed to calculate the O_2 uptake (BOD) curve. Instead, a new unit should be started up using a lower concentration of carbon source or a slightly higher K_2 value.

In summary, it may be concluded that the effect of reaeration rate constant on oxygen uptake is small during the increasing rate phase of O_2 uptake unless the K_2 values differ greatly. A rough rule of thumb, based upon experiments such as those shown in Figures 2 and 6, might be taken as differences in K_2 on the order of a factor of two. In general, the data indicate that the greater the reaeration rate constant, the greater will be the total oxygen uptake. A survey of the summary data in Table II shows that, in those experiments in which none of the sag curves had a flat bottom (column 6), the total O_2 used (column 10) increased with K_2 (column 4). Also, it may be concluded that if a DO curve in the open reactor sags near zero for a period of more than an hour or so, a comparison cannot be made with sag curves not going to zero, because of the possible effect of low oxygen tension on the biochemical behavior of the bio-mass.

As discussed in Chapter II, much controversy has existed concerning the kinetics of the BOD curve. The Streeter-Phelps (2) first order decreasing rate description of the curve has since been improved by many authors (17)(18)(19). Extensive studies by Bhatla and Gaudy (7) have completely described the phasic BOD curve, including the plateau. Several theories were proposed to explain why the plateau and phasic nature of the BOD curve occur. For systems containing heterogeneous microbial populations, the second stage of carbonaceous O_2 demand was shown to be due to predators (protozoa) metabolizing the bacteria grown during the first stage of O_2 uptake, and the plateau was observed between stages, depending upon the relative rates of increase of the two populations and period of time between peak numbers of bacteria and protozoa.

In the present research, the oxygen uptake curve could best be described as a conventional S-shaped growth curve. As shown by the figures in the first section of Chapter IV, the oxygen uptake usually exhibited a lag period followed by a period of increasing rate of uptake. The lag period or slow decline in DO was found to be directly related to the type and percent of seed used. Also, McWhorter and Heukelekian (19) reported that an increase in seed concentration (by volume) reduced the lag period. In the present study, acclimation of the seed to the test substrate for a period of time not extending too long into the endogenous phase, was found to eliminate the lag period. At the inflection point, the increasing rate changes to a decreasing rate. The low point of the sag curve corresponds to a breakover in the O_2 uptake curve with very slow uptake afterward. This also marks the disappearance of the usable exogenous substrate. The DO will increase

from the minimum as the uptake curve remains flat or rises very slowly. If protozoa were initially present in the seed, their growth rate should increase after the bacteria have reached their maximum population. As the protozoa grow and multiply, using the bacteria as substrate, they exert an oxygen demand on the system which appears as a second increase in rate.

The time period between the attainment of the maximum bacterial population and the beginning of appreciable oxygen utilization by the protozoa corresponds to the length of the slow O_2 uptake period or plateau. If no protozoa are present, the slow uptake may continue with no second increase in O_2 uptake rate. In heterogeneous systems, not all bacteria may act as a food source for protozoa; also the protozoa may not reach a population large enough to exert an O_2 demand greater than the reaeration force. During the present research, many different variations of oxygen uptake curves were observed. However, the generally phasic type of O_2 uptake curves observed by Bhatla and Gaudy (7), Isaacs and Gaudy (24), Jennelle and Gaudy (9), McWhorter and Heukelekian (10), and Gates and co-workers (21)(27) were also observed in this study.

B. Experiments on the Prediction of Dissolved Oxygen Sag Curves in the Simulated Channel From Oxygen Uptake Curves Developed in the Open Jar Reactors

In this section of the study, experimentation was conducted using the open stirred reactors as "models" to predict a DO sag curve exerted by a specific waste concentration in a simulated receiving stream. The predicted curve was compared to an actual curve observed in the simulated stream apparatus.

This portion of the study included fourteen experiments using synthetic waste to check the method of predicting stream sag. The method has been explained in Chapter III and sample calculations are shown in the Appendix of this thesis. Two jars and the river were adjusted to predetermined reaeration rates. However, in some experiments at least one K_2 value would result in a sag curve which either approached or reached zero DO for an extended period of time, and these data were not used for prediction.

A seed was acclimated, in most cases, for a 24-hour period, which corresponded to the length of time employed in determining the reaeration rate of the jars and river. When a 0.5 percent seed was applied to the river, the decrease in DO started immediately; however, for the synthetic wastes, a 1.0 percent seed was necessary to start the DO decrease in the jars at the same rate. The lag in the DO removal curve naturally corresponds to a lag in the O_2 uptake curve. The mathematical integration method using the O_2 uptake curve calculates this lag into the predicted curve, which delays the time of occurrence of the sag compared to that in the river. As pointed out earlier, Isaacs (30) noted that the concentration of seed had an effect on the length of the lag period. Gates, et al. (27) stated that the greater the amount of biomass, the greater the substrate utilization, and this controls the falling limb of the O_2 sag curve. The conclusion of Gates, Marljar, and Westfield (27) concerning the influence of substrate concentration on the decreasing leg of the sag curve, i.e., the rapidly increasing portion of the O_2 uptake curve, agrees with the findings of Jennelle and Gaudy (9). From the results of their experiments, it was concluded that BOD bottle data cannot be used to evaluate conditions in a receiving

stream unless the substrate concentration is the same in both systems, because they observed that the kinetics of the O_2 uptake curve to the inflection point followed a Monod-type relationship (40) between O_2 uptake rate constant and substrate concentration. Further studies have recently been conducted in the bioenvironmental laboratories of Oklahoma State University by Kelly (28) to substantiate the existence of the hyperbolic relationship between O_2 uptake rate and substrate concentration using various methods to determine O_2 uptake. He found that a Monod-type curve could be constructed and, consequently, a direct relationship between initial substrate concentration and oxygen uptake rate can be formulated during the phase of exponential increase in O_2 uptake (downward leg of the DO sag). Kelly's work forms a part of the overall investigation on kinetic description of O_2 uptake or BOD exertion, and was conducted at the same time as the present study. The findings provide substantive support to the present results, and they are discussed in more detail by Kelly (28).

Some of the problems which can occur in using the techniques employed in the present studies may be seen in the data shown in Figures 7 - 15. It is noted in Figure 7 for the glucose-glutamic acid system that an 8-hour lag and the phasic declining leg of the DO profile in the open reactor delayed the time of occurrence of the minimum DO as compared to that in the river. If the lag is "calculated out," the sags occur at the same time, as seen in Figure 9. For this particular run only, a 0.5 percent fresh sewage seed from the primary clarifier launder of the municipal treatment plant at Stillwater, Oklahoma, was used, and thus, there was a slower DO removal for both the river and jar. The lag in the open jars is much greater in Figure 10 for a glucose system,

and there was a much larger phasic shift during the downward leg of the DO profile. This lag may also be ignored or "calculated out" in making a prediction of the river profile, but the change in phase remains and delays the predicted DO sag bottom by 10 hours (see Figure 10). This experiment also had two very different recovery stages, which averaged out later. In Figure 14, the shape of the O_2 uptake curve for the open reactor was closer to the monomolecular shape than any other obtained in this study. This curve predicts a sag which is delayed 13 hours from that observed in the river. The delay is partly due to the phasic nature of the downward leg of the sag curve observed in the jar. Also, it is noted that there was no evidence for the "plateau" in the open jar reactor, whereas there was in the river. This does not infer that the first order kinetic BOD curve could be employed in predicting DO profile, because even though the plateau was "masked" or did not occur in the jar, this curve did exhibit an apparent first order increasing portion during the first 12 hours. In order to eliminate, or in any event, reduce the problems caused by the long lag due to acclimation time, the investigator must use an acclimated seed. The use of a thoroughly acclimated seed certainly seems justified, since the actual receiving stream will naturally become acclimated to the waste effluent.

The phasic declining limb occurred in several experiments, including those in which glucose was the sole carbon source. Gates, et al. (21) noted phasic removal of substrates with some combinations of compounds, with a recovery phase before the second sag due to the second substrate. Considerable work has been done in our laboratories concerning sequential substrate removal with heterogeneous populations. Gaudy, Komolrit, and Bhatla (20) cited several mechanisms explaining the

phenomenon for various ages of the biological system. In young cell systems, the suppression of enzyme function as well as repression of enzyme induction were demonstrated to be possible mechanisms. For the glucose system in the present study, the organisms may have changed a portion of the substrate into other substrate(s), creating a multisubstrate system, resulting in phasic substrate utilization which was manifested in phasic O_2 depletion in the downward leg of the profile. This type of curve is very clearly seen in Figure 10 (jar one). It is worthy of note here primarily to delineate the fact that occurrence of such curves is not exceptional. The phasic nature of substrate removal and/or O_2 utilization has been observed in many systems, and its existence provides a strong argument for the use of the DO prediction method herein employed rather than the sag curve approach of the Streeter-Phelps type which requires formal mathematical description of the O_2 uptake curve.

Microscopic examinations were made during the experiments at various times mainly to note changes in protozoan population. As discussed briefly earlier, and as extensively delineated by Bhatla and Gaudy (7), the protozoa population is believed to be the most general cause for the second major uptake in the BOD curve. In most observations, the protozoan population was very sparse during the declining leg of the sag curve. When a large increase in protozoa occurred, it was after the DO profile had recovered from the sag bottom. During this time, the O_2 uptake rate had decreased to a period of very slow increase or had undergone a flat period with zero increase, i.e., the plateau had occurred. In some cases, protozoa could be observed to be "grazing" on the floc particles. This process of self-clarification due to predator

activity has been reported by many; such observations have been reported by Bhatla and Gaudy (7) and by Isaacs (30). The metabolism of bacteria by protozoa has been shown to be a prominent cause of the second stage O_2 uptake, and the delay time between the creation of protozoan food source and attainment of rapid protozoan population increase has been shown to define the plateau. A plateau was not always observed in this study, but a substantial protozoan population developed in each run. Also, each system exhibited self-clarification by the end of five days. The lack of a plateau in many runs implies a smooth transition in the predator-prey relationship. Differences in occurrence of a plateau may be due to differences in the number (and type) of protozoa present initially in the different seeds. High initial protozoan populations may, in some instances, foster a more rapid increase of protozoan numbers, thus melding the two stages of O_2 uptake and eliminating the plateau.

Figures 16 - 27 described the results of several experiments to test the sag prediction method using actual wastes. A quantity of fresh sewage was acclimated to each waste prior to each experiment. Also the mineral salts, buffer, and nitrogen were added for each waste.

In the experiment using slaughterhouse waste (Figures 16, 17, 18), the seed concentration was 1.0 percent in the jars, and 0.5 percent in the river. It can be seen in Figure 16 that this extra seed in the jars was not warranted, and probably caused the DO removal rate to be somewhat greater for the jars than the river. The small second sag in the jars and later in the river may have been due to some type of remaining substrate or to O_2 uptake by the protozoa. A high concentration of predators was present initially; also COD values of samples taken at

the bottom of the sag and after five days, were equal. Therefore, the probable reason for the small second uptake is unknown.

The probable effect of the initial seed concentration may be seen in Figure 17. The difference in O_2 uptake or time to attain the plateau was approximately five hours. In Figure 18, it was seen that this caused a 5-hour differential in time to attain the low point of the DO sag. The difference in K_2 values of the river and jar two was rather substantial--nearly two-fold. However, the predicted curves were very similar. Unit one had a K_2 closer to that of the river, and the predicted curve fell one mg/l DO below the actual. This margin of error is adjudged small for a seven mg/l actual deficit, and it is felt that without the difference in seed, the prediction would have been even closer to the observed profile.

In experiments on the hardboard pulping waste (Figures 19, 20, 21), the K_2 values of the jars bracketed that of the river, and all were rather closely grouped. The resulting O_2 uptake curves were S-shaped and nearly superimposable during the critical phase of O_2 uptake (see Figure 20). Again, protozoa were present and clarification occurred during the experiment. The predicted curves were practically traces of the observed curve in the simulated river. The difference in predicted and observed minimum DO level was only 0.7 mg/l.

The most complex whole waste used was the kraft digester blow-down liquor. However, most of the indicated COD of this material was lignin, which is not a utilizable substrate, and which remained in the system after five days. The lag phase in the units probably would have been two or three days if the seed had not been acclimated for two weeks. These experiments were shown in Figures 22, 23, and 24. The lower K_2 of

the river caused this system to exhibit the greatest deficit. The effect of K_2 on O_2 uptake was not evident until the recovery stages of the DO, as can be concluded from Figure 23. With an acclimated seed, such as should exist in the river, the most important stage of the sag curve and thereby the O_2 uptake curve, is the declining leg (rapidly increasing phase for O_2 uptake) which occurs during the first two days after the waste enters. In these experiments, the time to reach maximum deficit and the amount of deficit were the same for the predicted and actual curves. A second small sag in the jars before recovery from the first sag (Figure 22) caused the predicted sag (Figure 24) to exhibit a longer time period at the minimum DO than was observed in the river. As with the previous experiments using actual wastes, the predicted sag curves are adjudged to provide rather good estimates of the DO profile.

In order to study a very complex substrate, a combination of slaughterhouse and hardboard wastes was used in the final set of experiments in the artificial river. In this case, the microorganisms were acclimated to a mixture of the two wastes. The combination was removed in 16 hours and with one major DO sag (Figure 25). A second small sag in the jars was noted at approximately two days. This effect was also noted for the slaughterhouse waste experiment. The O_2 uptake curve was much greater in the open jar which was operating at the high K_2 value. All three curves were S-shaped and exhibited an apparent exponential (increasing) phase of O_2 uptake. After this initial rapid first order increasing uptake, the curves "broke over" for a period of time, and then a second large increase in uptake took place. Follett and Gaudy (5) also observed the occurrence of a "plateau" with complex substrates,

such as paper mill wastes.

An attempt to use this combination of wastes in a standard BOD bottle test led to many problems. Many trial runs were made in an effort to find the right substrate concentration and seed percentage with the limited amount of initial DO available with the standard dilution technique. The dilution of stock CODs of several thousand down to approximately 10 mg/l was difficult and resulted in measured CODs of 18 mg/l per bottle. The same 0.5 percent seed concentration used in the jars and river was used in the bottles.

The two curves in Figure 19 calculated from the BOD bottle O_2 uptake curve predict a very large DO sag. The Streeter-Phelps equation gave the typical rounded bottom with first order decreasing limbs. The numerical integration method using the same curve and including the lag phase of uptake, predicted a more phasic sag curve with a V-shaped bottom. It can be seen that the O_2 uptake curve from the open stirred reactor (Figure 27) predicted a DO profile which was much closer to the actual curve for this combination of wastes than did the calculations using the O_2 uptake curve developed in the BOD bottle.

As discussed in Chapter II, many of the topics of research concerning stream assimilative capacity have involved the addition of terms and factors to the Streeter-Phelps equation. The effect of benthic deposits and various plant life (autotrophy) are not included in the Streeter-Phelps equation and are not included in the method proposed here. These are indeed complex biological phenomena in themselves, and they require mathematical description of equal or greater complexity than the exertion of carbonaceous BOD due to entry of waste to streams. The two opposing factors of the Streeter-Phelps equation are, however, the major

ones affecting the DO profile, and understanding their interrelationships should ideally precede consideration of the other factors affecting the DO balance.

The main purpose of the present study was to apply the "new kinetics" of BOD exertion to predict effects on the kinetic course of the DO balance in a stream, and to develop a laboratory procedure which approaches the conditions in an actual stream, thus enhancing the engineering capability of predicting the profile. These two important practical aspects have been largely overlooked by many investigators who appear to be content with attempts to add additional terms to an equation for description of the more complex situations. Such attempts provide more sophisticated and complex equations, but do little to provide practical and useful predictive technique for control of stream pollution. The general approach to prediction of the DO profile herein studied has been outlined in brief by Jennelle and Gaudy (9) and developed further by Gaudy (10). The present investigation was intended to test the approach, to refine and revise, where need be, the general concepts involved, and to provide recommended methodology for practical employment of the technique. The results of the present study using the simulated river channel apparatus to assess the credibility of the profile predicted from the open jar O_2 uptake curve indicate that the approach has considerable potential and a tentative recommended procedure based upon these findings is given in the following section. It might be argued that the best test of the procedure would be its use to predict the profile in an actual receiving stream, followed by a monitoring program to check the general accuracy of the predicted sag or critical DO level. Considerable space could be devoted to arguing the

pros and cons as to whether this would be the best test of the scientific predictions of the approach (e.g., consider the problems involved in measuring the K_2 values in various reaches of natural stream). In any event, it is worthy of noting that the general approach was recently employed by Gaudy (personal communication) in estimating the effect of treated effluent on the DO resource in a natural stream. Subsequent monitoring of the stream over a sufficient period of time should provide field data regarding the usefulness of the predictive technique.

In summary, the procedure used in this research eliminates the "plug in" values and the inadequate monomolecular BOD kinetics usually assumed to exist. The open jars and stirrers may be set up to operate at the actual waste dilution expected in a stream and at the expected range of reaeration rates in the stream. This allows a closer approach to the actual conditions which will exist in the receiving stream and therefore must produce data of greater predictive value than can be derived from the standard BOD dilution technique.

C. Recommended Procedure

The equipment needed for the laboratory tests includes two or three battery jars, a small, dependable, adjustable speed motor with shaft and propeller for each jar, and a DO meter with probes. The jars used in the present study were 15-liter capacity; larger capacity jars would also be usable. Smaller working volumes are not desirable because errors in making up dilutions are magnified, and large ranges of K_2 values may be difficult to attain and hold steady throughout the experimental period. The Bodine motors used herein needed no maintenance, and can be expected to run continuously for long periods of time. If

the voltage in the laboratory is variable, a voltage regulator may be necessary to maintain constant stirring speed. Because the probe membrane is rather delicate, and since the probe loses sensitivity, more than one probe is required to allow for problems during an experiment. The sensitivity of the probes must be checked versus the Winkler DO method in Standard Methods (37); therefore, a few bottles and reagents are needed.

The system should be run at the "design" temperature, i.e., the critical temperature for which the prediction of the DO profile is to be made. Since this is usually the warmest expected temperature, a refrigerated system is not needed. Temperature control can best be attained by immersing the jar reactors in a water bath; thus one temperature controller can be used for duplicate (or triplicate) reactors.

It is believed that sodium sulfite with cobalt chloride catalyst is the easiest and cheapest way to remove the DO from the water. Very small quantities of these reagents are needed for each run. These chemicals, those for the DO test, and the mineral salts listed in Table I are the only needed reagents.

To begin a run, the jars should be filled with water from the receiving stream, which is then allowed to reach an equilibrium temperature. The motors should be set by rheostat control to a stirring speed that will provide a reaeration rate in the approximate range of that expected in the river. The reaeration of the receiving stream may vary from reach to reach, but in general the most important reaeration rate or rates are those expected during the first one or two days of flow time from the point of entry of waste to the river. A family of laboratory sag curves developed in the jar at K_2 values bracketing

those expected in the river will give the best estimate of the downward leg and the bottom of the actual sag curve in the river. The K_2 of the river may be estimated by one of the many existing methods, for example, the formula of Isaacs and Gaudy (8).

When the temperature of the water in the reactor becomes stable and the stirrers are set, one adds the sulfite and cobalt catalyst. The DO will immediately decrease and should reach a minimum value between zero and 1.0 for the test results in generating reaeration data to calculate K_2 . Unless far too much sulfite was added, it should all have reacted within 30 minutes. The investigator should record DO every 15 minutes after addition of the chemicals in order to establish zero time for the reaeration experiment. The reaeration may be allowed to proceed until the saturation value for the operating temperature is approached.

It was found that the most consistent method for checking probe sensitivity was to use a separate container of water at approximately the same temperature as the test jar. A two-liter beaker was used in this study, and was aerated for a few minutes with a magnetic stirrer. The probe was inserted for a reading while a BOD bottle was filled by carefully submerging it in the beaker. This may be done throughout the run at least twice a day; thus the probe is checked without removing water from the battery jar reactor.

The investigator may add the waste to the jars at any time after sufficient DO has been added by reaeration to permit easy calculations for K_2 . (A useful calculation procedure for K_2 was given in Chapter IV). This initial DO for the experiment may vary somewhat from the initial deficit value expected in the receiving stream, because this is taken

into account in the prediction calculations. However, it is just as easy to "pollute" the jar at an initial DO deficit close to that expected in the river as at any other, and such a procedure provides the investigator with a direct preliminary estimate of the river profile.

The dilution to be employed, i.e., ratio of receiving water to waste effluent, depends upon the conditions and purposes for which the DO profile is being estimated. For example, in a case where the degree of treatment of the waste prior to discharge has been determined by considerations other than stream assimilation capacity (e.g., by state law), a sample of the treated effluent (presumably a sample from a pilot plant operation or a waste similar to the one expected at the site in question) can be used at a dilution which is determined by the estimated daily volume of waste and the design or minimum flow condition of the receiving stream (the average daily flow of the driest seven consecutive days of flow of 10-year occurrence is often employed). Other dilutions should also be employed. It is important to stress that in accordance with the findings of Jennelle and Gaudy (9), as well as Kelly (28), dilution (i.e., substrate concentration) affects the kinetic expression of the BOD exertion curve. Therefore, separate experimentally determined O_2 uptake curves are needed for each dilution of waste and river water. Water is siphoned from the jar, waste is added, and then the volume is readjusted to the initial value with river water and seed suspension.

If extra nutrients are believed necessary, they should be added with the waste. In the interest of providing a conservative engineering estimate and in order to ensure that the carbon source is the limiting nutrient, the usual inorganic chemical supplements (nitrogen

and phosphorus) should be added. The investigator may or may not take the view that even if these essential inorganic chemicals are not present in the river water or effluent now, they may be at some time in the future. This is really a matter of engineering judgment, and such addition depends upon the purpose of making the study.

The seed must be pre-acclimated to the waste being studied. Therefore a separate unit (e.g., a two-liter beaker) may be used to acclimate organisms to the waste. One can use a small batch-fed reactor to maintain an acclimated seed population. A DO reading should be taken when the volume has been readjusted in the jar to establish a zero reading. The investigator must follow the DO throughout the sag and recovery stages, obtaining sufficient DO values to construct an accurate picture of the profile from which to calculate the O_2 uptake curve. In all cases in this study, the exertion was essentially complete, with good recovery of DO, in five days.

Some important guidelines to be observed during the deoxygenation study are: (1) the faster the change in DO, the more often readings should be taken; (2) microscopic examinations should be made to note the increase in bacterial growth and later the protozoan growth; (3) the speed of the stirrers should be checked daily to guard against variations in speed; (4) the sensitivity of the DO probe must be checked (small changes in probe sensitivity are to be expected); (5) the jars should become more turbid, then show signs of clearing; (6) phasic legs of the sag curve can be expected; (7) in order not to let algae grow in jars, shielding from light may be necessary; (8) the DO should not go to zero, and on the other hand, (9) the sag should not be too slight, since calculation of the O_2 uptake (BOD) curve depends upon

production of a well defined sag curve.

The calculations for O_2 uptake and the prediction curve are presented in the Appendix. These computations are not particularly laborious; however, a calculator with a memory cell greatly facilitates the calculation.

TABLE VI

CONCLUSIONS

The results of this study support the following conclusions:

1. The effect of reaeration rate on O_2 uptake requires further definition. However, from this study, the apparent practical range for effect of reaeration rate constant was established as follows: If one K_2 value was double another, the system with higher K_2 value exhibited a greater O_2 uptake throughout the experiment.

In order to compare the O_2 uptake curves obtained at different reaeration rates, the sag curves from which the O_2 uptake curves are calculated must have shown reasonably well defined sags, e.g., considering an initial DO of 8.0 mg/l, a sag which fell below 6.0 mg/l but did not go to zero. Since the DO is obtained electronically, two or three jars are no more difficult to operate than one, and with the jars set at various K_2 values in the range of those expected in the river, the investigator may observe the effect of reaeration rate on the sag curve. If a flat bottom sag curve is obtained with the DO hovering near zero, it must be assumed that oxygen tension will have affected O_2 uptake, and such a curve should be disregarded.

2. When using an added microbial seed population, it should always be acclimated to the waste under study. The organisms in the river will become acclimated to an existing waste; those existing in

the waste (e.g., treated effluent) are already acclimated. Therefore, the comparability of the laboratory O_2 uptake curve and that which will exist in the river is enhanced by employing an acclimated seed in the experimental work.

3. The type of BOD kinetics observed in this study compared favorably with data on O_2 uptake dilute systems from this laboratory using untreated effluents or a pure carbon source. The O_2 uptake curves were never of first order decreasing kinetic form. With the dilute substrate concentrations used, an autocatalytic curve was obtained for both the open stirred reactors and the artificial river.

4. The presence of protozoa was noticed in each experiment, and an increase in their numbers corresponded to the clarification of the units. Although the plateau was not always manifest, its occurrence was dependent on the size of the protozoan population and the time interval between the maxima in the bacterial and the protozoan growth cycles. The above statements are based solely on microscopic observations which did not involve attempts to make precise direct counts of bacteria and protozoa. They substantiate results of quantitative experimentation on population changes made in a previous study in the bioenvironmental engineering laboratories.

5. The motor with long shaft and propeller was found to provide reliable and constant speed stirring. The volume of reactor liquor in the jar and in general the "scale" of the experimental setup seem adequate as adjudged by the fact that the results compared favorably with those obtained in the larger scale "artificial" river.

6. The calculations for oxygen uptake and for the predicted sag are very easily facilitated with slide rule or calculator. The

proposed method to predict the DO profile in a stream does not require forcing the O_2 uptake data into any definable kinetic order. Rather, an attempt is made to simulate in the open reactor jars, conditions extant in the receiving stream. The present results indicate that this approach can be successfully employed.

CHAPTER VII

SUGGESTIONS FOR FUTURE WORK

1. Additional studies should be conducted to further define the effect of reaeration constant on oxygen uptake. A higher K_2 value did not always result in greater O_2 uptake compared to a lower K_2 value. A definite conclusion on the relation of agitation with O_2 uptake could not be reached.

2. Continued improvements may be made in the prediction method by including ways to assess the effects of benthic deposits and/or plant life on the DO concentration in the stream. There may be cases wherein one or both of these factors exert a greater demand on the stream than that due to the utilization of the waste. Work to determine relative magnitude of effect on the DO profile could prove useful in adjusting the prediction calculations.

3. Assessment of the method in the field should be continued to find areas in the procedure which might be refined.

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APPENDIX

A. Calculation of Oxygen Uptake from Open Jar Reactors

The reaeration rate of the open stirred reactor(s) must be known in units of hr^{-1} (base e), and this rate should roughly approximate the reaeration rate in the reach(es) of the river under study. The method used to determine the K_2 in the jar was explained in the text.

From the DO values recorded during the experiment, the deficit at each time may be found by subtracting the DO from the saturation value for the operating temperature employed. Table III includes the complete data used to determine the O_2 uptake for experiment 23 for a single jar.

Column 1 shows the time of the DO reading, and column 2 lists the deficit at each time. The reaeration rate for the jar is multiplied by the deficit and recorded in column 3. Column 4 lists the time interval between DO determinations.

The amount of DO put into the system during a specific time interval by reaeration is determined by multiplying K_2 , deficit, and the length of the interval; these values are listed in column 5. Column 6 lists the DO reading, and the change in DO during each interval is the difference in DO recorded in column 7. The oxygen utilized during the time interval is given in column 8 and is equal to the DO added by reaeration minus the change in DO concentration in the system, i.e., column 5 minus column 7. Column 9 shows the summation of the values

TABLE III
CALCULATION OF OXYGEN UPTAKE FROM OPEN JAR REACTORS

1	2	3	4	5	6	7	8	9
Hour	D mg/l	K_2D mg/l-hr	Δt hr	$K_2D\Delta t$ mg/l	DO mg/l	ΔDO mg/l	5-7 mg/l	O_2 Uptake mg/l
0	1.50	0.15			7.20			0
6.25	0.88	0.09	6.25	0.74	7.82	.62	0.12	0.12
9	0.88	0.09	2.75	0.24	7.82	0	0.24	0.36
11.5	0.97	0.10	2.5	0.23	7.73	-.09	0.32	0.68
22	2.95	0.29	10.5	2.04	5.75	-1.98	4.02	4.70
24.5	3.90	0.39	2.5	0.85	4.80	-.95	1.80	6.50
26.5	4.22	0.42	2	0.80	4.48	-.32	1.12	7.62
28.5	4.53	0.45	2	0.87	4.17	-.31	1.18	8.80
29.75	4.74	0.47	1.25	0.57	3.96	-.21	0.78	9.58
31.5	5.16	0.51	1.75	0.86	3.54	-.42	1.28	10.86
33.5	5.99	0.59	2	1.11	2.71	-.83	1.94	12.80
35.5	6.62	0.66	2	1.25	2.08	-.63	1.88	14.68
40.25	7.87	0.78	4.75	3.41	0.83	-1.25	4.66	19.34
46	7.55	0.75	5.75	4.40	1.15	.32	4.08	23.42
49	6.62	0.66	3	2.11	2.08	.93	1.18	24.60
53	5.68	0.56	4	2.44	3.02	.94	1.50	26.10
57.5	4.95	0.49	4.5	2.37	3.75	.73	1.64	27.74
70.25	4.82	0.48	12.75	6.17	3.88	.13	6.04	33.78
75.5	4.00	0.40	5.25	2.29	4.70	.82	1.47	35.25
83.5	2.88	0.29	8	2.72	5.82	1.12	1.60	36.85
96	2.16	0.21	12.5	3.13	6.54	.72	2.41	39.26
107.5	1.88	0.19	11.5	2.30	6.82	.28	2.02	41.28
120.5	1.30	0.13	13	2.05	7.40	.58	1.47	42.75
124.25	1.30	0.13	3.75	0.48	7.40	0	0.48	43.23

$$C_s = 8.70 \text{ mg/l}$$

$$K_2 = 0.099 \text{ hr}^{-1}$$

given in column 8. The quantities listed in column 9 can now be plotted versus time (column 1) to obtain the curve of accumulated oxygen uptake. This curve is shown in Figure 8 in the text.

B. Calculation of DO Profile From Experimentally Determined Oxygen Uptake Curves

Calculation of a DO profile from an experimentally determined O_2 uptake curve is, in a sense, a reversal of the previous calculation. The K_2 value(s) employed are those estimated for the receiving stream and the initial deficit employed is that for the receiving stream at the temperature of interest for the stream. The calculations shown in Table IV were made using the O_2 uptake curve developed in Table III of the Appendix (plotted in Figure 8 of the text).

Column 1 indicates the times at which values from the O_2 uptake curves were chosen. The sample calculation starts with hour 12 because the lag phase in O_2 uptake was ignored and this time is assumed to be zero. The basis of the integration method is the assumption that within an increment of time the reaeration rate remains the same. Consequently, it is best to select as small an increment as is practical. The length of each interval is given in column 2.

The values from the uptake curve at each time are listed in column 3. The amount of oxygen utilized in each interval is the difference between the values in column 3, and this change in oxygen uptake is given in column 4.

The initial deficit of the stream is the starting deficit for the calculations in column 5. To obtain the values in column 6, the K_2 value of the stream is multiplied by the initial deficit for the

TABLE IV
 CALCULATION OF DO PROFILE FROM EXPERIMENTALLY-DETERMINED
 O₂ UPTAKE CURVES

1	2	3	4	5	6	7	8
Hour	Δt hr	O ₂ Uptake mg/l	ΔO_2 mg/l	D mg/l	K ₂ D Δt mg/l	ΔDO mg/l	DO mg/l
12		0.80		1.96			6.84
16	4	2.05	1.25	2.27	0.94	.31	6.53
18	2	2.85	0.80	2.52	0.55	.25	6.28
20	2	3.75	0.90	2.81	0.61	.29	5.99
22	2	4.70	0.95	3.09	0.67	.28	5.71
24	2	5.95	1.25	3.60	0.74	.51	5.20
26	2	7.20	1.25	3.99	0.86	.39	4.81
28	2	8.30	1.10	4.13	0.96	.14	4.67
30	2	9.90	1.60	4.74	0.99	.61	4.06
32	2	11.20	1.30	4.90	1.14	.16	3.90
34	2	13.00	1.80	5.52	1.18	.62	3.28
36	2	15.00	2.00	6.20	1.32	.68	2.60
38	2	17.00	2.00	6.71	1.49	.51	2.09
40	2	18.80	1.80	6.90	1.61	.19	1.90
42	2	20.40	1.60	6.84	1.66	-.06	1.96
44	2	21.90	1.50	6.70	1.64	-.14	2.10
46	2	23.40	1.50	6.59	1.61	-.11	2.21
48	2	24.15	0.75	5.76	1.58	-.83	3.04
52	4	25.70	1.55	4.54	2.77	-1.22	4.26
56	4	27.20	1.50	3.86	2.18	-.68	4.94
60	4	28.80	1.60	3.61	1.85	-.25	5.19
64	4	30.65	1.85	3.73	1.73	.12	5.07
68	4	32.65	2.00	3.94	1.79	.21	4.86
72	4	34.30	1.65	3.70	1.89	-.24	5.10
76	4	35.45	1.15	3.07	1.78	-.63	5.73
84	8	37.00	1.55	1.67	2.95	-1.40	7.13
92	8	38.45	1.45	1.52	1.60	-.15	7.28
100	8	39.90	1.45	1.51	1.46	-.01	7.29
110	10	41.60	1.70	1.40	1.81	-.11	7.40
120	10	42.70	1.10	0.82	1.68	-.58	7.98

$$C_s = 8.80 \text{ mg/l}$$

$$K_2 = 0.120 \text{ hr}^{-1}$$

interval and the length of the interval. The product, in mg/l, is the amount of oxygen added by reaeration, and this is subtracted from the amount of O_2 assimilated, i.e., column 4 minus column 6. The change in dissolved oxygen is listed in column 7 and is a positive number when the amount of oxygen used is greater than that added to the system. A negative change in dissolved oxygen indicates that the amount of O_2 added by reaeration exceeds oxygen uptake. A new deficit value is established for the next interval by adding or subtracting, according to the sign of DO, the change in DO from the preceding deficit. Column 8 is the difference between column 5 and the saturation value. These DO values are plotted versus the time in column 1 to obtain the predicted sag curve. The resulting curve is compared to the actual river sag in Figure 9 of the preceding text.

VITA

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Doctor of Philosophy

Thesis: STUDIES ON THE PREDICTION OF THE DISSOLVED OXYGEN PROFILE IN RECEIVING STREAMS

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