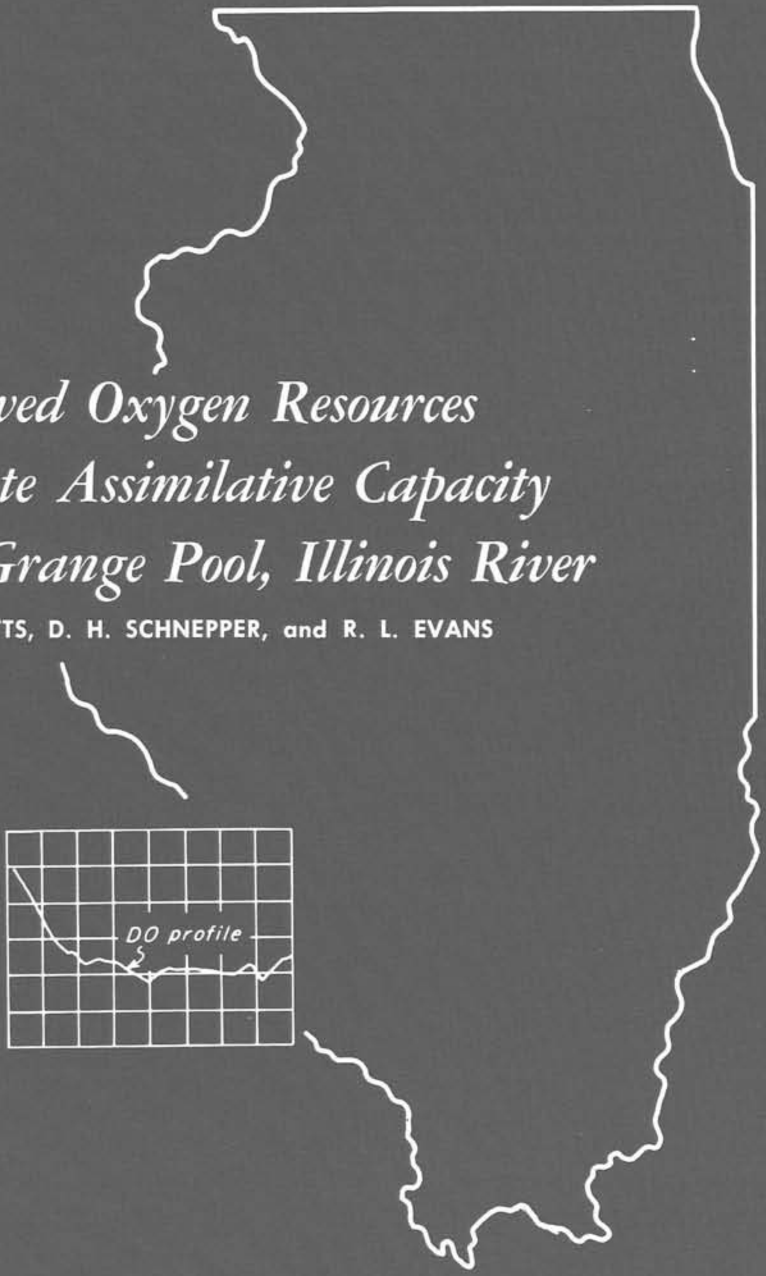
REPORT OF INVESTIGATION 64

STATE OF ILLINOIS

DEPARTMENT OF REGISTRATION AND EDUCATION

Dissolved Oxygen Resources and Waste Assimilative Capacity of the La Grange Pool, Illinois River

by T. A. BUTTS, D. H. SCHNEPPER, and R. L. EVANS



ILLINOIS STATE WATER SURVEY

URBANA

1970

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Abstract: The La Grange navigation pool, a 77.4-mile reach of the Illinois River below Peoria, frequently experiences low dissolved oxygen concentrations which fall below 4.0 mg/1, the minimum standard Weighted average DO concentrations as low as 1.65 mg/1, with a minimum DO of 0.9 mg/1, have been observed. Mathematical models were developed by statistical regression methods for predicting average and minimum pool DO concentrations. A variety of methodologies were investigated to determine the best procedure for defining the pool waste assimilative capacity; the Velz modification of the Black and Phelps procedure was selected A quality control chart was designed to detect DO trends which deviate from expected patterns The ability of the pool to assimilate organic wastes has been restricted because man has drastically altered the natural hydraulic and hydrologic characteristics of the river A significant cause of DO depletion appears to be nitrification; this fact must be considered in future waste treatment requirements if significant water quality improvements are to be realized.

Reference: Butts, T. A., D. H. Schnepper, and R. L. Evans. Dissolved Oxygen Resources and Waste Assimilative Capacity of the La Grange Pool, Illinois River. Illinois State Water Survey, Urbana, Report of Investigation 64, 1970

Indexing Terms: biochemical oxygen demand, dissolved oxygen, Illinois, nitrification, oxygen sag, reaeration, rivers, sanitary engineering, time-of-travel, waste assimilative capacity, water management, water pollution, water quality control, water temperature.

STATE OF ILLINOIS
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CONTENTS

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by T. A. Butts, D. H. Schnepper, and R. L. Evans

ABSTRACT

A study of the dissolved oxygen resources of the La Grange navigation pool in the Illinois River during 1965—1967 provides concepts which can be of assistance to regulatory agencies responsible for making decisions for water quality management.

Dissolved oxygen water quality standards for the La Grange pool require the maintenance of 5 milligrams per liter (mg/1) or more during at least 16 hours of any 24-hour period and not less than 4 mg/1 at anytime. Conditions in the pool were observed to fall consistently below these standards. Weighted average pool dissolved oxygen concentrations were found to be as low as 1 65 mg/1, with a minimum of 0.9 mg/1.

Three objectives were established: 1) to relate observed dissolved oxygen concentrations to flow, temperature, and oxygen demand; 2) to develop a waste assimilative capacity model; and 3) to develop a statistical water quality control chart to aid in the interpretation of data generated by continuous monitoring. This report describes the methodologies tried and selected to achieve these objectives.

Statistical regression methods were used to develop relationships for achieving the first objective Mathematical models were formulated permitting the prediction of average and minimum dissolved oxygen concentrations in the pool waters. The Black and Phelps method with Velz's modification was found to be the most appropriate approach for defining the waste assimilative capacity of the pool. To meet the third objective a one-sided quality control chart was designed to detect trends deviating from an expected pattern. Proper data input and interpretation permit decisions regarding whether the water quality system is in-control, out-of-control, or indecisive.

SUMMARY

The field procedures followed in undertaking a waste assimilative study of the 77.4-mile-long La Grange pool differed little from those used by many investigators in determining the oxygen resources of a stream. Basically, measurements for dissolved oxygen, temperature, and 5-day biochemical oxygen demand were made at selected points throughout the stream reach and recorded. Cross-section data were obtained that permitted calculations for determining time-of-travel by the volume displacement method; stream gages maintained by the U. S. Geological Survey provided the data for streamflows. Field investigations were performed during critical low flow and high temperature stream conditions.

In addition to basic measurements, an effort was made to define the character of the oxygen demanding (BOD) substances in the river, i.e., the relationship between carbonaceous and nitrogenous demand.

This study departs from similar ones in that numerous methodologies have been rigorously investigated to determine the mathematical expressions which best fit observed stream conditions. The principal measured factors included 5-day biochemical oxygen demand (BOD_5), dissolved oxygen (DO), temperature *(T),* streamflow *{Q),* deoxygenation *(K_1)*, reoxygenation *(K_2)*, carbonaceous demand (Y_5c), nitrogenous demand (Y_{5N}), stream depth *(H),* stream width, and time-of-travel *(t).*

Soundings taken by the U. S. Army Corps of Engineers (Peoria Office) at 0.2-mile intervals throughout the 77.4-mile reach provided excellent data for time-of-travel computations. The volume displacement method was programmed into an IBM 360/50 computer for determining time-of-travel at 46 locations along the pool length. For rapid estimates, a logarithmic regression equation was developed relating the computer calculated time to gaged flows upstream at Kingston Mines (Q_h) and downstream at Meredosia (Q_m).

The developed equation *(see equation 1 in text),* where *t* is in days, is:

$$t = 4058 Q_k^{-0.5609} Q_m^{-0.2161}$$
$$r = -0.995$$
$$SE = 0.0912 \text{ days}$$
$$\text{Limits: } Q_k = 3560 \text{ to } 9800 \text{ cfs}$$
$$Q_m = 6270 \text{ to } 11{,}500 \text{ cfs}$$

The use of multiple regression techniques allowed the development of dissolved oxygen prediction equations. The initial assumption was that the average pool temperature (T_A), time-of-travel (t), and BOD_5 were the principal components affecting the average (DO_A) and minimum (DO_M) dissolved oxygen in the pool. Upon examination, a consistent meaningful relationship between BOD_5 and DO could not be derived. A review of similar data reported by Wisely and Klassen[1] from a 1936 study supported these findings, i.e., no significant correlation between BOD- and DO. Of interest was the minor variation between the means and standard deviations of BOD- determined in 1936 and those observed during this investigation. Standard deviations were estimated to be less than 0.9 mg/1 for all stations during both studies.

Time-of-travel and water temperature were found, independently, to be highly correlated to dissolved oxygen concentration. This led to the development of prediction equations involving these two factors. The equation *(see equation 2 in text)* for average pool dissolved oxygen *(DOA)* is:

$$\begin{aligned} DO_A &= 30.24 \exp\left[-(0.2761t + 0.03944T_A)\right] \\ r &= -0.94 \\ SE &= 0.26 \text{ mg/l} \\ \text{Limits:}\quad t &= 4.1 \text{ to } 6.6 \text{ days} \\ T_A &= 23 \text{ to } 29 \text{ C} \end{aligned}$$

Similarly, the prediction equation *(see equation 3 in text)* for the minimum dissolved oxygen *(DOM)* , with the same limits of *t* and *TA,* is:

$$\begin{aligned} DO_M &= 41.71 \exp\left[-(0.3487t + 0.05576T_A)\right] \\ r &= -0.92 \\ SE &= 0.29 \text{ mg/l} \end{aligned}$$

An analysis of these equations was made to determine the relative effects of temperature and time-of-travel on the dissolved oxygen resources of the pool. Under the flow and temperature conditions of this study, the effect of time-of-travel is approximately three times that of the average pool temperature. This would appear to be a pertinent finding and one to take into consideration when proposals regarding deepening or widening a navigational pool are reviewed. For example, a chart was prepared to show the effect on the DO in the pool caused by deepening the channel 2 feet. The average decrease on 12 dates for average and minimum DO concentrations was 12 and 16 percent, respectively.

The prediction equations have been formulated without including BOD- as a variable, which in effect assumes the waste load in the stream to be reasonably constant. The assumption appears valid and allows the advantage of obtaining rapid estimates of dissolved oxygen conditions in the pool during low flow summer conditions. However, the prediction equations were used in conjunction with a probability procedure to devise a means of detecting any changes in the river waste load. This was accomplished by passing planes (equations) through points defined by the mean of a DO sample plus or minus two standard deviations and parallel to the prediction planes (equations). Observed DO's falling consistently above or below the 2.5 percent limits indicate probable changes in river waste loads.

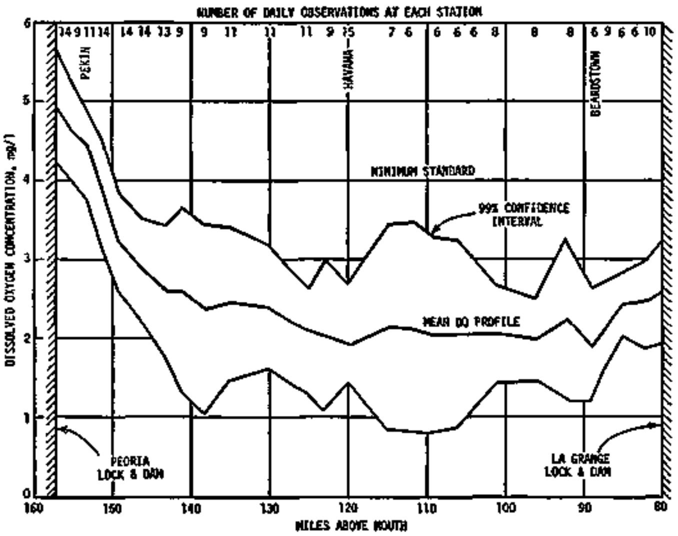

Figure. 1. Mean dissolved oxygen profile during summer months

The La Grange pool has been designated as an Aquatic Life Section of the Illinois River requiring the dissolved oxygen concentration to be at least 5 mg/1 during 16 hours of any 24-hour period and not less than 4 mg/1 at anytime. Figure 1 shows the observed oxygen-sag curve for average DO's at 27 stations during streamflows of less than 7020 cfs measured at Kingston Mines. The number of observations used for computing the averages are tabulated at the top. The confidence intervals represent the range in which the true mean is expected to fall. For example, at milepoint 120 with a mean DO of 1.92 mg/1, a 99 percent chance exists that the true mean will be between 1.42 and 2.42 mg/1. The widening of the confidence bands at some stations is due primarily to fewer samples rather than to an increase in the variability of samples, since larger samples give better estimates of the true mean. Thus, the assimilative capacity of the La Grange pool, under current waste loads and during summer months, is not capable of preventing the dissolved oxygen concentration from falling below the stream quality criteria specified for the reach.

Many methodologies and combinations thereof for defining mathematically the observed oxygen-sag curve were tried. Observed DO-sag curves could not be consistently duplicated using BOD's and K_1's derived from laboratory results by the methodologies developed by Streeter and Phelps,[0] Black and Phelps,[2] or Phelps.[3] However, use of the observed DO's and reaeration determined from the Velz curve[4] made it possible to determine BOD's and K_d's that provided a curve fitting the observed data. This approach eliminated using analytical biochemical oxygen demand data and relies solely upon observed DO and reoxygenation estimates proposed by Velz. The basic equation *(see text page 17)* is:

$$DO_{used} = (DO_a - DO_{net}) + DO_{rea}$$

where $(DO_a - DO_{net})$ represents the difference in observed DO between upstream and downstream stations.

The value of a mathematical model that adequately reflects observed stream DO's lies in being able to evaluate realistically the degree of waste removal necessary to maintain specified dissolved oxygen levels. Figure 2 not only indicates the fit of computed DO's to those observed during one period of the study but also demonstrates waste treatment needs to achieve specified DO levels during conditions of the period. The percent reduction noted must be applied to the total oxygen demand imposed upon the stream.

Analyses of the oxygen demand characteristics of waters within the La Grange pool indicate that a significant nitrogenous demand exists at the upper end. The composition represents about 54 percent of the total oxygen demand. Although the existence of nitrification in the Illinois River has been previously reported, the seriousness it poses to the dissolved oxygen balance has not been fully emphasized. During one 3-day period the rate of the nitrogenous demand was estimated to be greater than the carbonaceous demand to the extent that 34,000 pounds of nitrogenous BOD was used during one day of travel time whereas only 14,000 pounds of carbonaceous BOD was satisfied. Most of the nitrogenous demand was satisfied in the pool.

Since conventional waste treatment plants are designed principally to remove carbonaceous demand, approximately 54 percent of the total oxygen demand would remain if 100 percent removal of the carbonaceous demand could be accomplished. As illustrated in figure 2, complete treatment, as conventionally considered, would not produce the specified dissolved oxygen levels for the pool.

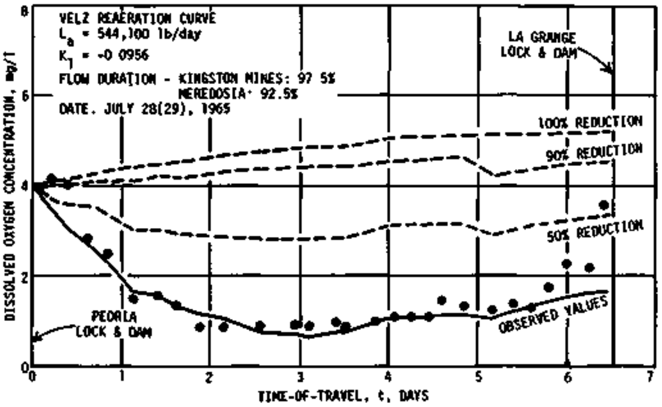

Figure 2. Computed DO-sag curve, July 1965

Statistical and waste assimilative evaluations demonstrate that the oxygen resources in the pool are under severe pressure during summer streamflows. Conventional secondary treatment, applied uniformly to all municipalities and industries, will not yield dissolved oxygen levels commensurate with the water quality criteria that have been established. Either treatment must be initiated on a selective basis to remove the major nitrogenous demands imposed upon the pool, or the dissolved oxygen in the pool must be augmented.

In the absence of a program for such selective removal or augmentation, a statistical water quality control chart was designed to show improvements or deterioration of the water quality by detecting trends which deviate from the normal or expected (historical record). The system can be particularly useful in evaluating the effectiveness of treatment additions in and above the pool. The principles considered pertinent to developing the system and the step-by-step procedures are described in the text.

INTRODUCTION

Insight into the relationships that exist between liquid wastes imposed upon a stream's water and the ability of the stream to assimilate the load is a basic requirement for the intelligent development of a water quality management program. Such a program is particularly important to the rapidly developing Illinois River Valley.

Knowledge of the waste assimilative capacity of streams can provide a more rational basis for water quality rules and regulations than a program developed around uniformity of treatment based primarily upon effluent standards without regard to the capacity of the receiving stream.

It is the purpose of this report to define the mechanics of self-purification under existing organic loads in a 77.4-mile navigational pool of the Illinois Waterway, and to present findings that will provide direction toward a rational approach in maintaining that purity of water specified in water quality standards for the pool.

Scope of Study

The Illinois Waterway, in a series of eight navigational pools, extends 327.2 miles from its confluence with the Mississippi River to Lake Michigan at Chicago. The La Grange pool commences at milepoint 80.2 and extends 77.4 miles to the vicinity of Peoria. Four major rivers, the Mackinaw, Spoon, Sangamon, and La Moine, are tributary to the pool. The Peoria metropolitan area lies immediately above the pool; the city of Pekin and the Pekin industrial complex are located along the upper-most stretch of it. The cities of Havana and Beardstown are located farther downstream. Principal features of the pool are shown in figure 3.

The dissolved oxygen resources and waste assimilative capacity of the La Grange pool were investigated during the summer months of 1965, 1966, and 1967. Determina-

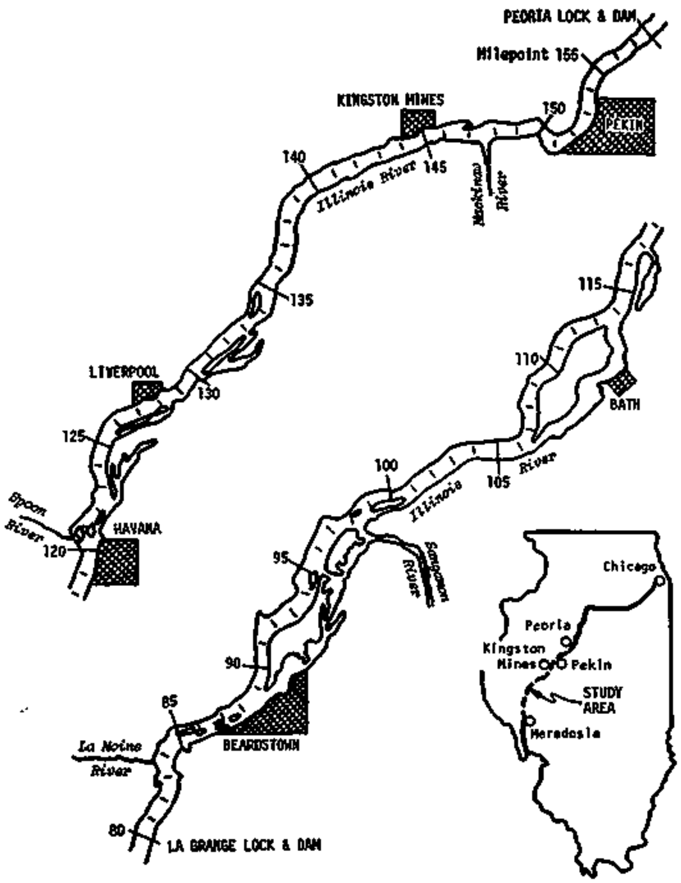

Figure 3. Study area—La Grange pool, Illinois River

tions for dissolved oxygen (DO) and 5-day biochemical oxygen demand (BOD_5) were made within the pool and from the four major tributaries at or near their confluence. Waste discharges from municipalities and industries were not sampled. Dissolved oxygen measurements were made along the length of the pool on 13 days: July 28(29) and August 10, 11, 12, and 13 during 1965; July 22, August 18, 19, 24, 25, 26, and September 29 during 1966; and July 11 during 1967. The July 28(29), 1965, date is considered one sampling date since the upper half of the pool was sampled on the 28th and the lower half on the 29th, under similar hydrologic and waste load conditions. On 14 other days DO measurements were made in either the upper or lower half of the pool. Samples for BOD_5 were collected throughout the pool on July 13, 14, 27, and August 10, 12, and 13 during 1965; and on August 24, 25, and 26 during 1966. Twenty-nine stations (milepoints) were sampled during 1965, and from 8 to 19 were sampled during 1966 and 1967. Although some traverse sampling was conducted, all measurements used to assess the oxygen resources and waste assimilative capacity of the pool were made at 3-foot depths along the centerline of the navigation channel. Analyses were made for carbonaceous, nitrogenous, and total BOD. On several occasions light and dark bottle samples were attached to buoys for incubation in the river near collection points, but the results were inconclusive and are not incorporated in this report.

All sampling was done by boat and usually commenced in the upper portion of the pool at 9:00 a.m. and terminated in the lower reach at 2:00 p.m. The Alsterberg modification of the Winkler method and/or a galvanic cell oxygen analyzer were used for measuring dissolved oxygen concentrations. During 1965 standard dilution techniques were used for determining BOD. During 1966 and 1967 incubated BOD samples were not diluted but were replenished with oxygen, when necessary, by reaeration. The temperature of the river water was recorded at each sampling point.

Data were obtained on the physical characteristics of the pool for computing river velocity, depth, and flow. These parameters were used with observed DO and BOD values to evaluate and compare various methodologies for waste assimilative determinations. Particular emphasis was placed on the river reoxygenation and deoxygenation computational procedures, and estimates were made of the degree of waste reductions required for the pool to maintain certain dissolved oxygen concentrations.

The effect of nitrification (second-stage BOD) on the dissolved oxygen resources of the pool was also investigated. Relationships based upon percent composition were established between second-stage BOD and total BOD.

A statistical quality control chart was developed as a tool for water quality management. The chart was designed to assist in interpreting water quality data generated by a continuous monitor; however, the methods used to construct the DO control chart can be utilized in developing controls for other parameters pertinent to water quality.

Plan of Report

The material in this report is presented in two main sections. The first section describes the methods and basic equations used for evaluating the data; it reviews methodologies for assessing dissolved oxygen relationships in a stream and discusses the functions of each factor involved.

The second section presents and discusses the computed times-of-travel, the dissolved oxygen prediction equations with suggestions for their application, the waste assimilative capacity of the pool, and a series of water quality control charts. Notations for symbols used throughout this report are given in the back (*page 27*).

Acknowledgments

This study was conducted under the general supervision of Ralph L. Evans, Head of the Water Quality Section, and William C. Ackermann, Chief, Illinois State Water Survey. Many other Water Survey personnel contributed. Field measurements and compilation of cross-section data were performed to a considerable extent by engineering assistants Arlin D. Dearing, Ronald E. Peterson, J. Larry Arvin, Robert J. Lapping, Allen R. Thompson, and Michael E. Gregg. The Fortran program required for time-of-travel computations was developed by Shunndar Lin, Assistant Hydrologist. The statistical analyses required for

the velocity constants and ultimate BOD relationships were performed by Dr. James C. Neill, Survey Staff Statistician; Robert Sinclair, System Analyst, provided liaison and programming advice in using the computer service of the University of Illinois. Katherine Shemas, Clerk-Typist, typed the original manuscript; Mrs. J. Loreena Ivens, Technical Editor, edited the final report; and John Brother, Jr., Chief Draftsman, prepared the illustrations.

Extensive cooperation was extended to the authors by Patrick Murphy, Engineer in Charge, U. S. Army Corps of Engineers (Peoria) and his staff; William Starrett, Aquatic Biologist, Illinois Natural History Survey (Havana) ; and Herman Wibben, Engineer in Charge, U. S. Geological Survey (Peoria).

DATA EVALUATION

Time-of-Travel

The U. S. Geological Survey furnished data on Illinois River and tributary flows for the gaging stations listed in table 1. The milepoints listed for the tributaries are their confluence locations on the Illinois River.

Incremental increases in flow in terms of cubic feet per second per mile (cfs/mi) were computed by subtracting the tributary flows from the difference between the gaged values for Meredosia and Kingston Mines and dividing by the distance between the two stations. Flows for the specific sampling points were estimated by using the incremental flow increases and adding tributary flows when appropriate.

Time-of-travel *(t)* determinations were computed by the theoretical volume displacement method in which *t* equals volume divided by average flow. Data for cross sections at 0.2 milepoints were supplied by the U. S. Army Corps of Engineers for volume computations. The cross-sectional areas were adjusted to fit the river stages at the time of sampling. Corps of Engineers staff-gage readings were available at 10 locations for making stage adjustments relative to the mean pool elevation. The average area for a reach was found by summing all the areas in the reach and dividing by the number of areas. This procedure was considered adequate because all the cross-sectional areas were uniformly spaced giving each equal weight. The volume was computed by multiplying the average area by the reach length. Average depths *(H)* were computed by dividing the summation of areas by the summation of widths for a reach.

A flow-duration curve for the Illinois River at Kingston Mines, developed by Mitchell[5] for water years 1940 through 1950, was updated to include the water years 1951 through 1965. These curves are presented in figure 4. The two curves essentially coincide above the 67 percent level. Also, a flow-duration curve for the summer low flow period (June 16—September 16) for the years 1951 through 1965 was constructed. Figure 4 also gives the duration curve for the river at Meredosia for the water years 1921 through 1950. The Meredosia curve was not updated because of its long record and because the updated Kingston Mines curve had varied little from the unadjusted curve. Figure 5 shows duration curves for the four major streams tributary to the La Grange pool. These curves have not been updated.

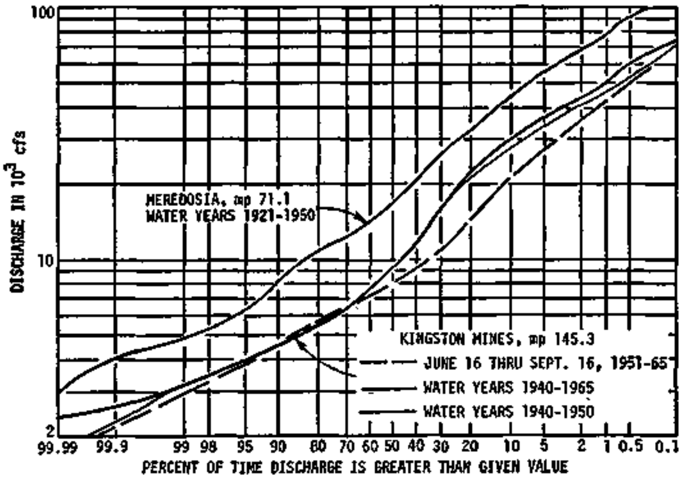

Figure 4. Flow duration curves for La Grange pool

Table I. Streamflow Gaging Stations Relevant to the La Grange Pool

River	Gaging station	Milepoint	Drainage area (sq mi)
Mackinaw	Congerville	147.8	764
Illinois	Kingston Mines	145.3	15,200
Spoon	Seville	120.5	1,600
Sangamon	Oakford	98.0	5,120
La Moine	Ripley	83.7	1,310
Illinois	Meredosia	71.1	25,300

Regression Analyses

Standard regression analysis procedures were used to evaluate the relationships between dissolved oxygen concentration and stream BOD_5, stream temperature, and time-of-travel through the pool. The model used to formulate these relationships was:

$$DO = D \exp (Ax_1 + Bx_2 + Cx_3)$$

where

DO = the dissolved oxygen concentration, in mg/l
exp = base of natural logarithms, 2.71828
A,B,C,D = constants determined by regression analysis
x_1,x_2,x_3 = stream parameter variables

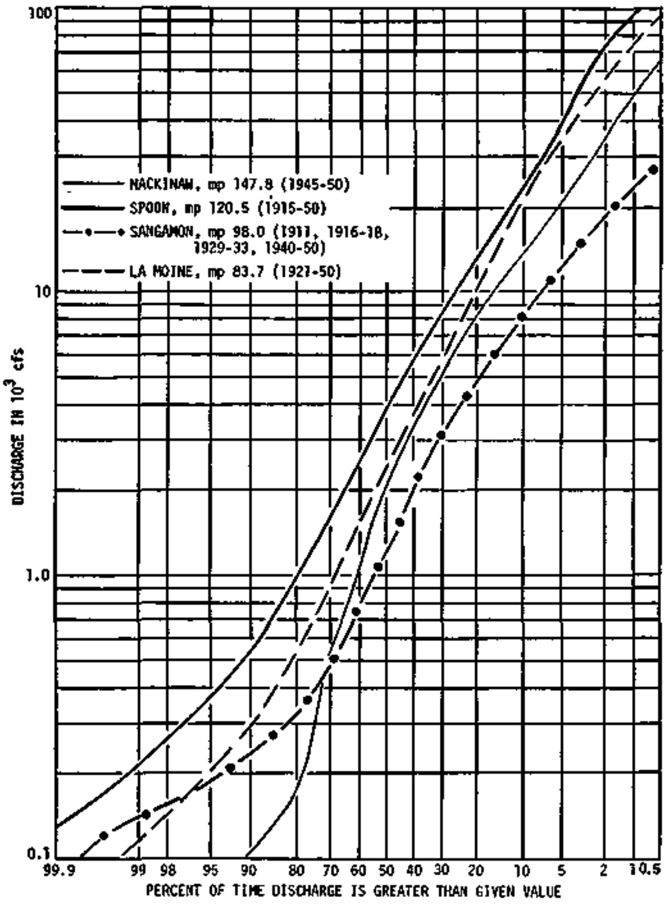

Figure 5. Flow duration curves for major tributaries

Product-moment correlation coefficients were determined between the DO and other stream parameters. A perfect direct correlation is +1.0; a perfect inverse correlation is —1.0. A direct or positive correlation exists between flow and DO; i.e., an increase in flow increases the dissolved oxygen concentration up to some limiting value in waters subjected to a constant organic pollutional load. An inverse or negative correlation exists between dissolved oxygen concentrations and water temperatures; i.e., as water temperatures rise, dissolved oxygen concentrations decrease.

A preliminary analysis indicated that the correlation coefficient between the river BOD_5 and DO was insignificant; i.e., no relationship appeared to exist between them. Analysis of variance was used to determine if the daily BOD_5 concentrations or loads varied significantly from day to day and from station to station.

Regression analysis was also used to develop an empirical equation for predicting the time-of-travel through the pool. Theoretical time-of-travel values, computed by the volume displacement method, were related to the gaged flows at Kingston Mines and Meredosia. The statistically derived equation is in the logarithmic form:

$$t = A x_3^B x_4^C$$

where

t = time-of-travel
x_3, x_4 = gaged flows at the upstream and downstream ends of the pool
A, B, C = constants determined by regression analysis

Dissolved Oxygen Relationships

The concentration of dissolved oxygen in a flowing stream, subject to an oxidizable pollution load, is a function of many variables. Physical forces are engaged in the replenishment of oxygen, through the mechanics of reoxygenation at varying rates. Biochemical reactions, dependent principally on bacteria (both heterotrophic and autotrophic), provide the sink mechanism that depletes oxygen. Small pigmented aquatic organisms, through the process of photosynthesis, may lend support to the physical forces of reaeration. Sludge deposits, when present, in turn support the forces of oxygen depletion. All of these responses are a function of time, temperature, and dissolved oxygen saturation. Even with considered judgment and experience only reasonable estimates can be derived in assessing the independent effects and rates of interplay of these conflicting stresses on the dissolved oxygen resources of a stream.

Oxygen-Sag Curve. The most widely used method for evaluating the waste assimilative capacity of a river is the Streeter-Phelps[6] oxygen-sag equation which was developed for use on the Ohio River in 1914. The basic equation is:

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

where

D = dissolved oxygen deficit at time t (D can be in lb/day or mg/l and t is in days)
D_a = initial oxygen deficit in lb/day or mg/l
L_a = ultimate BOD in lb/day or mg/l
K_1 = deoxygenation coefficient to the base e, day^{-1}
K_2 = reoxygenation coefficient to the base e, day^{-1}

This formula is based on two assumptions: 1) at any instant the rate of deoxygenation is directly proportional to the amount of oxidizable organic material present, and 2) the rate of reoxygenation is directly proportional to the dissolved oxygen deficit. Mathematical expressions for these assumptions are:

$$dD/dt = K_1 (L_a - L_t)$$

and

$$dD/dt = -K_2 D$$

The term dD/dt is the net rate of change in the dissolved oxygen deficit, and L_t is the BOD at any time t; the other terms have been previously defined. Combining the two differential equations and integrating between the limits of t equals zero at D_a and t equals any time-of-travel below D_a yields the basic equation developed by Streeter and Phelps.[6]

Computational Methods for K_1 and L_a. Many researchers have worked on developing and refining formulas and methods for use in evaluating the deoxygenation *(K_1)* and reaeration *(K_2)* constants and the ultimate BOD (L_a). In this study of the waste assimilative capacity of the La Grange pool, various methods and formulas were investigated to determine the ones most applicable for computing K_1, K_2, and L_a.

Six methods for computing K_1 and L_a were evaluated. These methods included 1) Thomas slope, 2) method of moments, 3) rapid ratio, 4) daily difference, 5) Reed-Theriault, and 6) least squares using BOD_5. Each method is based on laboratory incubated BOD's. Methods 1 and 4 are semigraphical solutions developed by Thomas[7] and Tsivoglou,[8] respectively; method 2 requires the use of special curves published by Moore et al.[26]; method 3 can be solved using curves developed by Sheehy[9]; method 5 is a least-squares fit of the monomolecular equation developed by Reed and Theriault[10]; and method 6 is a modification of a procedure recommended by O'Connor [11] for computing river deoxygenation constants. A digital computer program was used to determine K_1 and L_a by the Reed-Theriault method.

The ultimate BOD and K_1 values that were determined in the laboratory at 20 C were adjusted to river temperatures. The ultimate BOD correction formula used was:

$$(L_a)_T = (L_a)_{20}(0.02T + 0.6)$$

where $(L_a)_{20}$ is the ultimate BOD at 20 C and $(L_a)_T$ is the ultimate BOD at any temperature T. The K_1 correction formula used was:

$$(K_1)_T = (K_1)_{20}(1.047^{T-20})$$

where $(K_1)_{20}$ is the K_x value at 20 C and $(K_1)_T$ is the K_1 value at any temperature T. A discussion of the application of both formulas is given by Babbitt and Bauman.[12]

The O'Connor method consists of determining BOD_5's on water samples collected at various milepoints in the stream and plotting the BOD_5 (lb/day) versus time-of-travel (days) on semilog paper. The plot results in two straight lines if a waste load that is discharged at or near the beginning of the river reach is large compared with the river BOD load entering the reach. If the. waste discharge is relatively small compared with that upstream in the river, one straight line will result. A plot with a steep slope below an outfall indicates that settling and/or volatilization may be occurring. This initial physical activity does not create an immediate BOD in the stream; however, it should be considered in the basic Streeter-Phelps[6] equation. O'Connor makes an allowance in the basic equation by replacing K_1, the deoxygenation constant, with two constants K_r and K_d K_r represents the removal rate of potential oxygen-consuming wastes by biological and physical factors, and K_d represents the biological deoxygenation rate which may include the effects of biological extraction from benthic growths. The O'Connor modification of the basic Streeter-Phelps equation is:

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

If little or no settling or volatilization occurs, $K_r == K_d$ and the equation reduces to the basic form.

Because some BOD removal, presumably from settling, occurred in the Pekin area, the basic O'Connor approach was tried with some modification. In the O'Connor method K_r and K_d are determined by visually fitting curves to the data, whereas in this study K_r and K_g, were determined by least-squares statistical procedures.

O'Connor computes the ultimate BOD for the station at the beginning of the reach by one of the procedures mentioned above such as the Thomas slope[2] or method of moment.[26] The ultimate BOD determined thusly is used in conjunction with K_r and K_d in the modified Streeter-Phelps equation. The authors believe, however, that the river BOD plot should be used to compute the ultimate BOD since K_r and K_d were determined from it. The ultimate BOD can be determined from the 5-day river BOD plot by fitting the data by least-square regression procedures to the following general equation:

$$L_t = L_{at} \exp(-K_d t)$$

where

L_t = the BOD remaining at incubation time t (t = 5 days in this case)
L_{at} = the BOD at incubation time t for the beginning of a reach
K_d = deoxygenation constant
t = incubation time

After solving for L_{at} and K_d, one can determine L_a with the exponential equation $L_t = L_a \exp(-K_d t)$, where $L_t = L_{at}$.

Computation Methods for K_2. The factor that has stimulated much thought and research is the reoxygenation constant K_2. Several theoretical and empirical formulas have been developed to compute K_2 by relating it to stream velocity and depth. Considerable controversy persists as to which method or formula is best. O'Connor and Dobbins[13] developed the semiempirical formula:

$$K_2 = 24(D_L U)^{1/2}/H^{3/2}$$

where

D_L = coefficient of diffusion = 8.1×10^{-5} ft²/hr at 20 C
U = velocity in ft/hr
H = average depth in ft

A similar formula, empirically derived from full-scale stream studies by Churchill, Elmore, and Buckingham[14] is:

$$K_2 = 5V/H^{5/3}$$

where

V = average velocity in fps
H = average depth in ft

The O'Connor and Dobbins equation is based on theory more general than that for the formulas developed by several of the other investigators; consequently, it had been chosen originally as the only one to use in this study. The empirical formulas developed by Krenkel and Orlob[15] and that described above[14] appear to be more restrictive in their use. Langbein and Durum[10] of the USGS have analyzed and summarized the work of several investigators and have concluded that the most applicable formulation of the reaeration factor is:

$$K_2 = 7.63V/H^{1.33}$$

Comparisons of the reaeration coefficients obtained using these formulas[13,14,16] were made with computed Illinois River depths and velocities.

The K_2 values were corrected for river temperatures using the equation developed by Streeter, Wright, and Kehr[17]:

$$(K_2)_T = (K_2)_{20}\ (1.016^{T-20})$$

where $(K_2)_T$ is the K_2 value at any temperature T and $(K_2)_{20}$ is the K_2 value at 20 C.

Velz Reoxygenation Curve. Another approach for determining the waste assimilative capacity of a stream is a method first developed and used by Black and Phelps[2] and later refined and used by Velz.[4] For this method deoxygenation and reoxygenation computations are made separately, then added algebraically to obtain the net oxygen balance. This procedure can be expressed mathematically as:

$$DO_{net} = DO_a + DO_{rea} - DO_{used}$$

where

DO_{net} = dissolved oxygen at the end of a reach
DO_a = initial dissolved oxygen at beginning of a reach
DO_{rea} = dissolved oxygen absorbed from the atmosphere
DO_{used} = dissolved oxygen consumed biologically

The dissolved oxygen used (DO_{used}) is assumed to be a first-order biological reaction similar to that assumed in the derivation of the Streeter-Phelps equation.[6] Consequently, the oxygen usage can be computed from the expression:

$$DO_{used} = L_a\ [1 - \exp(-K_1 t)]$$

L_a and K_1 are determined experimentally in the same manner as for the Streeter-Phelps method.

The reaeration term (DO_{rea}) in the equation is the most difficult to determine. In their original work, Black and Phelps[2] experimentally derived a reaeration equation based on principles of gas transfer or diffusion across a thin water layer in a quiescent or semiquiescent system. A modified but equivalent form of the original Black and Phelps equation is given by Gannon[18]:

$$R = 100 - \left(\frac{1 - B_0}{100}\right)(81.06)\ \left(e^{-K} + \frac{e^{-9K}}{9} + \frac{e^{-25K}}{25} + \ldots\right)$$

where

R = percent of saturation of DO absorbed per mix
B_0 = initial DO in percent of saturation
$K = \pi^2 am/4L^2$ in which m is the mix or exposure time in hours, L is the average depth in centimeters, and a is the diffusion coefficient used by Velz

The diffusion coefficient a was determined by Velz[19] to vary with temperature according to the expression $a_T = a_{20}\ (1.1^{T-20})$, in which a_T and a_{20} are the coefficients at T C and 20 C, respectively. When the depth is in feet $a_{20} = 0.00153$, and when depth is in centimeters $a_{20} = 1.42$.

Although the theory upon which this reaeration equation was developed is for quiescent conditions, it is still applicable to moving and even turbulent streams. Phelps[3] indicates this can be explained in either of two ways:

> a) "Turbulence actually decreases the effective depth through which diffusions operates. Thus, in a turbulent stream, mixing brings layers of saturated water from the surface into intimate contact with other less oxygenated layer from below. . . . The actual extent of such mixing is difficult to envision, but it clearly depends upon the frequency with which surface layers are thus transported. In this change-of-depth concept therefore there is a time element involved."
>
> b) "The other and more practical concept is a pure time effect. It is assumed that the actual existing conditions of turbulence can be replaced by an equivalent condition composed of successive periods of perfect quiescence between which there is instantaneous and complete mixing. The length of the quiescent period then becomes the time of exposure in the diffusion formula, and the total aeration per hour is the sum of the successive increments or, for practical purposes, the aeration period multiplied by the periods per hour."

Because the reaeration equation involves a series expansion in its solution, it is not readily solved by desk calculations. To facilitate the calculations, Velz[4,19] published a slide-rule curve solution to the equation. This slide-rule curve is reprinted here as figure 6 (for its use, consult reference 19). Velz's curve has been verified as accurate by two independent computer checks, one by Gannon[18] and the other by Butts.[20]

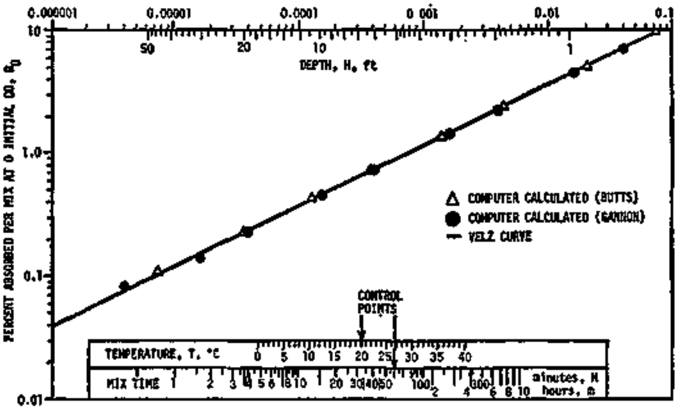

Figure 6. Standard reoxygenation curve

Although the Velz curve is ingenious, it is somewhat cumbersome to use. Therefore, a nomograph[21] was developed during this study for a quick, accurate desk solution of R at zero initial DO (B_0 = 0 in the Black and Phelps equation). The nomograph, presented in figure 7, was constructed on the premise that the exposure or mix time is characterized by the equation

$$M = (13.94)\log_e(H) - 7.45$$

in which M is the mix time in minutes and H is the water depth in feet. This relationship was derived experimentally and reported by Gannon[18] as valid for streams having average depths greater than 3 feet, as in the La Grange pool. For an initial DO greater than zero, the nomograph value is multiplied by $(1 - B_0)$ expressed as a fraction because the relationship between B_0 and the equation is linear.

The use of the nomograph and the subsequent calculations required to compute the oxygen absorption is best explained by an example:

Given:

H = 14.7 feet
T= 15 C
Initial DO of stream = 45 percent of saturation
DO load at saturation at 15 C = 10,000 pounds
Time-of-travel in stream reach = 0.10 days

Find:

M, mix time in minutes; R_0, the percent DO absorbed per mix at zero initial DO; and DO_{rea}, the total oxygen absorbed in the reach.

Solution:

Connect 14.7 feet on the depth scale with 15 C on the temperature scale; read 30 minutes on the M scale and 0.16 percent on the R_0 scale.

Since R_0 is the percent of the saturated dissolved oxygen absorbed per mix when the initial DO is at 100 percent deficit (zero DO), the oxygen absorbed per mix at 100 percent deficit will be the product of R_0 and the DO load at saturation. For the above example, it is 0.16%/100 times 10,000 pounds, or 16 pounds per mix per 100 percent deficit. However, the actual DO absorbed per mix is only 1 — (45%/100) times 16, or 8.8 pounds per mix because the amount absorbed is directly proportional to the deficit. Finally, the number of mixes per reach must be determined. The time-of-travel is given as 0.10 days or 144 minutes and the mix time (M) was found to be 30 minutes. Consequently, the number of mixes in the reach is 144/30 or 4.8. Reoxygenation in the reach is therefore equal to the product of the DO absorbed per mix times the number of mixes per reach or 42 2 pounds. The procedures and computations can be summarized by the expression:

$$DO_{rea} = \left(1 - \frac{\%\,\text{DO saturation}}{100}\right)\left(\frac{R_0}{100}\right)\left(\frac{t}{M}\right) \times (\text{DO saturation load})$$

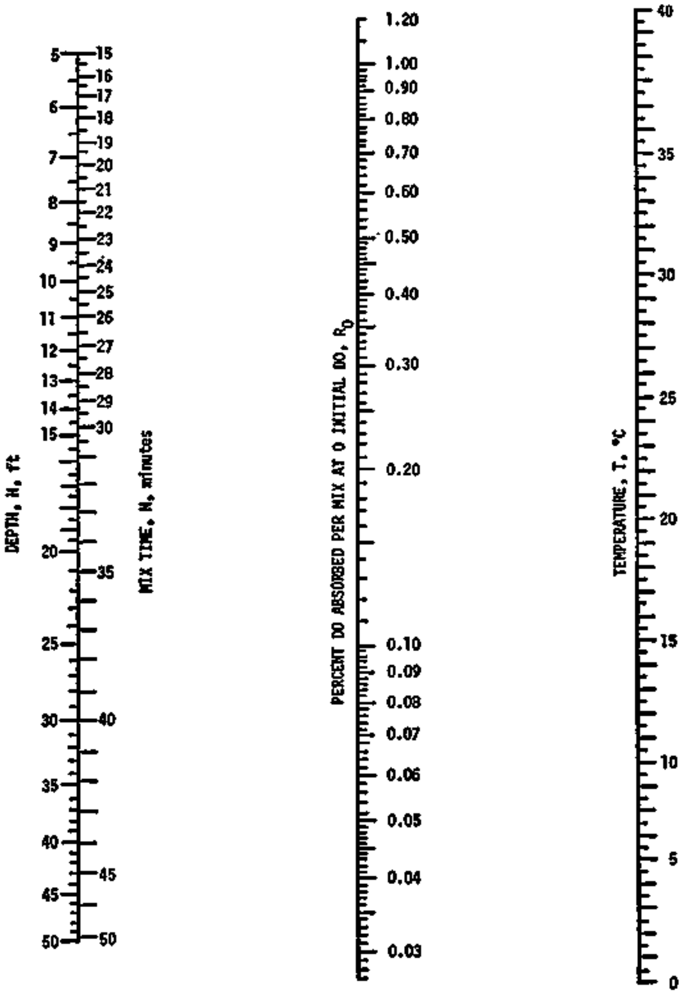

Figure 7. Oxygen absorption nomograph

The dissolved oxygen used (BOD) can be computed with only field-observed dissolved oxygen concentrations and the Velz reoxygenation curve. From the basic equation, the dissolved oxygen used in pounds per day can be expressed as:

$$DO_{used} = (DO_a - DO_{net}) + DO_{rea}$$

The terms DO_a and DO_{net} are the observed field dissolved oxygen values at the beginning and end of a subreach, respectively, and DO_{rea} is the reoxygenation in the subreach computed by the Velz curve. If the dissolved oxygen usage in the river approximates the first-order biological reaction, a plot of the summations of the DO_{used} versus time-of-travel can be fitted to the equation, $DO_{used} = L_a\,[1 - \exp(-K_1 t)]$. The fitting of the computed values to the equation must be done by trial and error, and a digital computer was utilized to facilitate this operation. A program originally written for use by the State Water Survey for determining the relationship of well-loss coefficients with well parameters was modified and adapted to this problem.

The program makes a first approximation of L_a and K_1 by setting L_a equal to the total DO used in the reach and K_1 equal to an arbitrary value of 0.55. Initial step sizes of K_1 are set at 0.5 and 0.05. The larger step is used if the first approximation of K_1 is found to be greatly in error. When a close approximation is reached, the step size is changed to 0.05. Usually 35 iterations are made; however, for some of the data over 700 cycles were required to get a good fit. During each cycle, K_1 is changed by its step size, and the DO_{used} for each subreach is calculated. A comparison is then made between the computer calculated values and the observed values. The errors between the calculated and observed values for each observation are squared and summed. By successively changing K_1 and recalculating and summing the resulting errors and adjusting K_1 accordingly over 35 cycles (or more in a few cases), various fits of the data are obtained. From the best fit, the ultimate BOD (L_a) and the deoxygenation coefficient (K_1) are estimated. This program is essentially equivalent to the Reed-Theriault method of fitting laboratory BOD data to the monomolecular equation.

RESULTS AND DISCUSSION

The flow characteristics of a navigational pool, biased by controls uncommon to natural streamflow, permit assessment of its dissolved oxygen resources in terms of minimum and average DO. Temperatures also can be considered in terms of averages. Equally important is the relative constancy of volume and depth, within limits, regardless of flow patterns. Accurate time-of-travel data are particularly important in analyzing the waste assimilative capacity of controlled flow existing in a navigational pool. The procedures used, and findings developed in an effort to relate these elements in proper proportions follow.

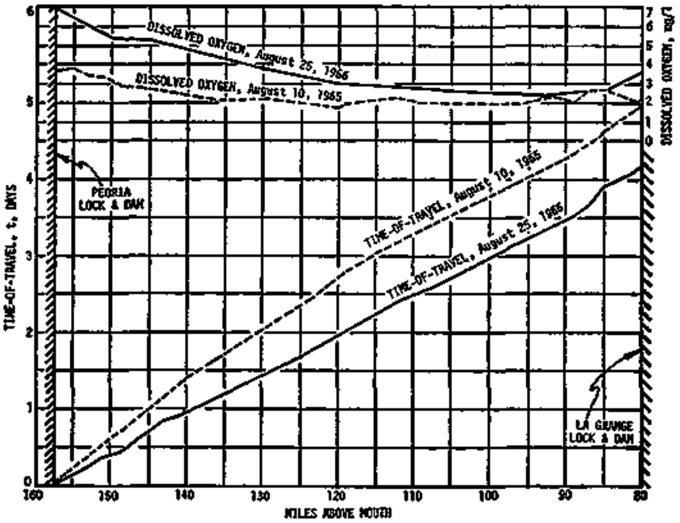

Figure 8. Time-of-travel versus dissolved oxygen

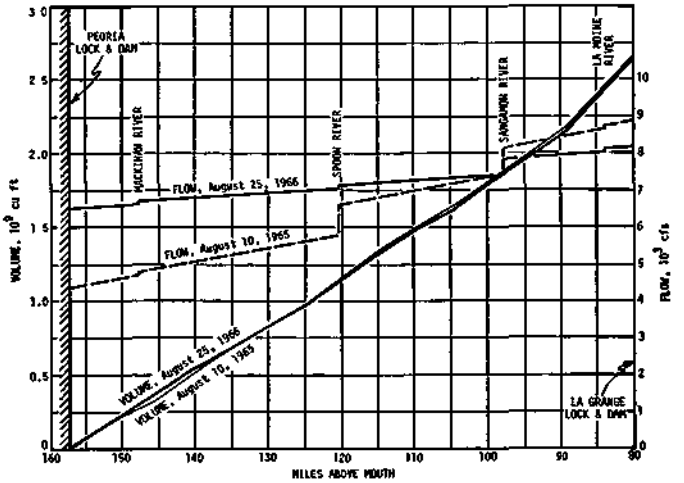

Figure 9. Flow-volume relationship

Time-of-Travel

Soundings taken by the U. S. Army Corps of Engineers at 0.2-mile intervals provided excellent data for use in making time-of-travel computations. The volume displacement method was programmed into a IBM 360/50 computer for determining time-of-travel and other parameters at 46 locations within the pool. These locations included cross sections where DO and BOD_5 determinations were made at least once during regular sampling days. The program can be easily modified for use in computing travel times for any stream or river for which cross sections are available. Included in the computer printout, in addition to time-of-travel data, are subreach average depths, widths, and cross-sectional areas; subreach lengths and volumes; average flows within the subreaches; and flows at each cross section.

Figures 8 and 9 illustrate the relationships between dissolved oxygen, time-of-travel, flow, and pool volume for two sampling days. The pool BOD_5 loads and water temperatures were essentially the same during both periods. However, on August 10, 1965, the average pool DO was 36 percent less than that on August 25, 1966. This difference can be attributed primarily to the increase in time-of-travel since the difference in the average pool flows was less than 11 percent (figure 9). Solely on rhe basis of dilution, the DO should have decreased only 11 percent instead of 36 percent. The pool volumes are essentially equal (figure 9) for both dates irrespective of the differences in flow. On another date, July 11, 1967, even though the flow was 58 percent greater than the flow on August 10, 1965, the volume was only 8 percent greater. This demonstrates that the pool operates like a huge holding tank during intermediate to low flows. Control of the pool elevation, a requirement for navigation purposes, creates this effect.

A rapid means of computing the total time-of-travel *(t)* through the pool was obtained by developing a logarithmic regression equation relating the computer calculated times to the gaged flows at Kingston Mines (Q_k) and Meredosia (Q_m) • The equation, where t is in days, is:

$$t = 4058 Q_k^{-0.5369} Q_m^{-0\ 2161} \tag{1}$$

$$r = -0.995$$

$$SE = 0.0912 \text{ days}$$

$$n = 14$$

$$\text{Limits: } Q_k = 3560 \text{ to } 9800 \text{ cfs}$$

$$Q_m = 6270 \text{ to } 11{,}500 \text{ cfs}$$

Table 2 summarizes the time-of-travel values calculated with the computer and by equation 1. A twofold increase in time occurs between the lowest and highest values. The lowest time-of-travel (higher flow) is for a flow duration (percentage of time a given flow is equaled or exceeded) of approximately 62 percent; the highest time-of-travel is for a flow duration of 87 percent. The arithmetic average flow for the pool has a duration of approximately 40 percent. These duration percentages are average values for the Kingston Mines and Meredosia gages.

Time-of-travel prediction equations can be readily developed for any location in the pool. A series of equations would be useful in predicting times for use in computing oxygen-sag profiles.

Table 2. Time-of-Travel in La Grange Pool Calculated with Computer and Regression Equation

Date	Time (days)		Date	Time (days)	
	Computer	Equation		Computer	Equation
7/11/67	3.3049	3 2218	8/19/66	4 8264	4 8736
8/26/66	4 1874	4 2896	8/18/66	4 8329	4.7572
8/25/66	4 1944	4 2628	8/10/65	4 9641	4 9602
8/24/66	4 4165	4 4601	8/4, 5/66	5 1553	5 1750
8/12/65	4.4886	4.5031	7/22/66	5 2582	5 2589
8/13/65	4 6275	4 6921	9/29/66	5.4983	5.4029
8/11/65	4.7613	4 7281	7/28(29)/65	6.5067	6 2766

Dissolved Oxygen Prediction Equations

Multiple regression techniques were used to develop empirical equations for predicting the weighted average and minimum dissolved oxygen concentrations in the pool. The assumption was made that the average pool water temperature (T_A), time-of-travel (t), and biochemical oxygen demand (BOD) are the principal parameters which affect the average (DO_A) and the minimum (DO_M) dissolved oxygen. The temperature versus DO and time versus DO relationships were found to fit an exponential model best. The daily BOD_5 level in the pool appeared to remain relatively constant. Eleven days of data were available for analyzing the relationships between the variables during low summer flows. Several days of data were available for higher flows or for cooler water conditions but were not used in developing prediction equations.

Dissolved Oxygen and Temperature. The equation developed to relate the average pool dissolved oxygen concentration to the average pool temperature was:

$$DO_A = 50.89 \exp(-0.1123 T_A)$$

The equation implies that as the temperature increases the DO decreases exponentially. The sample correlation coefficient between the logarithms of the average DO's and the average temperatures is —0.83; this value is significant at a 1 percent level or less. Consequently, over a 99 percent chance exists that a true exponential relationship exists between the two variables. The 95 percent confidence limits for the correlation coefficient is — 0.47 to — 0.95. This means that only a 2.5 percent chance exists that the true population correlation is less than —0.47 or greater than —0.97.

The equation developed to relate the minimum pool DO to the average pool temperature was:

$$DO_M = 79.50 \exp(-0.1474 T_A)$$

The sample correlation coefficient and the 95 percent confidence limits are the same as for the DO_A -T_A relationship.

Dissolved Oxygen and Time. The equation developed to relate the average pool DO to the time-of-travel through the pool was:

$$DO_A = 17.12 \exp(-0.3658 t)$$

The average pool DO also decreases exponentially with increases in time-of-travel. The sample correlation coefficient is — 0.92, and the 95 percent confidence limits are — 0.77 to — 0.98. The relationship between *DOA* and t is highly significant, which emphasizes the importance of time-of-travel on dissolved oxygen.

The equation relating the minimum pool DO to the time-of-travel was:

$$DO_M = 18.06 \exp(-0.4678 t)$$

The sample correlation coefficient is —0.90, and the 95 percent confidence limits are — 0.63 to — 0.97. The time-of-travel influence on DO_M is approximately the same as for DO_A .

Time and Temperature. Because t and T_A are inversely and exponentially related to the dissolved oxygen, the relationship between them should be positive and linear with t being the independent variable. The equation, $T_A = 2.297t + 14.302$, was developed to express this relationship. The sample correlation coefficient is + 0.78; the 95 percent confidence limits are + 0.33 to + 0.93.

Dissolved Oxygen and BOD_5. An analysis of data collected during this study, as well as that made by Wisely and Klassen[1] in 1936, indicates that daily DO and BOD_5 variations in the river below Peoria are not highly correlated. The BOD_5 values at a given station appear to vary or fluctuate little during summer low flows. For example, the mean and standard deviation of 38 BOD_5's reported by Wisely and Klassen for the river at Peoria during steady summer flow conditions are 5.2 and ± 0.8 mg/1. This means that 68 percent of the BOD_5 values

Table 3. Statistical Comparison of 1936 and 1966-1967 5-day BOD-DO Data

Location	Mile point		Number of samples		Mean of BOD (*mg/l*)		Standard deviation of BOD (*mg/l*)		BOD_5-DO correlation	
	1936	1966-67	1936	1966-67	1936	1966-67	1936	1966-67	1936	1966-67
Peoria	166.1		38		5.2		0.8		+.32	
Pekin	152.9	157 or 153	37	18	9.4	5.5	1.9	1.7	—.37	—.05
Kingston Mines	145.5	146.0	42	9	8.0	6.0	1.6	0.9	—.56	—.57
Havana	119.6	120.0	45	11	5.9	5.1	1.5	1.7	—.26	+.49
Beardstown	88.6	87.0	37	8	4.5	5.9	1.3	1.2	—.52	—.63

were expected to range between 4.4 and 6.0 mg/1. Table 3 summarizes some statistical comparisons between the stations sampled during 1936 and similar ones sampled during this study.

For the summary in table 3 all BOD- data were adjusted to a common base of 8160 cfs, the average flow experienced at Peoria during the 1936 study. The variance in BOD_5 during both periods was relatively small. Since the BOD_5 test accuracy is probably less than ±15 percent, the true variance in the BOD_5 from day to day is small. For example, subtracting 15 percent of the mean values from the standard deviations results in standard deviations of less than 0.9 mg/1 for all stations during both periods. No statistical difference was found between the standard deviations either between periods for a given station or between stations except for Kingston Mines.

The correlation coefficients given in table 3 demonstrate that consistent, meaningful BOD, and DO relationships probably cannot be derived for the Illinois River at or below Peoria under the narrow range of BOD_5's found in the waterway. A surprising result is that positive correlations occurred for the relatively large DO and BOD_5 sample at Peoria in 1936, as well as for the small sample at Havana during this study. If these coefficients were truly significant, BOD increases could cause increases in DO, but this is unlikely.

Dissolved Oxygen-Time-Temperature Relationships. The development of a dissolved oxygen prediction equation using only time-of-travel and water temperature was conceived since both factors were found to be highly correlated to DO while BOD, was not. The river BOD- appears to change little with time at a given station, and any such changes that do occur are not necessarily in accordance with DO changes. The development of a prediction equation without a BOD_5 factor assumes that the river waste load is constant. Such an assumption appears justified in this study and can be used to advantage in analyzing and assessing the dissolved oxygen resources in the pool. For instance, knowing that historically the BOD_5 remains reasonably constant from day to day makes it possible to predict the DO using time-of-travel (or flow) and water temperature; if the predicted DO deviates from the observed by a value greater than the limits of accuracy of the prediction equation, a change in the system has probably occurred. The equation, in essence, can be used as a warning device.

The multiple regression equation developed for predicting the average pool DO using time-of-travel and average pool water temperature is:

$$DO_A = 30.24 \exp\left[-\left(0.2761t + 0.03944T_A\right)\right] \qquad (2)$$

$$r = -0.94$$

$$SE = 0.26 \text{ mg/l}$$

$$\text{Limits:}\quad t = 4.1 \text{ to } 6.6 \text{ days}$$

$$T_A = 23 \text{ to } 29 \text{ C}$$

Similarly, the equation developed for predicting the minimum DO, with the same limits of t and T_A, is:

$$DO_M = 41.71 \exp\left[-\left(0.3487t + 0.05576T_A\right)\right] \qquad (3)$$

$$r = -0.92$$

$$SE = 0.29 \text{ mg/l}$$

Equations were developed for predicting dissolved oxygen concentrations which are expected to be either greater or less for 2.5 percent of the time under a given set of temperature and time-of-travel conditions. This was accomplished by passing planes (equations) through points defined by the mean of the DO sample plus or minus two standard deviations and parallel to the prediction planes (equations). Observed DO's falling consistently above or below the 2.5 percent limits indicate that a change in the river waste load has probably occurred.

The following equations represent the average pool DO which is expected to be greater or less 2.5 percent of the time:

$$DO_{A<2.5} = 24.84 \exp\left[-\left(0.2761t + 0.03944T_A\right)\right] \qquad (4)$$

$$DO_{A>2.5} = 35.64 \exp\left[-\left(0.2761t + 0.03944T_A\right)\right] \qquad (5)$$

Similarly, the equations for the minimum pool DO are:

$$DO_{M<2.5} = 28.83 \exp\left[-\left(0.3487t + 0.05576T_A\right)\right] \qquad (6)$$

$$DO_{M>2.5} = 54.60 \exp\left[-\left(0.3487t + 0.05576T_A\right)\right] \qquad (7)$$

The limits for equations 4, 5, 6, and 7 are the same as for equations 2 and 3. These equations are empirically derived from statistical manipulation of observed data and therefore should be used only with t or T_A values within or close to the derivation limits.

Table 4 shows the average and minimum dissolved oxygen concentrations computed by equations 2 and 3 in comparison with the 11 observed values used to develop the equations.

Table 5 gives a comparison of computed minimum dissolved oxygen concentrations and values observed at or near the area in the pool where the low point on the oxygen-sag curve usually occurs. The time-of-travel values

Table 4. Computed DO versus Observed DO

Date	DO_A (mg/l) Observed	DO_A (mg/l) Computed	DO_M (mg/l) Observed	DO_M (mg/l) Computed
7/28(29)/65	1.65	1.63	0.9	0.88
8/10	2.45	2.97	1.9	1.92
8/11	3.19	3.10	2.3	2.03
8/12	3.26	3.32	1.9	2.22
8/13	2.99	3.08	1.9	2.00
7/22/66	2.27	2.41	1.2	1.45
8/18	2.94	2.71	2.0	1.69
8/19	2.52	2.73	1.8	1.70
8/24	3.75	3.56	3.0	2.45
8/25	3.85	3.73	2.4	2.58
8/26	4.20	3.81	2.4	2.67

Table 5. Computed versus Observed Low Dissolved Oxygen Concentrations

Date	Q_h (cfs)	Q_m (cfs)	t (days)	T_A (°C)	DO_M (mg/l) Observed	DO_M (mg/l) Computed
7/13/65	5,510	12,100	4.3935	27.0	2.7	2.0
7/14/65	5,550	11,600	4.4069	27.6	1.6	1.9
7/22/65	3,440	9,650	5.9840	26.4	1.2	1.2
7/27/65	3,690	7,320	6.1431	28.1	0.4	1.0
7/30/65	3,780	6,680	6.1686	28.2	1.0	1.0
7/27/66	5,830	7,380	4.7609	28.5	1.8	1.6
8/1/66	6,280	11,100	4.1500	27.4	2.4	2.1

were computed by equation 1; the temperatures are averages of values extending over at least one-half of the pool length.

The relative effects of time and temperature on dissolved oxygen can be determined by taking the total derivative of the empirical equation for the average dissolved oxygen concentrations:

$$dDO_A = f_t(t,T_A)\,dt + f_{T_A}(t,T_A)\,dT_A$$

Therefore:

$$dDO_A = \frac{\partial DO_A}{\partial t}\,dt + \frac{\partial DO_A}{\partial T_A}\,dT_A \qquad (8)$$

$$\frac{\partial DO_A}{\partial t} = (-0.2761)\,(30.24) \times \exp[-(0.2761t + 0.03944T_A)] \qquad (9)$$

$$\frac{\partial DO_A}{\partial T_A} = (0.03944)\,(30.24) \times \exp[-(0.2761t + 0.03944T_A)] \qquad (10)$$

Substituting 9 and 10 into 8 and factoring terms yields:

$$dDO_A = (0.2761dt + 0.03944dT_A)\,30.24 \times \exp[-(0.2761t + 0.03944T_A)] \qquad (11)$$

This indicates that, for small incremental changes in the average dissolved oxygen concentration (dDO_A), t and TA are related by the proportion $0.2761dt{:}0.03944dT_A$.

TA has been shown to be related to t by the formula $TA = 2.297t + 14.302$. Differentiating TA with respect to t yields $dT_A = 2.297dt$. If $2.297dt$ is substituted for dT_A in equation 11, the ratio of the effects of t and TA on the average dissolved oxygen becomes:

$$0.2761dt{:}(0.03944)\,(2.297dt) = 3{:}1$$

Thus, during low summer flows the time-of-travel has approximately three times more effect on the dissolved oxygen concentration than does the average pool temperature.

Similarly, for equation 3 which relates t and TA to the minimum dissolved oxygen concentration in the pool, the ratio of the effects of t and TA is:

$$\begin{aligned} 0.3487dt{:}0.05576dT_A &= 0.387dt{:}(0.05576)\,(2.297dt) \\ &= 2.7{:}1 \end{aligned}$$

Apparently, temperature influences the minimum dissolved oxygen concentration slightly more than it does the average dissolved oxygen concentration.

Application of Equations. The regression equations can be useful in obtaining rapid estimates of the dissolved oxygen conditions in the pool during summer low flow conditions. For example, aa investigator might want to estimate probable conditions in the pool at flows of 95 and 90 percent duration at Kingston Mines and Meredosia, respectively, and at an average water temperature of 25 C.

First, the time-of-travel through the pool can be estimated. From figure 4, Q_h and Q_m are determined to be 4000 and 8200 cfs, respectively. Substituting these flows into equation 1 gives a reasonable estimate of the time-of-travel :

$$t = 4058(4000^{-0.05369})\,(8200^{-0.2161}) = 5.680 \text{ days}$$

Then, the average and minimum dissolved oxygen concentrations in the pool can be estimated from equations 2 and 3:

$$\begin{aligned} DO_A &= 30.24 \exp[-(0.2761)\,(5.68) + (0.03944)\,(25)] \\ &= 2.4 \text{ mg/l} \\ DO_M &= 41.71 \exp[-(0.3487)\,(5.68) + (0.05576)\,(25)] \\ &= 1.4 \text{ mg/l} \end{aligned}$$

The equations were used to check the dissolved oxygen resources observed throughout the pool on July 11, 1967. The observed average and minimum pool dissolved oxygen concentrations were 4.37 and 2.5 mg/1, respectively, and flows at Kingston Mines and Meredosia were 9800 and 11,500 cfs, respectively. These flows give an estimated time-of-travel from equation 1 of 3.2218 days compared with a displacement calculated flow time of 3.3049 days. The time is somewhat less than the lower limit for which the DO equations were derived but reasonable results should be achieved. The average pool temperature was 26.7 C. Therefore the predicted DO's are:

$$\begin{aligned} DO_A &= 30.24 \exp[-(0.2761)\,(3.2218) + (0.03944)\,(26.7)] \\ &= 4.32 \text{ mg/l} \\ DO_M &= 41.71 \exp[-(0.3487)\,(3.2218) + (0.05576)\,(26.7)] \\ &= 3.1 \text{ mg/l} \end{aligned}$$

The predicted DO_A agrees very closely with the observed. However, the observed DO_M is approximately 20 percent less than the calculated value. Consequently, a check was

Table 6. Predicted DO Conditions for a 2-Foot Navigation Channel Depth Increase

	Dissolved oxygen concentration (mg/l)							
	Average (Existing)				Minimum (Existing)			
Date	Observed	Computed	Predicted	% Decrease*	Observed	Computed	Predicted	% Decrease*
7/28(29)/65	1 650	1 630	1.367	16 2	0 9	0.884	0 705	20 3
8/10	2 451	2 968	2 489	16 2	1 9	1 923	1 543	19.7
8/11	3 186	3 103	2 752	11.3	2.3	2.031	1.752	13 7
8/12	3 264	3 319	2 960	10 7	1 9	2 219	1.914	13.7
8/13	2.989	3 083	2 737	11.3	1 9	2 002	1.721	14.0
7/22/66	2 267	2 410	2.084	13.3	1 2	1.449	1 210	16.5
8/18	2 937	2 713	2 393	11 8	2 0	1 665	1.439	14.6
8/19	2 521	2 729	2 393	12 4	1.8	1 704	1 443	15 3
8/24	3.746	3 564	3 181	10 7	3 0	2 448	2.113	13.7
8/25	3.854	3.730	3 338	10 6	2 4	2 578	2 244	22.8
8/26	4 195	3 812	3 405	10 7	2 4	2.665	2 319	23 0
7/11/67	4.371	4.236	3.916	7 4	2 5	2.966	2.703	8.7

** Percentage decrease between existing computed DO and predicted DO*

made using equation 6 to determine if the difference was possibly due to an increased waste load.

$$DO_{M<25} = 28.83 \exp[-(0.3487)\ (3.2218) + (0\ 05576)\,(26.7)] = 2.1 \text{ mg/l}$$

Since the observed DO_M of 2.5 mg/1 is greater than that expected to occur only 2.5 percent of the time or less, it is concluded that the observed concentration is not due to an increased waste load although it is lower than the predicted value.

The regression equations can also be used to assess the effect of navigation channel depth increases on the oxygen resources of the river. Since the average and minimum dissolved oxygen concentrations are inversely related to the pool retention time, an increase in depth will result in lower dissolved oxygen concentrations for a given flow.

The U. S Army Corps of Engineers tries to maintain a 300-foot wide navigation channel in the La Grange pool. Table 6 shows the effects of a 2-foot increase in the navigation channel depth. The average decrease in DO for the 12 dates included in table 6 is 12 percent for the average pool DO and 16 percent for the minimum DO. Figure 10 shows the effects of various increases in channel depths on the dissolved oxygen concentrations during low and intermediate flow conditions.

A lowering of the DO_M by as much as 20 percent as predicted for conditions similar to those which existed on August 10, 1965, (table 6) would be highly significant. The observed DO_M on this date was well below acceptable limits.

Waste Assimilative Capacity

The statistical methods and models which have been developed herein provide means of predicting the dissolved oxygen conditions in the pool under existing waste discharge conditions. The development of the equations was based on the premise that the river BOD_5 load is constant at low flows. If a large increase or reduction in waste load occurs, the equations will not give valid estimates of the true DO. Therefore, the biochemical oxygen demand must be considered when the waste assimilative capacity of the pool is evaluated.

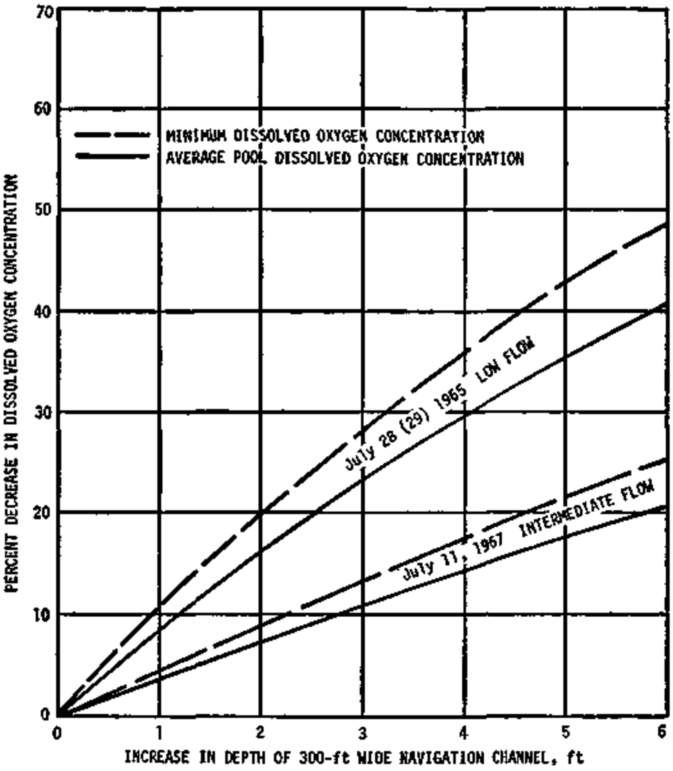

Figure 10. Effects of increasing channel depths

The objective is to select a model or method which is capable of simulating observed oxygen-sag profiles over a wide range of waste loads and flows. The ultimate BOD and the deoxygenation and reaeration constants must be determined. A diversity of formulas and methods are available for determining these parameters, but certain assumptions or limiting conditions have been involved in their development. Consequently, discretion should be used in choosing methods for a realistic, useful model.

Observed Dissolved Oxygen-Sag Curves. Under present waste loads, the assimilative capacity of the La Grange pool cannot prevent the DO from falling below the Illinois Sanitary Water Board standards during the summer *(see figure 1).*

The line through 4.0 mg/1 in figure 1 represents the minimum DO specified in the Illinois Sanitary Water Board water quality standards. The La Grange pool is designated as an "Aquatic Life Section" in the standards. Rule 1.05 (a) of Section SWB-8 of the "Rules and Regulations" defines the requirements for the dissolved oxygen resources of an Aquatic Life Section for the Illinois River as follows: "For maintenance of well balanced fish habitats the dissolved oxygen content shall not be less than 5.0 mg/1 during at least 16 hrs. of any 24-hour period, nor less than 4.0 mg/1 at anytime."

Strict adherence to this standard is virtually impossible under existing conditions. Examination of the duration curves for Kingston Mines *(see figure 4)* shows that the flow is expected to be 7020 cfs or less 37 percent of the time during 92 summer days. This means that the average DO for 34 days (0.37 X 92) will be less than 4.0 mg/1 between milepoint 151 and the La Grange dam. Careful study of the characteristics of the wastes and the waste assimilative capacity is required if implementation of waste treatment programs is to be meaningful.

Models for Dissolved Oxygen-Sag Curves. The O'Connor[11] modification of the Streeter-Phelps[6] oxygen-sag equation was considered initially. It takes into account possible physical removal of BOD in a stream by settling, volatilization, and flocculation. Such physical removal was thought to occur below the Pekin industrial complex.

As previously stated, in the O'Connor equation the basic Streeter-Phelps deoxygenation velocity constant (K_1) is replaced by two coefficients, K_r and K_d. The coefficient K_r is the river rate constant for waste removal immediately below a pollutional discharge; this factor includes both biochemical (K_d) and physical (K_r — K_d) removal rates. The physical fraction usually contains only carbonaceous demand. However, the biochemical fraction may include both nitrogenous and carbonaceous demand since the nitrogenous demand is usually dissolved while the carbonaceous fraction may be either particulate or dissolved. A point is reached in a stream where both the physical and biochemical rate constant is replaced by a purely biochemical rate designated as K_d. These relationships are shown diagrammatically as figure 11.

Plots of BOD- versus time for three days of data collected on August 24, 25, 26, 1966, appeared to follow the O'Connor formulation. However, for three days of data collected on August 10, 12, and 13, 1965, the plots did not conform to this method. In fact, the 1965 BOD_5 load appeared to increase slightly in a downstream direction. This observation is not easily explained. The most rational explanation is that the BOD- test is not sufficiently sensitive to detect the true dilution effects that occurred downstream during 1965. The flow increased almost 100 percent between the upper and lower ends of the pool, while the detectable BOD- concentration decreased only about 35 percent. This type of flow-concentration relationship did not occur during the 1966 sampling period; the flow increased only 20 percent while the BOD_5 concentrations decreased 50 percent. The BOD_3 versus time plot for the 1966 data is shown in figure 12. K_r and K_d were found to be — 1.517 and —0.1189 day^{-1}, respectively. An ultimate BOD of 894,551 lb/day was determined near Pekin. These values and reoxygenation coefficients computed by the O'Connor-Dobbins formula were used to calculate a DO-sag curve. Very little agreement existed between the calculated and observed curves, as shown in table 7.

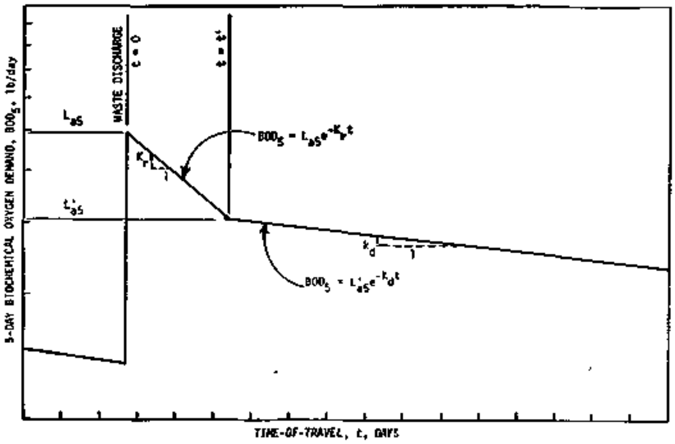

Figure 11. O'Connor stream deoxygenation rate constants relationships

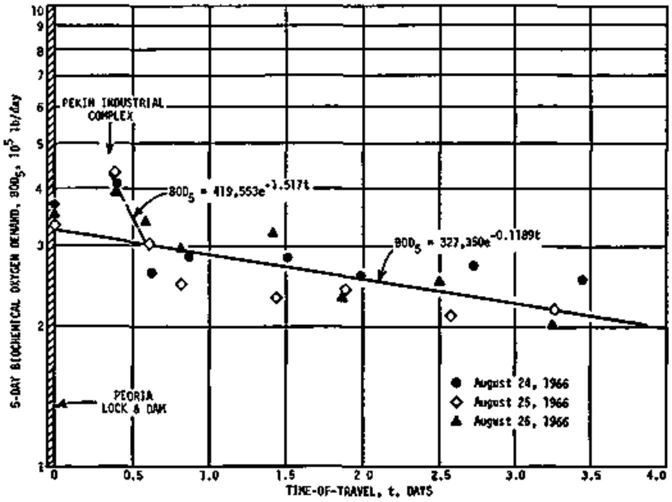

Figure 12. Biochemical oxygen demand profile

Because K_r is large and results principally from biological activity, the predicted DO immediately below Pekin (milepoint 150.0) drops very rapidly. Such a large drop in DO was not observed immediately below Pekin in more than 20 days of sampling in 1965, 1966, and 1967. The high BOD-'s at Pekin on the three August 1966 dates *(see figure 12)* may have been due to a poor sampling location, or the Pekin industrial waste discharges may not have been completely mixed with the river at the sampling station. Consequently, the observed K_r below Pekin appears to be a false rate.

Table 7. DO Values Computed by O'Connor Methodologies*

Milepoint	DO concentration (*mg/l*) Observed	DO concentration (*mg/l*) Computed
157.2		6 6
150.0	6.3	5 4
145.8	0.4	4.8
141.7	0.4	4 2
129.5	0.7	3.6
121.1	1.0	3.2
106.9	1.5	2.9
93.6	1.8	2 5
84.1	2.1	2 8
80.2	1 4	3.7

** Based on conditions in La Grange pool, August 24-26, 1966*

The basic Streeter-Phelps equation was used in conjunction with various methods of computing L_a, K_1, and K_2 in an attempt to better simulate the observed oxygen-sag curves. Table 8 gives a tabulation of $(L_a)_{20}$ and $(K_1)_{20}$ values computed by various methods for eight locations in the pool. The values have been computed as 3-day averages using a BOD sequence of 1, 2, 3, 5, and 7 days. In addition, an ultimate BOD at milepoint 157.2 was determined by extending the line representing K_d on figure 12 to $t = 0$ and converting the BOD_5 intercept to a value representative of ultimate BOD. This technique gave an L_a of 17.1 mg/1 in conjunction with a K_d of — 0.1189 day^{-1}. All the methods give different results to some degree although each computational procedure is based on a first-order BOD reaction.

Table 9 is a tabulation of K_2 values computed by four methods for nine reaches within the pool. The values are for the average water conditions in the pool during August 24-26, 1966. The Velz equivalent K_2 is the value K_2 must have in the Streeter-Phelps equation to achieve reoxygenation equal to that estimated by the Velz curve *(see figure 6).*

The reoxygenation coefficients differ depending upon the method used and the location within the pool Therefore, correct prediction of dissolved oxygen profiles by the Streeter-Phelps equation is partially dependent upon the reaeration formula selected. Only the USGS and O'Connor K_2 values show fairly good agreement. The Churchill formula gives the lowest estimates for rates of reoxygenation and the O'Connor formula the highest.

Twenty combinations of K_1 and K_2 are available for use in the oxygen-sag equation. Dissolved oxygen-sag curves were developed for each combination and the results are summarized in table 10, along with data from figure 12.

The rapid ratio method when used with the K_2's computed by the O'Connor formula gave good results; the average deviation from the observed was 0.26 mg/1. However, the other three reaeration formulas used in conjunction with the rapid ratio method gave fair to poor results. The observed results were best duplicated by using the Thomas slope method in conjunction with the equivalent Velz K_2. The Velz equivalent reaeration K_2's gave the smallest and most consistent differences between the computed and observed DO's with all the K_1 computational methods except the rapid ratio. Churchill's K_2 formula results in considerably less aeration than either the USGS or the O'Connor

Table 8. Deoxygenation and Ultimate BOD Values at 20 C Computed by Various Methods*

	Reed-Theriault		Thomas slope		Method of moments		Daily difference		Rapid ratio	
Milepoint	K_1 †	L_a †	K_1	L_a	K_1	L_a	K_1	L_a	K_1	L_a
157.2	.1600	17.56	.1495	18.82	.1750	16.28	.1050-	23 97	.1539	22 79
150.0	2230	17.86	.2490	16.88	.2517	16 74	.2127	18.40	.2333	17 87
145 8	.1260	18 23	.1203	18.00	.1374	18.74	1191	18.23	.1239	20.61
141.7	.1180	17.59	.1180	17 00	.1197	17.59	0781	25.18	.1157	24.97
129.5	0940	19.91	0728	24.55	.1143	18 38	.0800	23.15	0941	27 52
121 1	.1050	15 90	.0821	19 00	.1213	14 66	.0877	18.16	.1204	29 90
106.9	.0870	17.34	.0821	18 45	1220	15.02	.0747	20 37	1195	17.91
93.6	.1210	12.40	.0897	15.40	.1296	11.85	1081	13 30	.1569	11.01

** Values are based on 3-day averages for August 24-26, 1966, in La Grange pool*

† K_1 in day^{-1} and L_a in mg/l

Table 9. Reoxygenation Coefficients Obtained by Various Formulas*

Subreach milepoints	Avg flow (*cfs*)	Avg depth (*ft*)	Avg velocity (*fps*)	K_2 value at 20 C (*day*$^{-1}$) by given method: Velz equivalent	USGS	O'Connor	Churchill
157.2 – 150.0	6478	11.2	1.14	.1768	.3504	.3729	.1024
150.0 – 145.8	6557	11.3	1.15	.1709	.3467	3675	.1005
145.8 – 141.7	6616	11.6	1.10	.1816	.3192	.3445	.0923
141.7 – 129.5	6718	11.5	1.20	.1900	.3552	.3625	.1035
129.5 – 121.1	6798	10 8	1.12	.1980	.3594	.3999	.1062
121.1 – 106.9	6991	10.7	1.21	.2050	.3886	4001	1152
106.9 – 93.6	7475	11.6	1.17	.1907	.3426	.3590	.0997
93 6 – 84.1	7830	10.6	0.92	.2010	.2997	3571	0894
84.1 – 80.2	7949	12.2	0.86	.1924	.2338	.2820	.0668

** Values are averages for conditions in La Grange pool during August 24-26, 1966*

Table 10. Differences between Calculated and Observed DO's for Various Deoxygenation and Reoxygenation Methods in Conjunction with Streeter-Phelps Equation

Average and maximum differences between observed and predicted DO *(mg/l)* for given K_1, and K_t methods

Reaeration formula	Rapid ratio		Method of moments		Daily difference		Thomas slope		Reed-Theriault		Least-squares, figure 12	
	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max
Churchill	1.70	3.22	0 99	2.63	0 68	1.91	1 69	1.92	0.89	2 42	0.44	0.96
O'Connor	0.26	0.79	0.81	1.42	0 93	1 78	0 91	1.79	0 99	1 80	1 70	2.38
USGS	0.37	0.83	0 71	1 27	1.00	1.29	0.93	1.72	0.85	1.59	1.46	2.00
Velz equivalent	1.63	2.90	0.44	1.17	0.36	1.20	0 23	0.57	0.31	0 69	0.84	0 89

formulas, both of which give similar results although their resultant computed sag curves were considerably higher than the observed one.

Except for the least-squares method, the results in table 10 were obtained by replacing L_a and K_1 in the Streeter-Phelps equation with new values at the beginning of each subreach and resetting values for the initial DO equal to the calculated dissolved oxygen. The conventional procedure is to use only K_1 and L_a determined at the beginning of the whole reach; D_a is set at the initial observed concentration and is not reset downstream. This conventional procedure was tried using the L_a and K_1 values listed in table 8 for milepoint 157.2, but overall gave poor results.

Another method investigated utilized the Black and Phelps system of computing deoxygenation and reoxygenation separately and algebraically adding the two. Reaeration was computed from the oxygen absorption nomograph *(see figure 7).* Oxygen depletion was determined by substituting the L_a and K_1 values obtained from table 8 and figure 12 into the monomolecular equation. The results obtained were comparable but no better than those obtained with the Streeter-Phelps equation. The ultimate BOD and K_1 determined from figure 12 gave the best results; the maximum and average differences were 0.72 and 0 41 mg/l, respectively.

Method of Best Fit. The waste assimilative capacity of a stream can be assessed by the Black and Phelps concept without the benefit of analytical BOD- data. Only observed DO concentrations and reoxygenation quantities computed from either figures 6 or 7 are required. If it is assumed that photosynthesis is negligible and the Velz curve truly represents reoxygenation, the DO_{used} (or BOD) between two points of known dissolved oxygen concentrations can be expressed as:

$$DO_{used} = (DO_a - DO_{net}) + DO_{rea}$$

where $(DO_a - DO_{net})$ represents the difference in observed DO between upstream and downstream stations.

A first-order equation can be fitted to plots of the accumulated sum of the DO_{used} versus time to obtain L_a and K_d. Figure 13 shows a good fit of a first-order equation through data for August 24-26, 1966, with L_a equal to 345,700 lb/day and K_d equal to —0.3511 day"^{1}. If one computes the oxygen depletion by the formula shown on figure 13 and the reoxygenation by the Velz curve or nomograph, the average sag curve for the three days is reproduced very well, as shown by figure 14.

Since the computed curve fits the observed data, a realistic evaluation can be made of the degree of waste removal required to meet the minimum dissolved oxygen standards. Figure 14 shows that 35 percent removal of the 345,700 lb/day BOD load would not have been sufficient to maintain 4.0 mg/l throughout the pool; a 50 percent reduction would have increased the DO level above 4.0 mg/l but not above 5.0 mg/l.

A total of 13 individual days and two composites (one of three days and one of four) were analyzed with only observed DO's and reoxygenation to compute ultimate BOD and deoxygenation rates. The results are summarized in table 11. Except for three dates, the average deviation between the calculated and observed values was less than 0.5 mg/l. Of greater significance, however, is the fact that

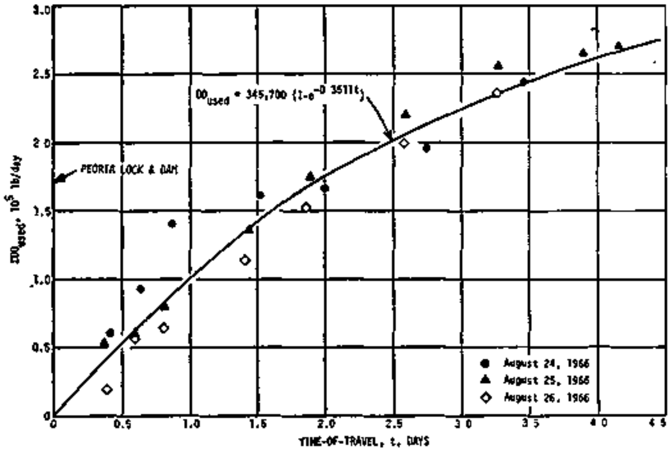

Figure 13. Computed BOD from DO observations

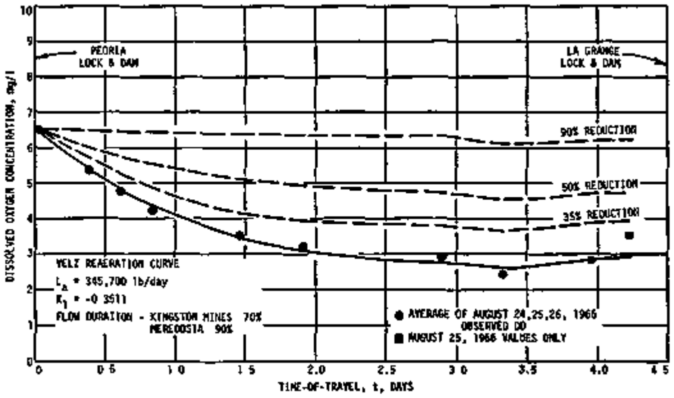

Figure 14. Computed DO-sag curve, August 1966

Table 11. Ultimate BOD and Deoxygenation Coefficients Computed from Observed DO's, and Deviations of Computed from Observed DO's

Date	L_a (10^5 lb/day)	K_d (day^{-1})	Deviation of computed from observed DO (mg/l)		Flow duration (% of days)	
			Avg	At sag	Kingston Mines	Meredosia
7/28(29)/65	5.441	.0956	0.31	0 29	97(98)	92(93)
8/10	6 638	.0711	0 42	0 33	87	87
8/11	6 618	.0886	0 47	0.39	83	86
8/12	6 815	.0891	0 40	0 02	79	84
8/13	6 325	.1098	0 89	0 57	82	85
7/22/66	3 112	4157	0 38	0.70	90	93
8/18	5 046	.2543	1 25	1.28	79	91
8/19	3 902	3766	0 25	0	80	92
8/24	2 390	7738	0 29	0 15	72	91
8/25	3 699	.3345	0 27	0 31	69	90
8/26	5.426	.1738	0 14	0 07	69	90
9/29	1.146	.3482	0 48	0	87	95
7/11/67	5 811	4303	1 12	0.81	47	76
8/10-13/65	7.554	.0749	0 54	0 53	83	86
8/24-26/66	3 457	.3511	0 18	0 15	70	90

the low points on both the observed and computed curves occurred at the same location and agreed closely in most cases.

For the dates having the higher deviations, corrections were made for downstream dissolved oxygen increases which could not be accounted for by reaeration alone. Photosynthesis appeared to be the main source of additional dissolved oxygen, but localized contributions from tributary inflows also appeared to be significant at times. The computed sag curve falls below the observed curve when a correction is made. The area between the two curves can be assumed to be primarily DO contributed by photosynthesis, as shown in figure 15.

Very low dissolved oxygen concentrations occurred during July 28(29), 1965, as was illustrated by figure 2 *(see page 3)*. The observed profile was reproduced very well except at the extreme lower end of the pool where photosynthetic oxygen production appeared to be significant. The removal of 90 percent of the waste load would maintain 4.0 mg/1 but not 5.0 mg/1 of dissolved oxygen. During very low flows, the reoxygenation capacity of the pool appears to be very poor as exemplified by the 100 percent reduction curve in figure 2. This curve indicates that if no waste load existed in the river to cause oxygen depletion and the DO below the Peoria dam was 4.0 mg/1, the dissolved oxygen concentration would increase downstream very slowly; a 5.0 mg/1 concentration would probably not be attained until almost 4 days travel time below the dam.

Figure 16 shows the percent reduction of river waste load needed to achieve specified DO levels under conditions similar to those observed during July 28(29), 1965. The extreme difference between this period and August 24-26, 1966, is partially the result of a 2-day increase in time-of-travel for July 28(29), 1965, *(see page 10)*.

Ultimate BOD versus Deoxygenation. An interesting inverse relationship appears to exist between the L_a and K_d values derived by using observed dissolved oxygen concentrations and the Velz reoxygenation curve. The values in table 11 show that, except for two days, an increase in L_a was generally accompanied by a decrease in K_d. The two exceptions occurred on July 11, 1967, a day of relatively high flow, and on September 29, 1966, a cool day in late summer. Figure 17 depicts this inverse relationship.

The L_a and K_d values in table 11 were determined by a computer using a hundred iterations to fit the DO_{used} summations to the monomolecular equation. L_a and K_d generally became stabilized toward the end of the hundreth iteration; however, significant changes still were occurring for the composite data of August 10-13, 1965, so the iterations were continued and results obtained for 200, 400, and 700 cycles. The results were:

Number of cycles	100	200	400	700
L_a (10^3 lb/day)	755	854	1003	1157
K_d (day^{-1})	0.0749	0.0652	0.0546	0.0468

At 700 cycles, L_a is 53 percent greater than at 100 cycles. However, K_d decreases proportionally so that all four sets of L_a and K_d values describe the same oxygen-sag curve. Therefore, a high BOD load utilized at a low deoxygenation rate can describe the same curve as a low BOD utilized at a high rate. This indicates that expressing waste strengths only in terms of BOD_5 can at times be misleading.

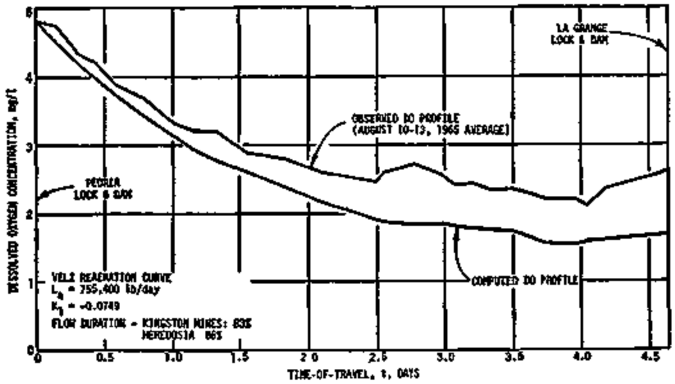

Figure 15. Computed versus observed DO-sag curve, August 1965

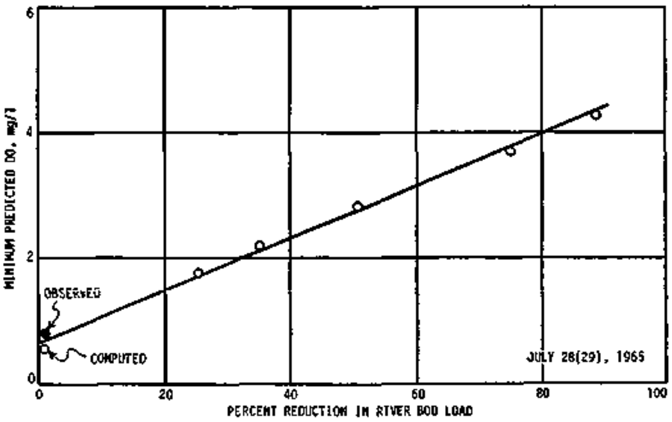

Figure 16. Waste load reduction versus predicted minimum DO

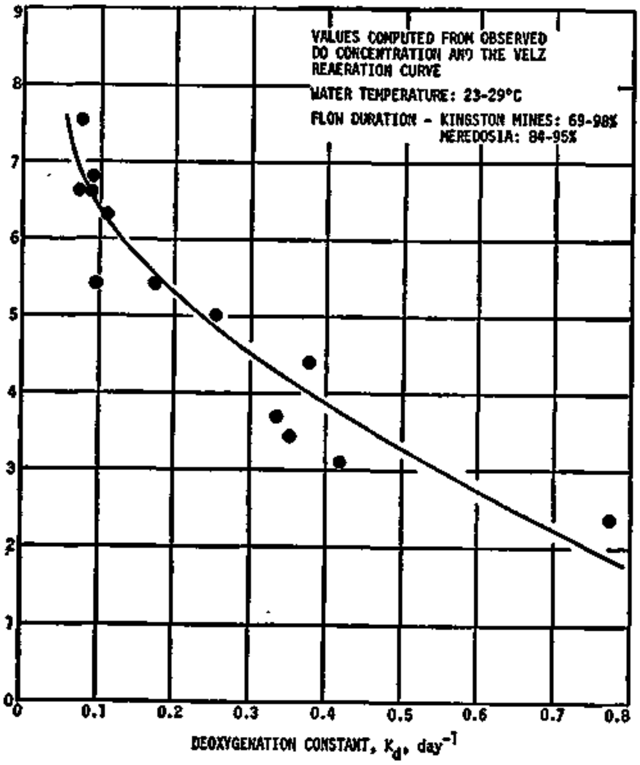

Figure 17. Ultimate BOD-deoxygenation relationships

A more accurate practice would be to specify both the BOD_5 and the deoxygenation coefficient when reporting BOD_5 results.

Nitrification. Nitrification, the oxidation of ammonia to nitrites and nitrites to nitrates, has been found to be a significant cause of oxygen depletion in the La Grange pool. The existence of nitrification has been reported in previous studies of the Illinois River. However, the seriousness of the problem has never been fully emphasized.

Hurwitz et al.[22] studied the effects of nitrification on the Illinois River Waterway from Chicago to Peoria. They found that nitrification started to progress rapidly at Marseilles, approximately 66 miles below Chicago. At Summit, immediately below Chicago Sanitary District outfalls, nitrification accounted for only 4.1 percent of the total BOD, whereas at Marseilles it accounted for 37.8 percent. At Henry, 51 miles below Marseilles, a peak percentage of *T6.2* was reached, and this peak slowly tapered to 54.5 percent at Peoria. These percentages are significant and meaningfur because they are averages of a large number of daily samples (from 40 to 150 depending upon the station). The Peoria results were based on an average of 95 daily samples.

Mohlman et al.[23] used Illinois River water to compare three modifications of the standard **BOD** test for isolating the carbonaceous from the nitrogenous demand. A significant percentage of the total BOD at Henry, Lacon, Peoria, and Pekin was found to be nitrogenous. For three summers of sampling, 1946 through 1948, the average percentage composition of nitrogenous BOD was 71.5 at Henry and 47.1 at Peoria. Mohlman and co-workers concluded that no justification exists, for, overlooking the nitrogenous BOD in the Illinois River and that ammonia is a liability to the dissolved oxygen balance. Contradictorily they imply that nitrogenous BOD must be accepted as a pollutant because complete oxidation of ammonia in present waste treatment processes is impractical and uneconomical.

In studying the water quality of Lake Peoria the State Water Survey has found ammonia (NH_3-N) concentrations as high as 5.45 mg/1. This concentration suggests a theoretical ultimate nitrogenous BOD of approximately 24 mg/1. This is a significant liability to the oxygen resources in the river below the lake in view of the fact that Zanoni[24] has found that nitrifying bacteria have a higher reaction velocity coefficient (K_1) than do heterotrophic bacteria.

Analyses of the BOD characteristics of waters within the La Grange pool support the findings of previous studies that a significant second-stage BOD exists in the Illinois River. The second-stage BOD was determined by subtracting the first-stage or carbonaceous demand from the total BOD. The carbonaceous demand was isolated from the total demand by use of the acid sterilization techniques developed by Hurwitz et al.[22] Table 12 summarizes the relative composition of the first- and second-stage BOD's for a number of dates and sampling locations. All the samples were incubated at 20 C except those on August 1,

Table 12. Carbonaceous and Nitrogenous BOD Percentages

Date	Milepoint	Incubation sequence (*days*)	Percent of total BOD	
			Nitrogenous	Carbonaceous
7/27/66	151.0	1, 2, 3, 5	53	47
	149.0		62	38
	146.0		35	65
8/1/66	157.2	1, 2, 3, 4, 5	51	49
	145.8		58	42
	141.7		75	25
8/12/66	157.2	1, 2, 3, 4, 5, 7	62	38
	150.0		53	47
	145.8		51	49
	141.7		38	62
8/24/66	157.2	1, 2, 3, 5	53	47
	150.0		77	23
	145 8		43	57
	141.7		66	34
	129.5		74	26
	106.9		77	23
	93.6		79	21
8/25/66	157.2	1, 2, 3, 5	51	49
	150.0		42	58
	145.8		63	37
	141.7		63	37
	106.9		67	33
8/26/66	150.0	1, 2, 3, 5	56	44
	145.8		68	32
	141.7		62	38
	129.5		37	63
	121.1		55	45
	106 9		51	49
	93.6		47	53
9/6/67	157.2	1, 2, 5, 7, 12	49	51
9/7/67	157.2	1, 2, 5, 7, 12	46	54
Average for all samples			57	43

1966, and September 7, 1967. On August 1, 1966, incubations were made in the river, in bottles secured to buoys at the sampling stations, at a river water temperature of approximately 28 C. The September 7, 1967, sample was incubated in the laboratory at an air temperature of 24 C.

The results indicate that, throughout the pool, a significant percentage of the total oxygen demand is nitrogenous. The composition at the Peoria end of the pool (near milepoint 157.2) is approximately 50 percent which agrees with the results obtained by earlier investigators.[22,23]

Figure 18 illustrates the total and carbonaceous BOD curves obtained on August 12, 1966, for four stations in the upper end of the pool. Basically they are typical of what can be expected, except the total BOD curves show a somewhat sharper break at approximately three days than has been observed for most of the other samples. This break indicates the time at which the second-stage demand started to progress very rapidly in the bottle. An important fact to note, however, is that both the first- and second-stage demands start simultaneously from the beginning of the incubation period.

Because the times at which the second-stage BOD's begin their rapid increase are less than low flow travel times through the pool *(see table* 2), much of the nitrogenous demand is satisfied in the pool. This causes a rapid decrease in the downstream nitrogenous load. A plot of the nitrogenous demand load versus time-of-travel for August 24-26, 1966, and a similar plot for the carbonaceous load are shown in figure 19. Although L_{a5N}, the 5-day nitrogenous load at *t* = 0, is only about two-thirds that of L_{a5c}, the velocity constant for the nitrogenous curve is almost four times greater than the carbonaceous constant. This means that the nitrogenous demand imposes a greater threat to the dissolved oxygen resources than does the carbonaceous demand. For instance, for one day time-of-travel 34,000 pounds of nitrogenous BOD was used, whereas only 14,000 pounds of carbonaceous BOD was used. Such a dramatic difference may not always occur; however, this does demonstrate the importance of nitrification and its effect on the oxygen resources in the Illinois River.

The data in table 12 indicate that the average percentage composition of carbonaceous load from milepoint 150.0 to 157.2 is approximately 46 percent. Since modern waste treatment plants are designed principally to remove the carbonaceous BOD and but little of the nitrogenous BOD, approximately 54 percent of the total load would remain if all the carbonaceous load was removed. As shown by figures 14 and 16, 100 percent removal of the carbonaceous load (46 percent total reduction) would not have raised the DO concentrations sufficiently to meet the minimum DO standards set for the pool.

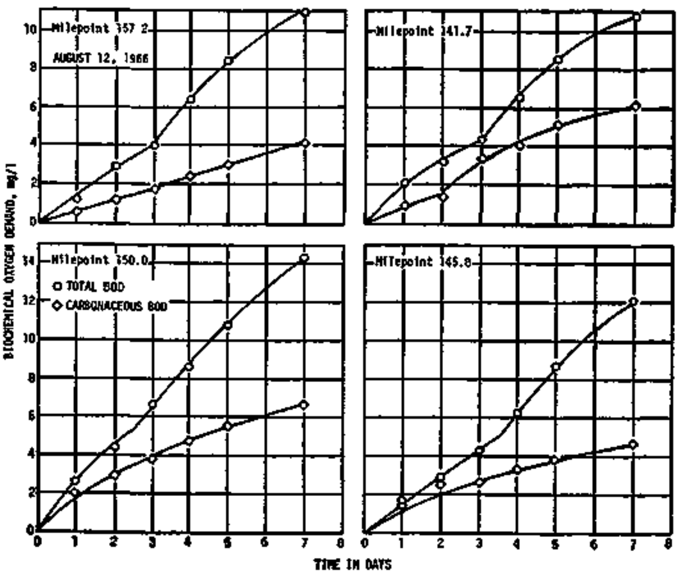

Figure 1 8. Nitrogenous versus carbonaceous demands, **laboratory**

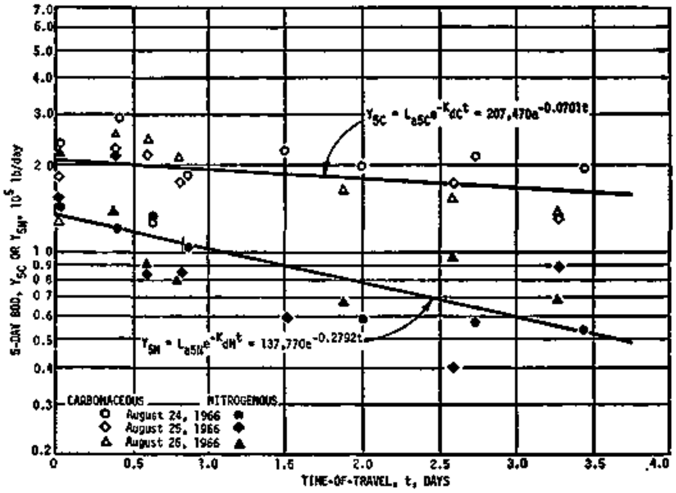

Figure 19. Nitrogenous versus carbonaceous demands, La Grange pool

Statistical and waste assimilative evaluations demonstrate that the oxygen resources in the pool are severely strained during summer low flows. Secondary treatment alone at all communities along the waterway will not improve conditions sufficiently to meet water quality standards. Treatment must be provided to remove nitrogenous BOD, or augmentation of the dissolved oxygen must be considered.

Water Quality Control Chart

Although DO standards probably cannot be met until steps are taken to remove nitrogenous BOD or to supplement the dissolved oxygen resources, information on the relative conditions of the river is needed in the interim to warn of further deterioration of quality. This can be accomplished by designing and implementing a statistical quality control program which would show trends deviating from the expected. For instance, if daily average dissolved oxygen concentrations are obtained and recorded by a continuous monitor, the raw data would undoubtedly show violations of the DO standards. This should not be too alarming in view of the results of this study. However, if the overall results are compared statistically with historical data (assumed to be representative of past conditions whether good or bad), a persistent deterioration of the water quality could be detected.

A quality control chart designed on principles developed by Wald[25] is suggested for use in detecting trends which deviate from the normal or expected. The chart is designed as a one-sided control chart since the dissolved oxygen can increase but it cannot decrease for extended periods without causing concern. The lower control limit *(LCL)* is a function of the water quality standard and several statistical parameters which are evaluated with historical data. An upper control limit *(UCL)* is also determined, but in the case of dissolved oxygen, this limit is strictly for control information and not for decision making. Newly generated data are compared with the control limits, and a decision is made as to whether the system is in-control or out-of-control.

Two types of errors (designated Type I and Type II) are associated with the design of control charts. A Type I error (α) is defined as the probability of rejecting an in-control sample, i.e., saying the sample is bad when in fact it is good. Conversely, a Type II error (β) is the probability of accepting a sample as good when it is actually out-of-control. Setting of the α and β probability values is based on judgment, reflecting the degree of risk the investigator is willing to accept. However, most statisticians recommend that both alpha and beta be set less than 0.15.

The equations used for computing the control limits are:

$$UCL = \frac{\sigma^2}{X_1 - X_0} \log_e \frac{1-\beta}{\alpha} + n \frac{X_0 + X_1}{2}$$

$$LCL = \frac{\sigma^2}{X_1 - X_0} \log_e \frac{\beta}{1-\alpha} + n \frac{X_0 + X_1}{2}$$

where

σ^2 = the population variance of historical data
X_0 = the population arithmetic mean of historical data
X_1 = the water quality standard
n = the sequential sample number

The *UCL* and *LCL* values vary according to *n*, the sample number. As previously indicated, the upper control limit has little significance in the construction of a chart for DO control except that it keeps the data in the no-decision region.

The features of the DO control chart are illustrated by figure 20.

The procedures required for establishing and using the control chart are:

1) Compute O^{-2} and X_0 from historical data (base period).
2) Choose appropriate α and β values and set the control standard X_1.
3) Compute *UCL* and *LCL* for the number of samples to be collected.
4) Plot the running sums of the *UCL* and *LCL* values versus *n* on arithmetic graph paper.
5) Collect samples at a regular frequency and plot the running sum of the results.
6) If the running sum of the observed data lies between *UCL* and *LCL,* continue plotting; if the sum goes above the *UCL,* STOP and conclude that the system is in-control; if the sum falls below the *LCL,* STOP and conclude the system is out-of-control.
7) If a stop is reached, take appropriate action, and then repeat steps 3 through 6.

Several examples are given to illustrate the use of this technique. No daily or routine dissolved oxygen data are available for the La Grange pool to establish a base period or to identify trends. However, equations 1 and 2 developed earlier in this report were used to estimate the average daily pool DO's during the warm low flow months of July and August. Water temperatures were estimated from records of water intakes serving industry on the pool. The Kingston Mines and Meredosia flows were obtained from the yearly U. S. Geological Survey publication, *Water Resources Data for Illinois - Part I - Surface Water Records.* In reviewing these records, 1963 appeared to be a good base year. The flows for July and August at Kingston Mines were in the general range of 4000 to 6000 cfs and only five values exceeded 10,000 cfs. The DO population mean and variance for the 2-month period

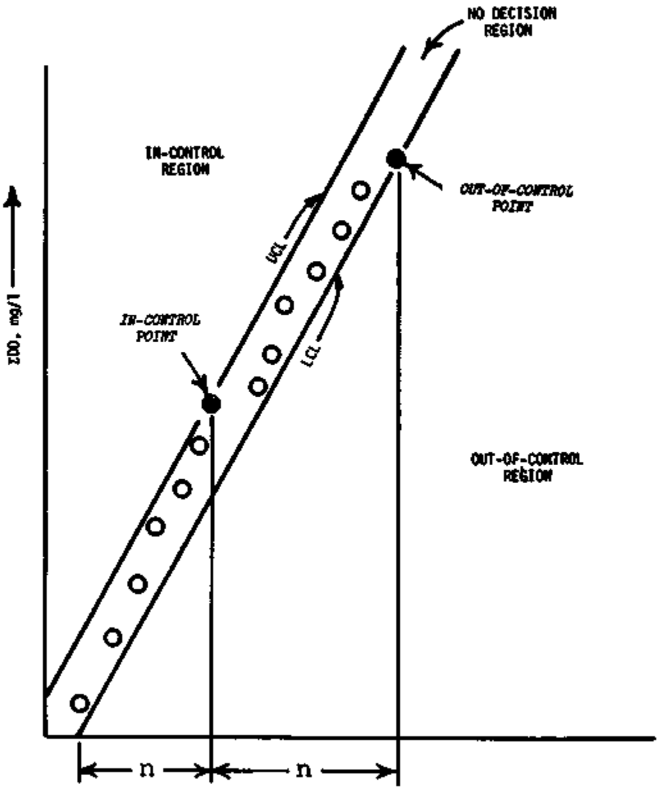

Figure 20. Schematic of control charts

Table 13. Control Limits for Values of Sequential Sample Numbers, Base Year 1963

$X_0 = 3.124; \sigma^2 = 0.732; X_1 = 4\ 0; \alpha = 0\ 10; \beta = 0.05$

n	UCL	LCL	n	UCL	LCL
1	5.44	1.14	32	115 87	111.57
2	9.01	4.71	33	119 43	115.13
3	12.57	8 27	34	122.99	118' 69
4	16.13	11.83	35	126.55	122 25
5	19 69	15.39	36	130.11	125 81
6	23 25	18 95	37	133.68	129 38
7	26 82	22 52	38	137.24	132 94
8	30 38	26.08	39	140 80	136 50
9	33 94	29.64	40	144 36	140 06
10	37 50	33 20	41	147 92	143 62
11	41.06	36 76	42	151 49	147 19
12	44 63	40.33	43	155 05	150 75
13	48 19	43 89	44	158.61	154 31
14	51.75	47.45	45	162 17	157 87
15	55 31	51.01	46	165.73	161 43
16	58 87	54.57	47	169 30	165.00
17	62.44	58.14	48	172 86	168 56
18	66 00	61.70	49	176.42	172.12
19	69 56	65 26	50	179.98	175.68
20	73 12	68 82	51	183.54	179.24
21	76.68	72.38	52	187 11	182 81
22	80 25	75.95	53	190 67	186 37
23	83 81	79 51	54	194 23	189 93
24	87.37	83 07	55	197.79	193 49
25	90.93	86 63	56	201.35	197 05
26	94.49	90.19	57	204 92	200.62
27	98.06	93 76	58	208 48	204.18
28	101.62	97.32	59	212 04	207.74
29	105.18	100 88	60	215.60	211.30
30	108 74	104 44	61	219.16	214 86
31	112.30	108 00	62	222.73	218.43

Table 14. DO Control Charts for July 1965, 1966, and 1967

Date	1965		1966		1967	
	n	ΣDO_A	n	ΣDO_A	n	ΣDO_A
1	1	1.67	1	4.03	1	5.11
2	2	3.62*	2	7.80	2	10.28**
3	1	1.92	3	11.37	1	5.44**
4	2	4.10*	4	14 74	1	5 75**
5	1	2.29	5	18.00	1	5.85**
6	2	4.44*	6	21.31	1	5.59**
7	1	2.35	7	24.72	1	4.78
8	2	5 55	8	28.09	2	9.07**
9	3	8.85	9	31.20	1	4.35
10	4	12.15	10	34 26	2	8.49
11	5	15 25*	11	37.19	3	12.91**
12	1	3.09	12	40.02*	1	4.45
13	2	6.01	1	2.88	2	8.93
14	3	8.92	2	6.05	3	13.38**
15	4	12 06	3	9.22	1	3.57
16	5	15.41	4	12.56	2	6 84
17	6	18 77*	5	15.90	3	9.86
18	1	2.82	6	18.75*	4	12.63
19	2	5 22	1	3.14	5	15.81
20	3	7.43*	2	6.65	6	19.05
21	1	2.13	3	9.55	7	22.68
22	2	4.14*	4	11.95	8	26.43
23	1	1.77	5	14.04*	9	30.24
24	2	3 35*	1	2.47	10	35.17
25	1	1.42	2	5.15	11	40.04
26	2	2.97*	3	7.82*	12	44.79**
27	1	1.76	1	2.82	1	5.29
28	2	3.58*	2	6.00	2	11.44**
29	1	1 65	3	10.46	1	6.08**
30	2	3.53*	4	14.54	1	6.08**
31	1	1.97	5	18.79	1	5.69**

* *Out-of-control*
** *In-control*

were estimated as 3.124 and 0.732 mg/1, respectively. Other parameters chosen were: a = 0.10; β = 0.05; and X_1 = 4.0 mg/1, the minimum permissible concentration set by the Illinois Sanitary Water Board. The resultant control equations are:

$$UCL = 3.562\ n + 1.881$$
$$LCL = 3.562\ n - 2.419$$

Control limits computed for 62 values of *n* are tabulated in table 13.

Running summations were made of the computed dissolved oxygen concentrations for July and August of 1965, 1966, and 1967. These were compared with the control limit values listed in table 13. If the summation fell between the *UCL* and *LCL* values, the system was in the no-decision region, and the summing was continued. If the summation was less than *LCL,* a 95 percent chance existed that the dissolved oxygen in the system was out-of-control, and that the water quality standard was not being met. When the summation exceeded the *UCL,* the *DO* standard was being met and the system was accepted as being in-control. Tables 14 and 15 show the tabulated values for the two months during three years. The control charts are shown diagrammatically as figures 21-23.

The charts show that the average dissolved oxygen pattern in the pool differed for each of the three years

Table 15. DO Control Charts for August 1965, 1966, and 1967

Date	1965		1966		1967	
	n	ΣDO_A	n	ΣDO_A	n	ΣDO_A
1	2	4.16*	6	22.34	1	4.72
2	1	2.21	7	25 58	2	9.14**
3	2	4.05*	8	28.72	1	3.87
4	1	2.10	9	31 40	2	7.38
5	2	4 57*	10	34.06	3	10.65
6	1	3.20	11	36.65*	4	14.04
7	2	6 50	1	2.86	5	18.12
8	3	9 54	2	5.92	6	22 96
9	4	12.29	3	9.47	7	27.89**
10	5	14.75*	4	13.43	1	4.32
11	1	3.19	5	17 64	2	8.74
12	2	6.35	6	21.64	3	12.79**
13	3	9.34	7	25.57	1	3.66
14	4	11 95	8	29 21	2	7.35
15	5	14.24*	9	32.74	3	10.86
16	1	2 19	10	35.99	4	14 07
17	2	4.16*	11	39.06	5	17.28
18	1	1.93	12	42 00	6	20.55
19	2	4.05*	13	44.52	7	24.24
20	1	2.24	14	47.24*	8	28.41
21	2	4.74	1	2.98	9	32.73
22	3	7.35*	2	6.35	10	37.21
23	1	2.50	3	9.98	11	41 96**
24	2	5.10	4	13.73	1	4.78
25	3	7.91*	5	17.54	2	9.20**
26	1	3.42	6	21.78	1	3.72
27	2	7.48	7	25.80	2	7.11
28	3	11.89	8	29 68	3	10.34
29	4	16.73**	9	33 49	4	13.58
30	1	5.36	10	37.18	5	16.60
31	2	12.95**	11	40.67	6	19.53

* *Out-of-control*
** *In-control*

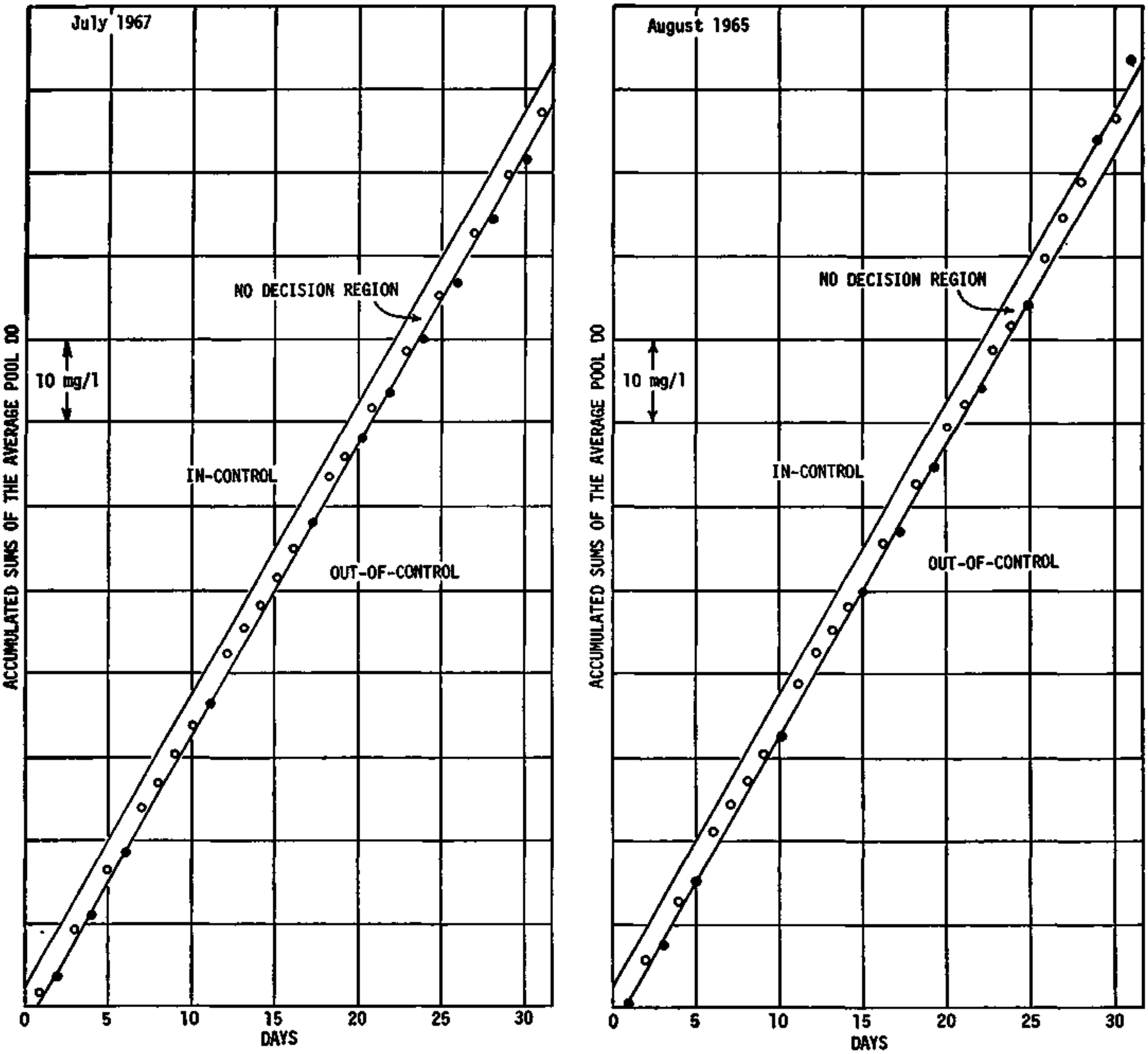

Figure 21. Dissolved oxygen control chart, July and August 1965

on the basis of the estimates made using the prediction equations. During 1965, the system was essentially out-of-control throughout the summer. Very low flows occurred during this period. During 1966, the system was never in-control, but it was out-of-control at infrequent intervals. During the summer of 1967, the flows were relatively high which prevented the system from going out-of-control. However, the system approached the out-of-control limits during the period July 18-23 and again at the end of August.

In these examples, the dissolved oxygen concentrations are estimated on the basis of time-of-travel and water temperatures. Therefore, all the out-of-control periods were the result of low flows and/or high water temperatures. For an actual situation with observed DO's, a decision must be made as to whether an out-of-control situation is caused by a waste load increase or by low flows and high river temperatures such as prevailed during the summer of 1965. Equations 4 and 6 can aid in making this decision.

For example, assume that the average dissolved oxygen in the pool is being determined daily and that after the fourth day (n = 4) the system went out-of-control. Assume an average pool DO of 3.1 mg/1 was observed on the fourth day at a water temperature of 24 C and a time-of-travel of 3.8 days. Substituting T = 24 C and t = 3.8 days in equation 4 gives an average DO of 3.4 mg/1. This indicates that the waste load probably has increased because only a 2.5 percent chance exists that the average

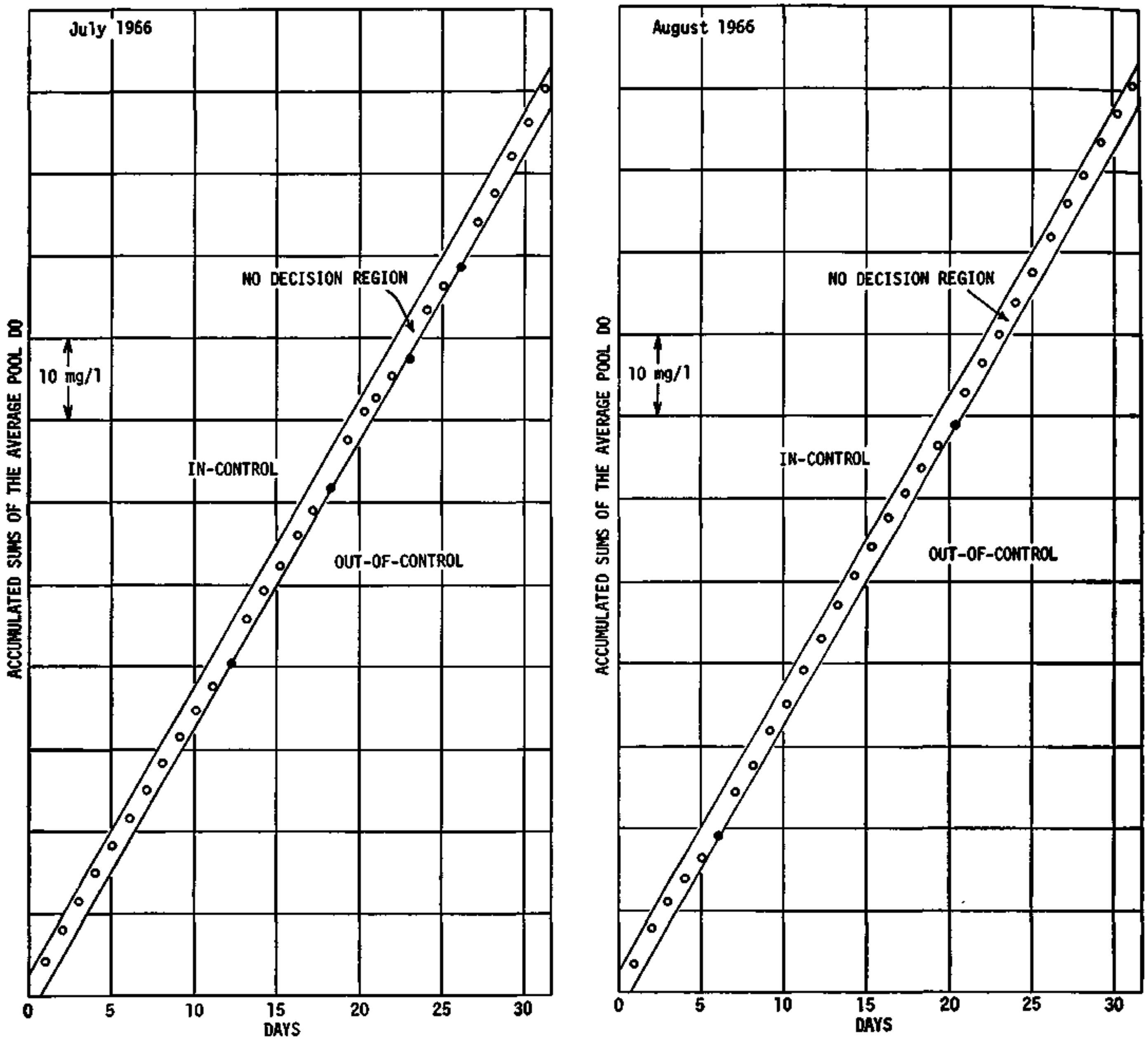

Figure 22. Dissolved oxygen control chart, July and August 1966

DO would have fallen below 3.4 mg/1 if the BOD had remained unchanged from that existing during the development of the equation.

A control system of this nature would be particularly useful in assessing the effectiveness of treatment additions at all municipalities and industries located in or above the pool. If conventional secondary treatment is effective in improving the DO level in the pool, in-control conditions should persist. However, a distinction has to be made between in-control conditions caused by increased flows and those resulting from the additional treatment. As an illustration, the condition during 1967 appeared much improved over that of 1965 as indicated in tables 14 and 15 and figures 21 and 23. However, this improvement would have to be attributed to higher flows during 1967. If secondary treatment had been implemented between 1965 and 1967, the improved conditions might have been improperly attributed to the additional treatment unless assessed by equation 4.

Although the discussion and examples have been centered around regression equations and control charts developed for the average dissolved oxygen in the pool, the same principles can be applied to a given station in the pool.

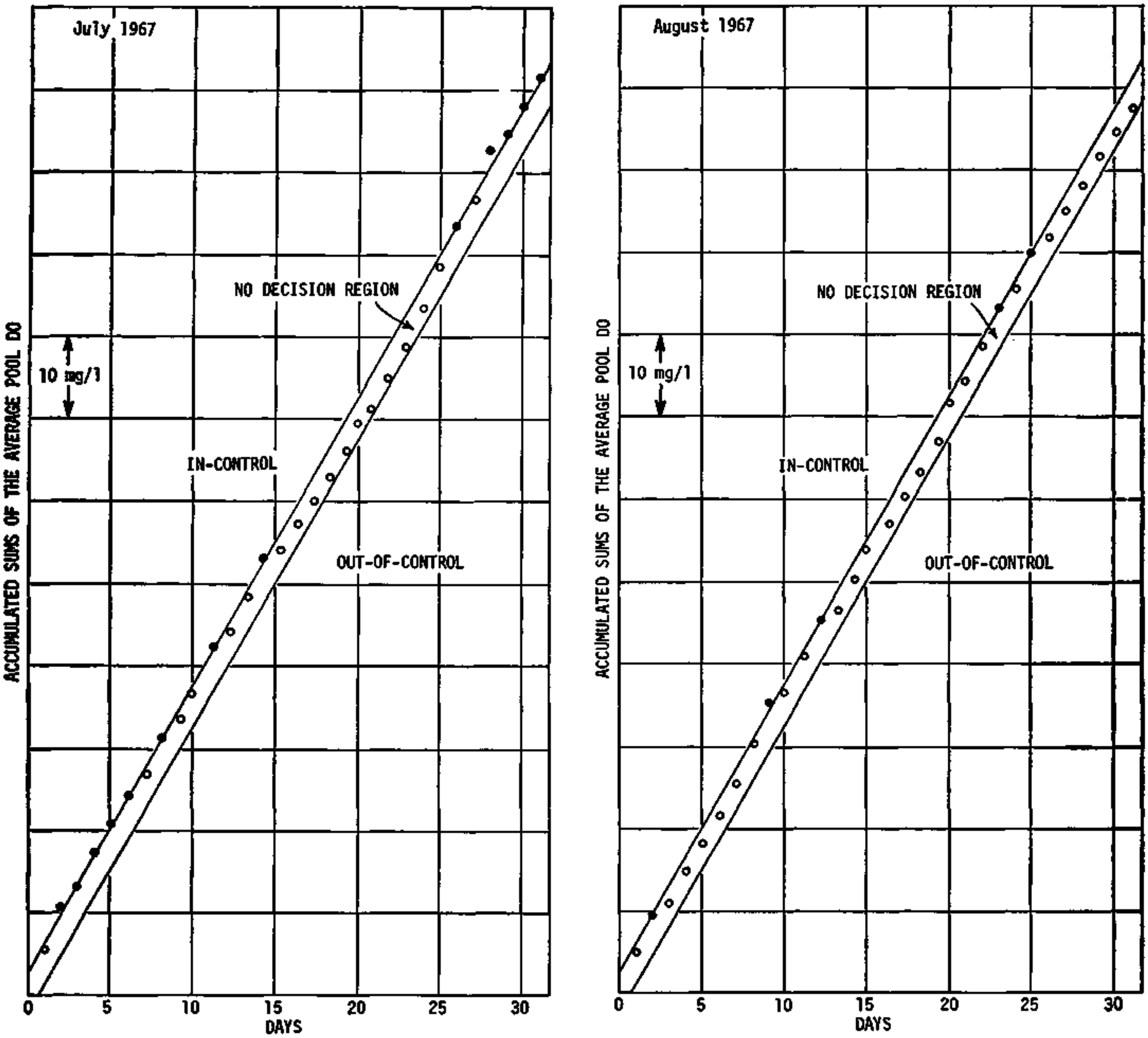

Figure 23. Dissolved oxygen control chart, July and August 1967

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NOTATIONS

a = diffusion coefficient used by Velz in Black and Phelps reaeration formula
a_T = Velz diffusion coefficient at any temperature T
a_{20} = Velz diffusion coefficient at 20 C
a = probability of rejecting an in-control sample
β = probability of accepting an out-of-control sample
B_0 = initial dissolved oxygen in percent saturation
BOD = biochemical oxygen demand without specifying time
BOD$_s$ = 5-day biochemical oxygen demand
D = dissolved oxygen deficit in mg/1 or lb/day at any time-of-travel t
D_a = initial DO deficit in lb/day or mg/1
D_L = diffusion coefficient in O'Connor-Dobbins reaeration formula
DO = a general expression for dissolved oxygen
DO_A = weighted average pool dissolved oxygen concentration in mg/1
DO_a = initial dissolved oxygen level in mg/1 or lb/day
DO_M — minimum pool dissolved oxygen concentration in mg/1
DO_{net} = dissolved oxygen at the end of a reach
DO_{rea} = dissolved oxygen absorbed from the atmosphere
DO_{Used} = dissolved oxygen consumed biologically
$DO_{A < 2.5}$ = weighted average pool DO expected to be less 2.5 percent of the time
$DO_{A > 2\cdot5}$ = weighted average pool DO expected to be greater 2.5 percent of the time
$DO_{M < 2.5}$ = minimum pool DO expected to be less 2.5 percent of the time
$DO_{M > 2.5}$ = minimum pool DO expected to be greater 2.5 percent of the time
exp, e = base of natural logarithms, 2.71828
H = average depth in feet
K = an exponent in the Black and Phelps reaeration equation
K_1 = deoxygenation constant to the base e in day^{-1} at any temperature
K_2 = reaeration constant to the base e in day^{-1} at any temperature
$(K_1)_T$ = deoxygenation constant to the base e in day^{-1} at temperature T
$(K_2)_T$ = reaeration constant to the base e in day^{-1} at temperature T
$(K_1)_{20}$ = deoxygenation constant to the base e in day^{-1} at 20 degrees Centigrade
$(K_2)_{20}$ = reaeration constant to the base e in day^{-1} at 20 degrees Centigrade
K_d = BOD removal rate due to biological activity in a river
K_r = BOD removal rate due to physical and biological factors in a river
K_{dc} = carbonaceous river deoxygenation coefficient in day^{-1}
K_{ac} = nitrogenous river deoxygenation coefficient in day^{-1}
L = average depth in centimeters, as used in Velz reaeration formula
L_a = ultimate BOD at any temperature
$(L_a)_T$ = ultimate BOD at a temperature T
$(L_a)_{20}$ = ultimate BOD at 20 degrees Centigrade
L_{at} = BOD at incubation time t at the beginning of a river BOD plot
L_{a5} = total 5-day BOD load in lb/day at time = 0 on a time-of-travel versus total BOD5 plot
L'_{a5} = total 5-day BOD load in lb/day at time = t' on a time-of-travel versus BOD5 plot
L_{a5}c = 5-day carbonaceous BOD load in lb/day at time = 0 on a time-of-travel versus carbonaceous BOD$_5$ plot
L_{a5N} = 5-day nitrogenous BOD load in lb/day at time = 0 on a time-of-travel versus nitrogenous BOD$_5$ plot
LCL = lower control limit
Lt = BOD remaining at time t
M = mix or exposure time in minutes
m = mix or exposure time in hours

NOTATIONS (Concluded)

n = sequential sample number
Q = streamflow in cfs
Q_k = gaged flow at Kingston Mines
Q_m = gaged flow at Meredosia
R = percent of saturation of DO absorbed per mix
R_0 = percent of saturation of DO absorbed per mix at zero initial DO
r = correlation coefficient
SE = standard error of estimate
O^{-2} = population variance of historical data
t = time-of-travel or incubation time in days
t' = the point on a time-of-travel versus total BOD_5 plot at which the deoxygenation coefficient changes from K_r to K_d
T = water temperature in degrees Centigrade
T_A — weighted average pool temperature in degrees Centigrade
U — velocity in ft/hr in the O'Connor-Dobbins reaeration formula
UCL = upper control limit
V = velocity in fps
$x_1 \ldots x_4$ = independent variables used in regression analysis
X_0 = population mean of historical data in mg/1
X_1 = water quality standard in mg/1
Y_{5c} = 5-day carbonaceous BOD at any time t
Y_{5N} = 5-day nitrogenous BOD at any time t