UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Water Resources Division

REAERATION
IN
OPEN-CHANNEL FLOW

by

J. P. Bennett and R. E. Rathbun

Open-file Report

Fort Collins, Colorado

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ILLUSTRATIONS

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TABLES

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Symbol	*Definition*
a	Parameter in the surface-renewal damped eddy diffusivity model (King, 1966).
a_1	Constant in the equation for consumption of dissolved oxygen by bottom deposits.
a_2	Constant in the Edwards and Rolley (1965) equation for rate of consumption of dissolved oxygen by bottom deposits.
a_0	Rate of addition of dissolved oxygen to the reach by drainage accrual, in milligrams per liter per day.
A	Temperature relation in the equation of Dobbins (1965); $A = 9.68 + 0.054 \, (T\text{-}20)$ where T is temperature in degrees Celsius.
$A_0, A_1, \ldots A_N$	Coefficients in the linear regression equation.
A_e	Parameter in the large eddy model (Fortescue and Pearson, 1967), in centimeters per second.
A_0	Rate of addition of dissolved oxygen to the reach by drainage accrual, in grams per square meter per hour.
A_s	Water surface area, in square meters.
A_x	Cross-sectional area of the reach at longitudinal position x, in square feet.
b	Proportion of available molecules in the surface layer that actually escape.

Symbol	Definition
b_1	Exponent on dissolved oxygen concentration in the Edwards and Rolley (1965) equation for rate of consumption of dissolved oxygen by bottom deposits.
B	Temperature relation in the equation of Dobbins (1965); $B = 0.976 + 0.0137 (30-T)^{3/2}$ where T is temperature in degrees Celsius.
B_i	Population regression coefficient.
B_F	Factor in the Dobbins (1965) equation, equal to $1 + F^2$ where F is the Froude number.
BOD	Biochemical oxygen demand, in milligrams per liter.
c	Concentration fluctuation, or the difference between the instantaneous concentration and the time-averaged concentration, in milligrams per liter or grams per cubic meter.
c_1, c_2, c_3, c_4, c_5	Constants in the equations of Dobbins (1964b, 1965).
c_1', c_3', c_5'	Constants in the Metzger-Dobbins (1967) model.
C	Dissolved oxygen concentration, in milligrams per liter or grams per cubic meter.
$\overline{C}$	Mean concentration of dissolved oxygen in the reach, in milligrams per liter.
$\overline{C}_1, \overline{C}_2$	Mean concentrations of dissolved oxygen in the reach for the two levels of dissolved oxygen concentration, disturbed equilibrium technique; in milligrams per liter.

Symbol	Definition
C_a, C_b	Dissolved oxygen concentrations at the upstream and downstream ends of the reach, respectively, at the first level of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter.
C_a', C_b'	Dissolved oxygen concentration at the upstream and downstream ends of reach, respectively, at the second level of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter.
C_i	Dissolved oxygen concentration at the gas-liquid interface, in milligrams per liter.
C_{di}, C_{df}	Initial and final concentrations, respectively, of dissolved oxygen in the dark bottle of the light- and dark-bottle test for photosynthesis, in milligrams per liter.
C_{li}, C_{lf}	Initial and final concentrations, respectively, of dissolved oxygen in the light bottle of the light- and dark-bottle test for photosynthesis, in milligrams per liter.
C_s	Dissolved oxygen concentration at saturation, in milligrams per liter or grams per cubic meter.
C_{s_1}, C_{s_2}	Saturation concentrations of dissolved oxygen for the two levels of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter.
$\overline{C}_s$	Mean saturation concentration of dissolved oxygen in the reach, in milligrams per liter.

Symbol	Definition
C_t	Dissolved oxygen concentration, in milligrams per liter; subscript t indicates variability with respect to time at a particular point in space.
C_G^*	Concentration of the tracer gas in the water, in milligrams per liter.
C_L	Dissolved oxygen concentration in the bulk liquid phase, in milligrams per liter.
C_L^*	Concentration of the conservative liquid tracer in the water, in milligrams per liter.
ΔC	Difference in dissolved oxygen concentration between upstream and downstream ends of the reach, in milligrams per liter.
ΔC_1	Difference in dissolved oxygen concentration between upstream and downstream ends of the reach at sunrise, in milligrams per liter.
d_1, d_2	Molecular diameters of gases 1 and 2, in Angstroms.
d_0	Rate of transfer of oxygen through the water surface, in milligrams per liter per day.
d_M	Depth of bottom deposit, in centimeters.
D	Dissolved oxygen deficit, or the difference between the saturation concentration and the concentration of dissolved oxygen, in milligrams per liter.
D_a	Dissolved oxygen deficit at upstream end of reach, in milligrams per liter.

Symbol	Definition
D'_a	Dissolved oxygen deficit at upstream end of reach at the second level of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter.
D_b	Dissolved oxygen deficit at downstream end of reach, in milligrams per liter.
D'_b	Dissolved oxygen deficit at downstream end of reach at the second level of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter.
D_i	Combination of the molecular and turbulent diffusion coefficients at the surface, Krenkel and Orlob (1963) model, in square feet per day.
D_m	Molecular diffusion coefficient, in square feet per day.
D_0	Rate of transfer of oxygen through the water surface, in grams per square meter per hour.
D_x	Longitudinal dispersion coefficient, in square feet per day.
D_B	Parameter that includes the effect of photosynthesis, respiration and removal of dissolved oxygen by benthal layer, in milligrams per liter per day.
D_M, D_E	Average dissolved oxygen deficit in the reach at that time in the morning and evening, respectively, when the production of oxygen by photosynthesis is zero, in milligrams per liter.
DO	Dissolved oxygen.

Symbol	Definition
E	Rate of energy dissipation per unit mass of liquid, equal to $U\,S\,g$ for open-channel flow, in ergs per second per gram.
E'	Combination of the activation energies for molecular diffusion and viscous flow, in degrees Kelvin.
$\overline{E}$	The average kinetic energy of a roll cell, large eddy model (Fortescue and Pearson, 1967), in square centimeters per second per second.
E_a	Activation energy for the absorption of oxygen by water, in calories per gram mole.
E_P	Percent standard error of estimate, for the reaeration coefficient, k_2, in percent.
E_S	Standard error of estimate, for the reaeration coefficient, k_2, in reciprocal days.
E_{SL}	Standard error of estimate for the reaeration coefficient, k_2, based on common logarithms.
E_V	Rate of energy dissipation per unit volume of liquid, in ergs per second per cubic centimeter.
E_ξ	Rate of energy dissipation per unit mass of liquid at the surface, in ergs per second per gram.
f	Dissolved oxygen exchange coefficient, in meters per hour.
$f(k_2)$	Functional relation of the reaeration coefficient, common logarithm base; used in the sensitivity analyses of the dissolved oxygen balance and disturbed equilibrium techniques.

Symbol	Definition
$f'(k_2)$	First derivative of the functional relation of the reaeration coefficient, common logarithm base; used in the Newton-Raphson iterative method for solving the dissolved oxygen balance and disturbed equilibrium equations for the sensitivity analyses.
$f_1(s)$	Rate of surface renewal function, Thackston and Krenkel (1969) model.
$f_2(H)$	Depth of flow function, Thackston and Krenkel (1969) model.
F	Volumetric water flow rate, in cubic meters per hour or cubic feet per second.
F_c	Source-sink term, in milligrams per liter per day.
$\overline{F}_c$	Source-sink term averaged over the depth of flow, in milligrams per liter per day.
F	Froude number, equal to $U/\sqrt{g\,H}$.
g	Acceleration of gravity, in feet per second per second.
G	General functional relation between dependent and independent variables in linear regression analysis.
h	Henry's Law constant, in liters per milligram.
H	Mean depth of flow, in feet or meters.
H'	Depth above minimum low water stage, Streeter-Phelps (1925) prediction equation for the reaeration coefficient, in feet.
j	Exponent on depth of flow in the general form of the empirical prediction equation for the reaeration coefficient.

Symbol	Definition
J	Constant in the Thackston and Krenkel (1969) model.
k_1	Deoxygenation coefficient or rate constant for biochemical oxidation of carbonaceous material, common logarithm base, in reciprocal days.
k_2	Reaeration coefficient or rate constant for oxygen absorption from the atmosphere, common logarithm base, in reciprocal days.
$(k_2)_c$	Reaeration coefficient calculated from the results of an experimental test, common logarithm base, in reciprocal days.
$(k_2)_e$	Reaeration coefficient estimated from a linear regression analysis equation, common logarithm base, in reciprocal days.
k_3	Rate constant for the removal of BOD by sedimentation and adsorption, common logarithm base, in reciprocal days.
k_L	Overall mass-transfer coefficient based on liquid phase, equivalent to k_2H, in centimeters per second or feet per day.
K_1	Deoxygenation coefficient or rate constant for biochemical oxidation of carbonaceous material, natural logarithm base, in reciprocal days.
K_2	Reaeration coefficient or rate constant for oxygen absorption from the atmosphere, natural logarithm base, in reciprocal days.

Symbol	Definition
K_{2_G}	Mass transfer coefficient for the tracer gas, in reciprocal days.
K_3	Rate constant for the removal of BOD by sedimentation and adsorption, in reciprocal days.
K_G	Overall mass-transfer coefficient based on the gas phase, in milligrams per square centimeter per second per atmosphere.
K_L	Overall mass-transfer coefficient based on the liquid phase, in centimeters per second or feet per day.
K_N	Rate constant for the oxidation of nitrogeneous material, in reciprocal days.
L	Biochemical oxygen demand of carbonaceous material, in milligrams per liter.
L_a	Biochemical oxygen demand of carbonaceous material at upstream end of reach, in milligrams per liter.
L_b	Biochemical oxygen demand of carbonaceous material at downstream end of the reach, in milligrams per liter.
L_f	Film thickness, in feet or meters.
$\overline{L}_f$	Average film thickness, in feet or meters.
L_t	Biochemical oxygen demand of carbonaceous material, in milligrams per liter; subscript t indicates variability with respect to time at a particular point in space.

Symbol	Definition
L_R	Rate of addition of BOD along the reach, in milligrams per liter per day. (Includes addition of BOD with runoff, the diffusion of partially degraded waste from the benthal layer into the water, and the scour and resuspension of bottom deposits.)
m	Rate of addition of BOD to water from bottom deposits, in milligrams per liter per day.
M	Molecular weight.
M_s	Modulus of compression at the surface, in grams per second per second.
n	An integer.
n_s	Number of new surface layers exposed per unit of time, in reciprocal seconds.
N	Mass transport rate of oxygen, in milligrams per square centimeter per second.
$\overline{N}$	Average rate of mass transport of oxygen, in milligrams per square centimeter per second.
N'	Number of data sets in linear regression analysis.
N_x	Concentration of nitrogenous material at longitudinal position x, in milligrams per liter.
p	Rate of production of dissolved oxygen by photosynthesis, in milligrams per liter per day.

Symbol	Definition
p'	Rate of production of dissolved oxygen by photosynthesis at the second level of dissolved oxygen concentration of the disturbed equilibrium technique, in milligrams per liter per day.
$p(f)$	Distribution function for surface-renewal time or distance below the interface to which renewal occurs (f is dummy variable for either y_1 or t), Harriott (1962) model.
p_i	Partial pressure of the diffusing gas, oxygen, at the gas-liquid interface, in atmospheres.
p_t	Rate of production of dissolved oxygen by photosynthesis, in milligrams per liter per day; subscript t indicates variability with respect to time at a particular point in space.
$p_{x,t}$	Rate of production of dissolved oxygen by photosynthesis at longitudinal position x at time t, in milligrams per liter per day.
p_B	Barometric pressure, in atmospheres.
p_G	Partial pressure of the diffusing gas, oxygen, in the gas phase, in atmospheres.
P	Rate of gross primary production of dissolved oxygen by photosynthesis, in grams per square meter per hour.
P_l	Rate of production of dissolved oxygen by photosynthesis in the light bottle of the light- and dark-bottle test, in milligrams per liter per day.

Symbol	Definition
P_B	Gross rate of photosynthetic production of dissolved oxygen by attached plants, in grams per square meter per hour.
P_P	Gross rate of photosynthetic production of dissolved oxygen by phytoplankton, in grams per square meter per hour.
P	Péclet number, equal to $\Lambda A_e/D_m$.
q	Rate of change of dissolved oxygen content in the reach, in milligrams per liter per day.
q_1	Rate of change of dissolved oxygen content in the reach at sunrise, in milligrams per liter per day.
q_M, q_E	Rate of change of dissolved oxygen content in the reach at that time in the morning and evening, respectively, when the production of oxygen by photosynthesis is zero, in milligrams per liter per day.
Q_0	Rate of change of dissolved oxygen content in the reach, in grams per square meter per hour.
Q_1, Q_2	Average rate of change of dissolved oxygen concentration per unit area in the reach for the two levels of dissolved oxygen concentration, disturbed equilibrium technique; in grams per square meter per hour.
r	Rate of consumption of dissolved oxygen by plant respiration, in milligrams per liter per day.
r_e	Rate of entry of gas molecules into the surface layer, in grams per second.

Symbol	Definition
r_0	Rate of loss of gas molecules from a surface layer, in grams per second.
r_t	Rate of consumption of dissolved oxygen by plant respiration, in milligrams per liter per day; subscript t indicates variability with respect to time at a particular point in space.
$r_{x,t}$	Rate of consumption of dissolved oxygen by plant respiration at longitudinal position x at time t, in milligrams per liter per day.
R	Rate of dissolved oxygen utilization by all processes, in grams per square meter per hour.
R'	Ratio of the oxygen consumed by respiration at the two levels of dissolved oxygen concentration, disturbed equilibrium technique.
R_d, R_l	Rate of consumption of dissolved oxygen by respiration in the dark and light bottles, respectively, of the light- and dark-bottle test for photosynthesis, in milligrams per liter per day.
R_i	Equals the quantity $(A_i - B_i)/S_{bi}$, used to test the significance of the regression coefficient A_i.
R_B	Rate of consumption of dissolved oxygen by respiration of attached plants, in grams per square meter per hour.
R_{BOD}	Rate of consumption of dissolved oxygen by the oxidation of organic wastes in the stream water, in grams per square meter per hour.

Symbol	Definition
R_G	Ideal gas constant, in ergs per gram mole per degree Kelvin.
R_H	Hydraulic radius, equal to the cross-sectional area of flow divided by the wetted perimeter, in feet.
R_M	Rate of consumption of dissolved oxygen by bottom deposits, in grams per square meter per hour.
R_P	Rate of consumption of dissolved oxygen by respiration of phytoplankton, in grams per square meter per hour.
RMS	Root-mean-square, or square root of the mean value of the square of the deviations of the measured parameter from the mean parameter.
s	Average rate of surface renewal, in reciprocal hours.
S	Water-surface or channel slope, in feet per foot.
S_{bi}	Standard error of the regression coefficient A_i.
$SE_{x,t}$	Rate of removal of BOD by sedimentation at longitudinal position x at time t, in milligrams per liter per day.
t	Time, in days or hours.
t'	Flow time, or the time lag that must elapse between dissolved oxygen measurements at the two sampling points in a recirculating flume, in seconds.
t_1, t_2	The time at which sunrise occurred, and the time in the evening when the rate of change of dissolved oxygen content in the reach returned to its sunrise value, in hours.

Symbol	Definition
t_a, t_b	Times at which the concentrations of dissolved oxygen are measured at the upstream and downstream ends, respectively, of the reach, in hours; $t_b - t_a$ is the flow time or the time required for a slug of water to flow through the reach.
t_e	Age of surface at which surface elements are replaced, in days or hours.
T	Temperature, in degrees Celsius.
T'	Absolute temperature, in degrees Kelvin.
u_*	Shear velocity, equal to $\sqrt{g\,H\,S}$, in feet per second.
$\overline{u'}$	Longitudinal turbulent intensity, in centimeters per second.
u_e	Eddy velocity in the longitudinal direction, large eddy model (Fortescue and Pearson, 1967), in centimeters per second.
u_i	Velocity fluctuation in the x_i direction (tensor notation), or the difference between the instantaneous velocity and the time-averaged velocity, in feet per day.
$\overline{u_i c}$	Product of the velocity fluctuation and the concentration fluctuation, in milligrams per liter centimeters per second. (Overbar indicates average with respect to time.)
U	Mean flow velocity in the longitudinal direction, in feet per day.

Symbol	Definition
U_i	Velocity in the x_i direction (tensor notation), in feet per day.
v_e	Eddy velocity in the vertical direction, large eddy model (Fortescue and Pearson, 1967), in centimeters per second.
V	Volume of the system, in cubic centimeters.
w	Exponent on velocity in the general form of the empirical prediction equation for the reaeration coefficient.
W	Width, in feet or meters.
W_G	Weight of gaseous tracer (krypton) injected for a tracer-procedure determination of the reaeration coefficient, in pounds.
W_L	Weight of conservative liquid tracer (tritiated water) injected for a tracer-procedure determination of the reaeration coefficient, in pounds.
W_{0G}	Weight of gaseous tracer (krypton) injected per unit of cross-sectional area of flow, equal to W_G/A_x, in pounds per square foot.
W_{0L}	Weight of conservative liquid tracer (triated water) injected per unit of cross-sectional area of flow, equal to W_L/A_x, in pounds per square foot.
x	Longitudinal position or direction, in feet.
x'	Longitudinal position in a coordinate system moving with the mean flow velocity, equal to $x - Ut$.

Symbol	Definition
x_a, x_b	Longitudinal positions of the upstream and downstream ends of the reach, in feet.
x_i	Coordinate direction in tensor notation; x_1 = longitudinal direction, x_2 = vertical direction, x_3 = lateral direction.
Δx	Length of reach, or $x_b - x_a$, in feet.
X	Distance between measurement points in a recirculating flume, in feet.
X_t	Amount of carbonaceous waste oxidized up to time t, in milligrams per liter.
$X_{1i} \; X_{2i} \; \ldots X_{Ni}$	Independent variables in the linear regression equation.
y	Vertical position or direction, in feet.
y_1	Vertical distance below the interface to which surface renewal occurs, Harriott (1962) model, in feet.
Y	Dependent variable in linear regression equation.
Y_{ei}	Estimate of the dependent variable, Y_i, from the linear regression equation.
Y_i	Dependent variable i in linear regression equation.
Z	Constant in the Streeter-Phelps (1925) prediction equation for the reaeration coefficient.
α, β	Parameters in the distribution function for surface-renewal time or distance below the interface to which surface-renewal occurs, Harriott (1962) model.

| Symbol | Definition |

Symbol   *Definition*

β' Turbulence parameter for a flow layer in the Marchello-Toor (1963) model, equal to $s(L_f/2)^2$, in square feet per hour.

Γ Gamma function, $\Gamma(\alpha) = \int_0^{\infty} e^{-y} y^{\alpha-1} \, dy$.

δ The mean relative increase in flow velocity per 5-foot increase in gage height, Streeter-Phelps (1925) prediction equation for the reaeration coefficient.

ε Eddy diffusion coefficient for mass, equal to $\varepsilon_T + D_m$, in square feet per day (y and x subscripts indicate vertical and longitudinal directions, respectively; i and j subscripts are tensor notation).

ε_T Turbulent diffusion coefficient, in square feet per day (i and j subscripts are tensor notation).

ε_{υ} Eddy diffusion coefficient for momentum, in square feet per day.

η Exponent on velocity in the Streeter-Phelps (1925) prediction equation for the reaeration coefficient.

θ Temperature coefficient, equal to $(K_T/K_{20})^{\frac{1}{T-20}}$.

κ Slope parameter in logarithmic velocity distribution law of von Karman.

κ_G Gas film coefficient for mass transfer, in milligrams per square centimeter per second per atmosphere.

Symbol	Definition
κ_L	Liquid film coefficient for mass transfer, in liters per square centimeter per second.
Λ	Macroscale of turbulence, in centimeters.
μ	Absolute viscosity of the liquid, in grams per centimeter-second.
μ_0'	Velocity normal to the interface that a gas molecule must have to be able to leave the liquid, in centimeters per second.
ν	Kinematic viscosity of the liquid, in square centimeters per second.
ρ	Mass density of the liquid, in grams per cubic centimeter.
σ	Surface tension of the liquid, in dynes per centimeter.
$\phi(t)$	Distribution function for surface ages.
χ	Constant in the Isaacs and Gaudy (1968) equation.
ψ	Constant in the empirical prediction equation for the reaeration coefficient.
ω	Dissolved oxygen consumption rate by bottom deposits, in grams per square meter per hour.

REAERATION IN OPEN-CHANNEL FLOW

By J. P. Bennett and R. E. Rathbun

ABSTRACT

Reaeration, the physical absorption of oxygen from the atmosphere,
is the primary process by which a stream replaces oxygen consumed in the
biodegradation of organic wastes. The reaeration process in a stream is
characterized by its surface reaeration coefficient. Hence, knowledge
of the reaeration coefficient permits determination of the quantity of
waste that can be discharged into a stream without seriously depleting
the dissolved oxygen content of the stream.

The three basic methods for measuring the reaeration coefficient are
the dissolved oxygen balance, disturbed equilibrium, and tracer procedures.
The dissolved oxygen balance method consists of measuring the various
sources and sinks of dissolved oxygen and determining by difference the
reaeration needed to balance the equation. The disturbed equilibrium
method consists of artificially producing dissolved oxygen deficits by
the addition of sodium sulfite and subsequent measurement of upstream and
downstream concentrations of dissolved oxygen at two different concentration
levels. The tracer method consists of using an inert radioactive gas as
a tracer for oxygen and correlating the rate of desorption of the tracer
gas with the rate of absorption of oxygen.

Various theoretical models of the oxygen absorption process exist, however, these models are in general not suited for prediction of the reaeration coefficient in streams because the model parameters have not been adequately related to bulk-flow hydraulic variables. Semi-empirical and empirical equations developed from experimental data adequately predict reaeration coefficients for streams of the type on which the equations were based but large errors may occur when the equations are applied to other types of streams or to conditions outside the range of variables considered in the original correlation.

INTRODUCTION

The use of rivers and streams for the disposal of municipal and industrial wastes is generally accepted as proper (Hess, 1954). It is recognized (Hull, 1963) that this use is one of the most important factors contributing to the general health and welfare of the people of the United States. Discharge of wastes into a stream, however, does not simply dilute the wastes. Each stream and river has a natural capacity for oxidizing biodegradable wastes, thus naturally purifying the waters. This purification capacity is dependent upon many factors including the water discharge, the depth of flow, the velocity of flow, and the various sources and sinks of dissolved oxygen along the stream. It is expected, therefore, that the natural purification capacity of a stream will vary as the hydraulic conditions in the stream change with time.

Although the flow in a specific stream may vary greatly from day-to-day and year-to-year, the total annual runoff for the United States as a whole has shown only a small, apparently cyclic, variation with time for the years 1895 to 1955 (Leopold and Langbein, 1960). On the other hand, the population and the number of industrial facilities have increased tremendously and this growth has placed an ever-increasing burden on the rivers and streams of the United States. In many instances, the purification capacities of streams and rivers have been exceeded.

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However, the fact that municipal and industrial wastes are discharged into a stream does not necessarily mean that the stream is polluted because the stream does have the capacity for self-purification. The definition of what constitutes "pollution" has received considerable attention. The Colorado Supreme Court in 1934 (Gindler, 1967, p. 5) defined pollution as follows:

"For the purpose of this case, the word 'pollution' means an impairment, with attendant injury, to the use of water that the plaintiffs are entitled to make. Unless the introduction of extraneous matter so unfavorably affects such use, the condition is short of pollution. In reality, the thing forbidden is injury. The quantity introduced is immaterial."

Other definitions have been discussed by Haney (1966) and he proposed that "pollution is the impairment of water quality, with resultant significant interference with beneficial water use." It is apparent from these definitions that the determination of when pollution exists depends both on the intended use of the stream and some water quality parameter that will insure that the water is of a quality adequate for the intended purpose.

Of the various indicators of water quality (such as the coliform bacteria count, the hydrogen ion concentration, and the concentrations of phosphates, nitrates, synthetic organics, and industrial chemicals), the one most often used as a measure of pollution by biodegradable organic wastes is DO (dissolved oxygen) concentration (Wolman, 1960). This report uses DO concentration as the principal measure of water quality. Thus the condition of a stream is determined from a DO balance which includes all of the sources and sinks of DO along the reach of interest. The various types of DO balances for streams and rivers that have appeared in the literature are discussed in the following paragraphs.

The purification capacity of a stream depends upon its DO resources and its ability to replace the oxygen consumed in the oxidation of organic wastes. One of the first studies of the DO balance was the classical study of Streeter and Phelps (1925). These authors assumed one sink and one source of DO.

The oxygen sink was the biochemical oxidation of carbonaceous wastes by bacteria in the stream. It is generally assumed that biochemical oxidation is a first-order process, that is, the rate of biochemical oxidation is proportional to the amount of carbonaceous material remaining to be oxidized. This process may be described by

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

where L is the BOD (biochemical oxygen demand) of the carbonaceous material, t is time, and K_1 is the deoxygenation coefficient or the rate constant for the oxidation of carbonaceous wastes. Note that the concentration of biodegradable waste is expressed in terms of the oxygen demand. The concentration of biodegradable waste in the stream is not directly measurable and is of importance only because it controls the demand for DO. The DO demand is determined by a BOD test and standard procedures for the test are described by the American Public Health Association (1965). If the DO concentration is expressed in terms of the saturation deficit, D, or the difference between the DO saturation concentration and the actual concentration at time t, then it follows that

$$\frac{dD}{dt} = - \frac{dL}{dt} \quad . \qquad\qquad (2)$$

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The oxygen source considered by Streeter and Phelps (1925) was reaeration or the physical absorption of oxygen from the atmosphere by the flowing stream. Adeney and Becker (1919, 1920) have shown that the absorption of oxygen by water is a first-order process, that is, the rate of absorption is directly proportional to the saturation deficit. This process may be described by

$$\frac{dD}{dt} = -K_2\, D \tag{3}$$

where K_2 is the reaeration coefficient or the rate constant for the absorption of oxygen from the atmosphere and D is the DO deficit.

Streeter and Phelps (1925) assumed that the DO deficit was determined by these two independent processes. Therefore, the DO balance was

$$\frac{dD}{dt} = K_1 \, L - K_2 \, D \quad . \tag{4}$$

The solution of equation 1 is

$$L = L_a \, \exp(- \, K_1 \, t) \quad . \tag{5}$$

Substituting equation 5 in equation 4, the solution of equation 4 is

$$D = \frac{K_1 \, L_a}{K_2 - K_1} \, [\exp(- \, K_1 \, t) - \exp(- \, K_2 \, t)] + D_a \, \exp(- \, K_2 \, t) \tag{6}$$

where L_a is the BOD of the carbonaceous material and D_a is the DO deficit just upstream from the point at which the waste is added to the stream. The time, t, is expressed in terms of flow time along the stream. If t is flow time, then dD/dt is equivalent to $U \, dD/dx$ where U is the mean flow velocity in feet per day and x is longitudinal distance in feet. The factors D and L are usually expressed in ppm (parts per million) or mg/ℓ (milligrams per liter) and K_1 and K_2 are usually expressed in reciprocal days (days^{-1}). A plot of D as a function of t gives the classical sag curve for dissolved oxygen deficit. An assumption inherent in equation 6 is that the initial pollution load is added at the upstream end of the reach and thereafter is affected only by biochemical oxidation and not by the addition of either pollution or dilution flow along the reach.

Streeter and Phelps (1925) were aware that the assumption of a slug injection of BOD was an over-simplification of the actual situation, and hence, also solved equation 4 for a BOD source uniformly distributed along the reach of interest. This BOD distribution resulted in a much more complicated solution. Other assumptions regarding the distribution of the BOD load are possible, and the complexity of the solution, equation 6, increases as the complexity of the assumed distribution for L increases.

An example of an oxygen sag curve for an L_a of 9.0 mg/ℓ, a D_a of 1.0 mg/ℓ, a K_1 of 0.1 days^{-1}, and a K_2 of 0.2 days^{-1} is presented in figure 1. Just below the point of addition of the pollution load, the

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Figure 1.--following here

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oxidation of the waste predominates and the DO deficit increases. However, reaeration begins as soon as a DO deficit develops and the rate of reaeration increases as the deficit increases. Finally at the minimum deficit of the oxygen sag curve, the rate of supply of oxygen by reaeration equals the rate of consumption of oxygen by biochemical oxidation. Thereafter, the reaeration process predominates and the DO deficit is gradually reduced to zero. Also shown in figure 1 is the increase in the DO deficit in the absence of reaeration (K_2=0).

The oxygen sag equation of Streeter-Phelps (1925) has been widely used and different forms of the equation have appeared in the literature. Some authors have used common logarithms (base 10) and the deoxygenation and reaeration coefficients under these circumstances are generally represented by k_1 and k_2, respectively, where

$$K_1 = 2.30 \ k_1 \tag{7}$$

and

$$K_2 = 2.30 \ k_2 \ . \tag{8}$$

A mathematical analysis of the Streeter-Phelps equations has been presented by Fair (1939).

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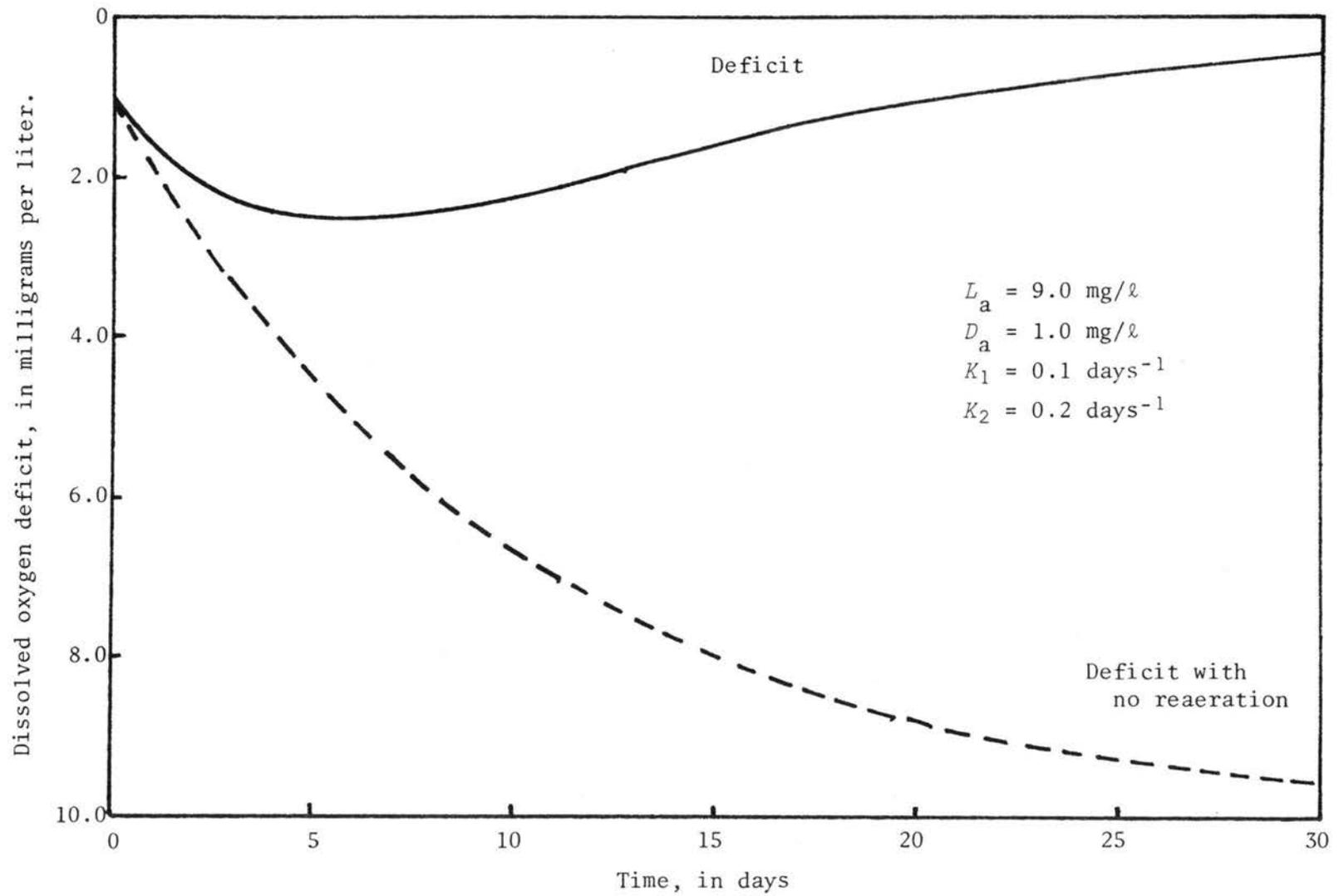
Figure 1.--Example of a dissolved oxygen deficit sag curve.

The figure shows a plot with "Dissolved oxygen deficit, in milligrams per liter." on the y-axis (ranging from 0 at top to 10.0 at bottom) and "Time, in days" on the x-axis (ranging from 0 to 30). The solid curve is labeled "Deficit" and the dashed curve is labeled "Deficit with no reaeration".

Parameters shown:

$L_a = 9.0$ mg/ℓ

$D_a = 1.0$ mg/ℓ

$K_1 = 0.1$ days^{-1}

$K_2 = 0.2$ days^{-1}

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Processes other than biochemical oxidation and reaeration also may be important in the DO balance of a stream. Although Streeter and Phelps (1925) chose to include only these two fundamental processes in their oxygen balance, they were aware of the possible effects of inflow along the reach, sedimentation and scouring in the reach, and photosynthesis (Streeter and Phelps, 1925, p. 22, p. 10). Other authors, notably Dobbins (1964b) and Camp (1963), have expanded the fundamental Streeter-Phelps equation to include in the oxygen balance these and other sources and sinks of DO.

Dobbins (1964b) included the removal of BOD by sedimentation or adsorption on bottom sediments, the removal of DO from the water by diffusion into the benthal layer, the removal of DO by plankton and fixed plant respiration, the addition of BOD along the reach by runoff and by scour of bottom deposits, the addition of DO by the photosynthetic process of plankton and fixed plants, and the continuous redistribution of the BOD and DO by the effects of longitudinal dispersion.

With these sources and sinks considered, the DO balance has the form

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + K_2 (C_s - C) - K_1 L - D_B \tag{9}$$

where C is the DO concentration, C_s is the saturation DO concentration, x is longitudinal distance along the reach, U is the mean stream velocity, D_x is the longitudinal dispersion coefficient, and D_B includes the net rate of removal of DO by the benthal layer and the effect of plants, both photosynthesis and respiration. Therefore, the algebraic value of D_B may be positive or negative, depending on the relative magnitudes of the three processes. Dobbins (1964b) used the convention that D_B is positive when the rate of removal of DO exceeds the rate of addition.

A BOD balance analogous to the DO balance may be written as follows

$$\frac{\partial L}{\partial t} + U \frac{\partial L}{\partial x} = D_x \frac{\partial^2 L}{\partial x^2} - (K_1 + K_3) L + L_R \tag{10}$$

where K_3 is the rate constant for the removal of BOD by sedimentation and adsorption and L_R is the rate of addition of BOD along the reach including the addition of BOD with runoff, the diffusion of partially degraded waste from the benthal layer into the water, and the scour and resuspension of bottom deposits.

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In general, steady state and uniform flow conditions are assumed in a DO balance study. With these assumptions, the $\partial C/\partial t$ and $\partial L/\partial t$ terms are zero and the water discharge, the input BOD load, the temperature, and the rate constants at each point in the reach are assumed independent of time. Other assumptions inherent in equations 9 and 10 are as follows:

(1) The DO and BOD are uniformly distributed over each cross section so that equations 9 and 10 can be written in the one-dimensional form.

(2) The processes described by the rate constants K_1, K_2, and K_3 are first order processes, that is, the rate of removal of BOD is proportional to the amount of BOD remaining and the rate of reaeration is proportional to the DO deficit.

(3) The processes represented by L_R and D_B are uniformly distributed along the reach.

(4) Only the carbonaceous demand of the waste is significant. If the nitrogeneous demand is important, an additional term must be added to equations 9 and 10.

Each of the terms in equations 9 and 10 represents a time-rate of change of the BOD or DO concentration and the units used are generally ppm per day or mg/ℓ per day.

Dobbins (1964b) solved equations 9 and 10 with these assumptions and the added assumption that the effect of longitudinal dispersion is negligible compared with the other terms for natural streams. For the BOD equation, the solution showed that the BOD may either decrease or increase along the reach, depending on whether L_a is greater than or less than $L_R / (K_1 + K_3)$ where L_a is the initial BOD load at the upstream end of the reach. Dobbins (1964b) suggested a procedure for the evaluation of the various constants and also discussed the D_B term which includes several different processes.

Camp (1963) has presented DO and BOD balance equations similar in form to equations 9 and 10. Primary differences are in the use of dC/dt and dL/dt as opposed to $U \, dC/dx$ and $U \, dL/dx$ and in the treatment of the D_B term. With the assumptions of steady state and uniform flow conditions,

$$\frac{d}{dt} = U \frac{d}{dx} \quad .$$ (11)

Therefore Camp's equations (1963, p. 295, 297) for the DO balance may be written as

$$\frac{dC}{dt} = K_2 (C_s - C) - K_1 L + p$$ (12)

and

$$\frac{dL}{dt} = - (K_1 + K_3) L + m$$ (13)

for the BOD balance. In equation 12, p is the rate of production of oxygen by photosynthesis and in equation 13, m is the rate of addition of BOD to the water from bottom deposits. For streams where longitudinal mixing is important, Camp (1963, p. 311) includes a $D_x (d^2/dx^2)$ term on the right-hand side of equations 12 and 13.

Other forms of DO balances have been used. The Water Pollution Research Laboratory group at Stevenage, England (Edwards and Owens, 1962; Edwards, 1962; Edwards and Owens, 1965; Owens, 1965) has used a DO balance which consists simply of an algebraic summation of the contributions or debits of the various sources and sinks of DO. The equation is

$$Q_0 = P \pm D_0 - R \tag{14}$$

where P is the rate of production of oxygen by photosynthesis, R is the rate of oxygen utilization, D_0 is the rate of transfer of oxygen through the surface of the stream, and Q_0 is the rate of change of DO content in the reach of interest. Equation 14 is an integral form of the DO balance with the various coefficients assumed to be independent of time and longitudinal position within the reach. It also assumes that the stream flow is constant and uniform over the reach of interest.

The factor Q_0 is defined by

$$Q_0 = \frac{F}{A_s} (C_b - C_a) \tag{15}$$

where F is the volumetric rate of flow of water, A_s is the water surface area of the reach, and C_b and C_a are the concentrations of DO at the downstream and upstream ends, respectively, of the reach at times t_b and t_a where $t_b - t_a$, is the time required for a slug of water to flow through the reach.

The factor D_0 is defined by

$$D_0 = f(\bar{C}_s - \bar{C}) \tag{16}$$

where f is the exchange coefficient for the reach and $\bar{C}_s$ and $\bar{C}$ are the mean saturation and the mean concentration of dissolved oxygen in the reach, respectively.

Each term in equations 14 to 16 has the dimensions of g/m^2 hr (grams per square meter per hour), or equivalent, and is a rate per unit of surface area. To put these equations in dimensions comparable to the dimensions of the Streeter-Phelps (1925), Camp (1963), and Dobbins (1964b) equations, each term must be divided by the mean depth of flow. Thus, the exchange coefficient, f, divided by the mean depth of flow is equivalent to the reaeration coefficient, K_2.

The basic DO balance, equation 14, was modified as needed to meet the conditions in the stream under study. For example, Owens and Edwards (1966) used

$$Q_0 = P_B + P_P - R_B - R_P \pm D_0 \tag{17}$$

where the B subscript refers to bottom deposits and attached plants and the P subscript refers to phytoplankton which live unattached in the water. In the River Lark just below a sewage works, Owens and Edwards (1963) found that the consumption of oxygen by the bottom deposits or mud was a very important factor. Thus the respiration term, R_B, for bottom deposits was divided into two terms, R_B and R_M, where the subscript B refers to attached bottom plants (benthos) and the subscript M refers to mud or bottom deposits. The resultant equation

$$Q_0 = P_B + P_P - R_M - R_B - R_P + D_0 \tag{18}$$

was discussed by Owens and Knowles (1968). If significant organic pollution exists in the water of the stream, then an additional oxygen sink, R_{BOD}, must be added to the right-hand side of equation 18.

Bain (1968) used a modified form of the Streeter-Phelps equation for predicting the variation of the DO concentration with time at a point. His DO balance was

$$\frac{dC_t}{dt} = p_t - r_t - K_1 L_t + K_2 (C_s - C_t) \quad , \tag{19}$$

where the t subscript indicates variability with time at a particular point in space. Bain (1968) wrote equation 19 for each of six 4-hour periods, giving a set of six simultaneous equations for each day of observation. These equations were solved by a numerical technique using sequential substitution and the result was a dynamic DO balance for a 24-hour period at a specific point in the stream.

O'Connell and Thomas (1965) considered the assumption of steady state conditions as the major fault of the Streeter-Phelps equation and therefore used

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = p - r + K_2 D - K_1 L \quad . \tag{20}$$

They solved equation 20 with the assumption that the p and r factors were constant with respect to time and position. Hence, the solution is applicable only at a point for a short interval of flow time.

Li (1962) presented a generalized solution of the Streeter-Phelps equation that was expanded to include the effects of BOD and runoff additions along the stream and of fluctuations of the BOD load and DO concentration at the point of addition of the pollution to the stream. He assumed that the variations in BOD load and DO concentration were cyclic and were repeated cycle after cycle.

O'Connor (1967) has written a general DO balance for a one-dimensional stream in which the oxygen demand of the waste was divided into the requirements for the carbonaceous material and the nitrogenous material. The result was

$$\frac{\partial C}{\partial t} + \frac{F}{A_x} \frac{\partial C}{\partial x} = K_2 (C_s - C) + p_{x,t} - K_1 L$$

$$- K_N N_x - r_{x,t} - SE_{x,t} \qquad (21)$$

where F is the volumetric rate of flow, A_x is the cross-sectional area of flow at longitudinal position x, K_N is the rate constant for the oxidation of nitrogenous material, N_x is the concentration of nitrogenous material at x, SE is the rate of removal of BOD by sedimentation, p is the rate of production of DO by photosynthesis, r is the rate of consumption of dissolved oxygen by plant respiration, and the x,t subscript indicates the longitudinal position x at time t. The oxygen demand of the nitrogenous material has not received as much attention as the oxygen demand of the carbonaceous material. However, work by Courchaine (1968), O'Connell and Thomas (1965), Wezernak and Gannon (1968), and O'Connor and others (1968) have shown the importance of nitrification on the DO balance of streams receiving discharges of municipal waste.

O'Connor (1967) solved the general DO balance (equation 21)
analytically with the assumptions that the photosynthetic rate varied
sinusoidally with time and the maximum rate of photosynthesis and the
factors $r_{x,t}$ and $s_{x,t}$ were independent of position and time. The solu-
tion was applicable to a sunlight period of 12 hours. O'Connor discussed
in general terms two limiting forms of the solution. In the first situa-
tion the stream is heavily polluted, shaded, and with large amounts of
suspended materials and/or small amounts of nutrient materials. Under
these conditions, $p_{x,t}$ and $r_{x,t}$ are small and negligible with respect
to the BOD factors and the assumption of steady state conditions is
reasonably valid. The solution reduces to the oxygen sag equation of
Streeter and Phelps (1925) with a term added for the oxygen demands of the
bottom deposits. In the second situation, the stream is in the latter
stage of self-purification. Oxidation of organic material is essentially
complete and bacterial respiration is negligible in comparison with
algae respiration. The assumption of steady state conditions is not
valid and the solution reduces to an equation that describes the temporal
distribution of DO as a result of photosynthetic activity.

The variety of DO balances that have appeared in the literature demonstrates an important fact: Each stream and each reach of a stream must be considered as a separate problem. Generalizations are possible, however. For example, McConnell and Sigler (1959) found in a shallow, swift stream that the effects of the stream metabolism on the DO content was negligible compared with reaeration. On the other hand, in the River Ivel where the water velocity seldom was greater than 6 cm/sec (centimeters per second), reaeration was relatively unimportant (Owens, 1965). Therefore, in an initial DO balance on a stream it is suggested that all possible sources and sinks of DO be considered. The unimportant factors may then be eliminated as they are shown to be negligible.

With the development of computers, the computation of DO distributions from complex analytical solutions of DO balances was simplified greatly. Frankel (1965) developed a dynamic model of the sag equation for computer solution. His model was an extension of the model of Li (1962) to include a variable DO source or sink caused by the presence of algae.

In addition to simplifying computations, computers also made possible numerical solutions that previously would not have been feasible. Dresnack and Dobbins (1968) presented numerical solutions of the BOD and DO equations where BOD and DO inputs varying with time and space prevented analytical solutions. These solutions were limited to steady state and uniform flow conditions. Three examples were considered. These were: (1) the effect of the longitudinal dispersion coefficient on the concentration profile of a conservative pollutant introduced at the upstream end of the reach in a periodically-varying manner; (2) the effect of sinusoidal inputs of BOD and DO at the upstream end of the reach on the BOD and DO profiles; and (3) the effects of sinusoidally-varying inputs of BOD and DO and a sinusoidal variation in the algae effects. Bella and Dobbins (1968) presented a modeling procedure using finite-difference techniques for BOD and DO profiles in streams and estuaries which considered temporal and spatial variations in hydraulic conditions.

The development of computers also has resulted in the advancement of the concepts of systems analysis and these concepts in turn have been applied to the modeling of the DO resources of a stream. A system may in general be defined as an entity which operates on or transforms an input to produce an output. Thus the system consists of the input, the output, and the transformation between the two. Thomann (1963) presented a general model for describing the variations with time of the DO in a finite number of sections of a body of water. This model was applied by Thomann (1965) to the Delaware River Estuary. He determined the transient response of the estuary to an instantaneous injection of waste, demonstrated the ease of extending the systems analysis model to two dimensions, determined the steady state conditions for the one-dimensional model, and applied the linear programming concept to the steady state conditions to determine the most economical combination of waste treatments for the various waste sources that would assure a minimum steady state concentration of DO of 2 mg/ℓ. The latter problem was solved for two values of the reaeration coefficient.

Liebman and Lynn (1966) applied dynamic programming in a simplified example of river basin planning based on data from the Willamette River, Oregon. The objective was to determine the amount of BOD removal required of each waste discharger so that the water quality standards for DO would be met with minimum total cost to the basin. The solution of the Streeter-Phelps equation was used with K_1 and K_2 assumed known and constant in each reach. The equation was modified, however, to account for changes in the saturation concentration, C_s, as a result of temperature changes. It was assumed that C_s varied linearly with distance downstream. Three situations were considered: (1) the configuration of treatment plants that would meet the DO standards with minimum cost; (2) same as (1) except that the minimum DO standard was reduced 0.1 mg/ℓ; and (3) same as (1) except with the added requirement that all plants provide the same percent of BOD removal.

The general application of the concepts of linear programming to the solution of the DO balance equation and the determination of the degrees of treatment required for minimum basin cost were discussed by ReVelle, Loucks, and Lynn (1967). The application of linear programming to the data from the Willamette River, Oregon, was discussed by ReVelle and others (1968). The results were essentially the same as those obtained with dynamic programming.

Most DO balances give one value for the DO concentration at a down-stream point. Similarly most DO quality standards do not distinguish as to the degree or duration of a violation. This consideration is important, however, because the presence of a DO concentration that is sufficient on the average to assure healthy fish does not prevent fish kills. Thayer and Krutchkoff (1967) presented a stochastic model applicable to steady state flow and input BOD and DO conditions that gives the probability distributions for the BOD and DO concentrations at downstream points. With the confidence limits determined from the distributions, it is possible to obtain the proportion of the time that the BOD will be greater than any specified concentration. The model can be used with any flow condition such as the expected minimum flow condition, provided the parameters K_1, K_2, K_3, and D_B associated with the flow condition are known.

Loucks and Lynn (1966) developed probabilistic models for predicting the probability distribution of minimum DO concentration at points down-stream from a waste treatment plant. The models were based on different mean daily stream and waste flow conditions. Loucks and Lynn suggested that the use of a maximum allowable probability of the DO concentration falling below a specified concentration for a given number of consecutive days was a more realistic approach than the deterministic DO standards generally used.

Kothandaraman and Ewing (1969) considered the effect of variations in K_1 and K_2 on the downstream DO distributions and developed procedures for taking the expected variations into account in predicting the DO. A Monte Carlo simulation technique was used to analogize the variations in K_1 and K_2. It was found that the variations of K_1 and K_2 within their practical ranges have significant effects in the prediction of the DO concentrations and that the errors increased with temperature increase.

Di Toro and O'Connor (1968) studied the effect of time-varying discharge and mean velocity on the BOD and DO distributions. It was found that the standard deviations of the resultant BOD and DO distributions were approximately equal to the coefficient of variation of the velocity multiplied by the BOD or DO distribution calculated using the mean velocity.

Despite the sophistication of the mathematical techniques permitted by the development of computers, it is still necessary to measure or estimate the various parameters of the DO balance. Thomann (1965) stated that his systems analysis study of the Delaware Estuary pointed out "the importance of good engineering evaluation of the system parameters of flow, diffusion, reaeration, and decay coefficients."

In the following pages is presented a critical analysis of previous theoretical and experimental work concerning the reaeration coefficient in open-channel flows. The discussion encompasses theoretical and empirical models for prediction of K_2, techniques for experimental determination of K_2, an analysis of previous experimental data, a suggested prediction equation, and suggestions for future research. From the introductory discussion of the DO balance for open-channel flows, it is apparent that if K_2 is to be calculated using a DO balance equation, all other parameters appearing in the equation must be known. The procedures for determining these parameters are therefore discussed also.

THEORIES FOR PREDICTING THE REAERATION COEFFICIENT

The gas absorption process at the interface between a flowing liquid and a gas has received considerable attention in recent years. The process is quite complicated and only superficially understood, so that theoretical treatments have been only partially successful. There is, however, considerable useful information concerning this phenomenon throughout the technical literature of chemical and sanitary engineering. The purpose of this section is to describe the various theories for predicting the coefficient of reaeration or gas-liquid mass transfer coefficient for open-channel flows.

Diffusion Equation

A gas moves into and through a flowing liquid by the process of diffusion. This process may be described by the general diffusion equation (Hinze, 1959)

$$\frac{\partial C}{\partial t} + U_i \frac{\partial C}{\partial x_i} = \frac{\partial}{\partial x_i}\left(D_m \frac{\partial C}{\partial x_i} - \overline{u_i c} \right) + F_c \quad , \tag{22}$$

given here in tensor notation. The capital letters represent time-averaged quantities, the lower case letters represent fluctuating components or the instantaneous deviations from the time-averaged quantities, C is the concentration of the diffusing substance, U_i is the velocity in the x_i direction, D_m is the molecular diffusivity of the dissolved gas in the liquid, F_c is a source-sink term, and the overbar on $\overline{u_i c}$ indicates an averaging procedure with respect to time. Equation 22 applies to a dispersant which is in solution in a steady-state flow of an incompressible liquid.

With the common assumptions that: (1) turbulent diffusion may be described by a turbulent diffusion coefficient, $\varepsilon_{T_{ij}}$, such that

$$\frac{\partial C}{\partial x_j} \varepsilon_{T_{ij}} = - \overline{u_i c} \quad ; \tag{23}$$

(2) the total diffusion may be described by a diffusion tensor, ε_{ij}, where the turbulent and molecular diffusion are independent and therefore additive, or

$$\varepsilon_{ij} = \varepsilon_{T_{ij}} + D_m \quad ; \tag{24}$$

and (3) the coordinate axes coincide with the principal axes of the diffusion tensor, Sayre and Chang (1968) have reduced equation 22 to

$$\frac{\partial C}{\partial t} + U_i \frac{\partial C}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\varepsilon_i \frac{\partial C}{\partial x_i} \right) + F_c \quad . \tag{25}$$

For uniform two-dimensional flow in a straight channel of constant cross section, equation 25 may be expressed as

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \varepsilon_x \frac{\partial^2 C}{\partial x^2} + \frac{\partial}{\partial y} \left(\varepsilon_y \frac{\partial C}{\partial y} \right) + F_c \quad . \tag{26}$$

Equation 26 is expressed in the coordinate system usually used for open channel flow situations, that is, the mean flow is in the x or longitudinal direction with U the flow velocity in that direction, y is in the vertical direction or the direction of the channel depth, and the mean flow in the y direction is zero.

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Defining averages of the type $\overline{C} = \frac{1}{H} \int_0^H C \, dy$, and noting that the mass transport across the lower flow boundary is zero $\left(\varepsilon_y \frac{\partial C}{\partial y} \Big|_{y=0} = 0 \right)$, one can average equation 26 over the flow depth H and obtain

$$\frac{\partial \overline{C}}{\partial t} + \frac{\partial}{\partial x} \left(\overline{UC} \right) = \frac{\partial^2}{\partial x^2} \left(\overline{\varepsilon_x C} \right) + \frac{1}{H} \left(\varepsilon_y \frac{\partial C}{\partial y} \right) \Bigg|_{y=H} + \overline{F}_c \quad . \tag{27}$$

Over a major portion of the flow depth of a turbulent open channel flow, mass transport in the y direction as a result of vertical diffusion is quite large compared to the mass transport through the surface. Hence, the vertical gradient of C generally is very small except near the surface so that within the bulk of the flow the value of C should approach $\overline{C}$. This has been verified by W. W. Sayre (written communication, 1968) who numerically solved the equation $\frac{\partial C}{\partial t} = \frac{\partial}{\partial y} \left(\varepsilon_y \frac{\partial C}{\partial y} \right)$. He assumed ε_y to be equal to the momentum transport coefficient of a flow having a logarithmic velocity distribution and solved the equation for C as a function of time at 50 points in the vertical using values of $\left(\varepsilon_y \frac{\partial C}{\partial y} \right) \Bigg|_{y=H}$ corresponding to the range of such values observed for streams in nature. Initially, the flow was assumed to be unsaturated except for the top increment and it was found that even for very short times, there was no appreciable concentration gradient in the vertical. In support of Sayre's work, it has been observed experimentally that the concentration of DO does not vary measurably in the vertical in natural streams. Churchill and others (1962) found no vertical concentration gradients for a series of dissolved oxygen measurements in a deep, low velocity stream, and Edwards and Owens (1962) found that the DO concentration of

a slow-flowing English stream was greater than 98 percent of the surface
concentration except in a relatively small area near the bed. Also
Whipple and others (1969, p. 116) concluded that the centerline DO
concentration at a depth of one foot was a good estimate of the mean
cross-sectional concentration of DO for the slow-flowing Passaic River.
When the concentration of the dissolved substance is constant in the
vertical, equation 27 may be written

$$\frac{\partial \overline{C}}{\partial t} + \overline{U} \frac{\partial \overline{C}}{\partial x} = \overline{\varepsilon}_x \frac{\partial^2 \overline{C}}{\partial x^2} + \frac{1}{H} \left(\varepsilon_y \frac{\partial C}{\partial y} \right) \Big|_{y=H} + \overline{F}_c \quad . \tag{28}$$

It is generally assumed that the diffusion equation in this form is
applicable to computing the longitudinal distribution of dissolved
oxygen in streams.

Because of the experimental and theoretical evidence indicating
no concentration gradient of dissolved oxygen in the vertical direction
of an open-channel flow, the overbar on concentration in equation 28
indicating an average with respect to the depth of flow is unnecessary.
Hency, this overbar on concentration will not be used in the remainder
of the report. For consistency, the overbar on the velocity will also
be dropped with the understanding, however, that U is the flow velocity
averaged over the depth of flow or the mean velocity of flow in the
longitudinal direction.

For reasons of convenience and tradition, completely aside from the fact that the turbulent transport process in open-channel flows is not sufficiently understood to permit evaluation of ε_y near a free surface, the second term on the right in equation 28 is generally expressed using one of two mass transfer coefficients, K_L or K_2. The more general coefficient K_L, the liquid-film coefficient, is defined as follows:

$$K_L = \frac{1}{(C_s - C_L)} \left(\varepsilon_y \frac{\partial C}{\partial y} \right)\Bigg|_{y=H} \tag{29}$$

where C_L is the dissolved oxygen concentration in the bulk liquid phase. From a comparison of equations 9 and 28 it is seen that the reaeration coefficient K_2, may be expressed in terms of the film coefficient as

$$K_2 = K_L / H \quad . \tag{30}$$

(Equation 9 is the same as equation 28, except the source-sink terms have been lumped into the term $\overline{F}_c$ in equation 28.) Theories for the prediction of K_L or K_2 may be checked in certain idealized situations by measurements of C_L, evaluation of the source-sink terms, and substitution into an integrated version of equation 28.

The prediction of mass transfer coefficients from solute and solvent properties and from the parameters of the flow is a problem which has received much discussion in the fluid mechanics literature. At the present time (1971) there are available fairly reliable theories for the prediction of heat and mass transfer coefficients for flows near the solid boundaries in straight circular pipes (Hinze, 1959). These fall into two general categories, the eddy diffusion or gradient diffusion theories and the renewal theories.

Because of the gas-liquid interface, side wall effects, and secondary currents, the mechanics of flow in straight open channels with uniform cross-sections are considerably more complex than the mechanics of flow in straight circular pipes. Furthermore, mass transfer coefficients usually are desired not for straight channels with uniform cross-sections, but for natural channels which are neither straight nor of uniform cross-section. Because of these complexities, reliable theories comparable to the eddy diffusivity theories for pipe flows have not been developed for the prediction of mass transfer coefficients from mean flow parameters in open-channel flows. The theories which have arisen are in general less rigorous, in the fluid mechanics sense, than are the eddy diffusivity theories. They fall into three general groups: (1) the conceptual theories, based on assumed mathematical models of the mass transfer processes within the flow; (2) the semi-empirical theories, qualitatively relating the mass transfer coefficients to some measurable flow property, the constants in the relation being determined by multiple regression; and (3) empirical theories resulting from dimensional analysis, again with the constants being determined by multiple regression techniques. The remainder of this section is devoted to a discussion of the models of these types which have appeared in the literature.

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Conceptual Models for the Gas-Liquid
Mass Transfer Process

Conceptual models derive from equations describing an interpretation of the physical conditions governing mass transfer at a gas-liquid interface. The equation generally used is the differential equation describing non-convective diffusion. The boundary conditions chosen vary from model to model. In some models, the parameters arising from the solution of the differential equation with the given boundary conditions are not clearly related to the mean flow parameters such as mean velocity, depth of flow, or turbulent intensity. In such models, discovering the relation of the former parameters to the latter is a problem requiring considerable thought and experimental verification. The models may be divided into the following general groups: (1) film; (2) renewal, including penetration, film-penetration, and surface renewal-damped eddy diffusivity; (3) kinetic theory; (4) large eddy; and (5) turbulent diffusion models. The usefulness of a particular model ultimately must be determined by how well it predicts reaeration coefficients for natural streams.

Film model

The earliest model for mass transfer at a gas-liquid interface was the two-film model of Lewis and Whitman (1924). They postulated that laminar films of gas and liquid exist at the interface between the two phases. Because mass transport in a direction perpendicular to the mean-flow direction in a laminar film is by molecular diffusion alone, a process much slower than the turbulent diffusion within the phases, the resistance to mass transfer is concentrated in the two films. The interface between the gas and liquid films seems to offer no resistance to mass transfer (Sherwood and Pigford, 1952). If the gas and liquid phases outside of the film region are assumed to be completely mixed, then the mass transport, N, of oxygen through the films for the oxygen-water system is

$$N = \kappa_L \left(C_i - C_L \right) = \kappa_G \left(p_G - p_i \right) \tag{31}$$

where C_L is the concentration of oxygen in the water phase, C_i is the concentration of oxygen at the interface, p_G and p_i are, respectively, the partial pressures of oxygen in the gas phase and at the interface, and κ_L and κ_G are, respectively, the liquid-film and gas-film coefficients. Equilibrium conditions usually are assumed at the interface so that C_i and p_i are related by Henry's Law or $p_i = h\, C_i$ where h is the Henry's Law constant.

The film coefficients are expected to be dependent on the properties of the liquid and the gas and on the flow parameters, but independent of the concentration of the dissolved gas in the liquid (Sherwood and Pigford, 1952).

However, because concentrations and partial pressures at the interface are difficult to measure, information on the individual film coefficients is difficult to obtain. Thus, equation 31 usually is written in terms of the overall liquid and gas-film coefficients, or

$$N = K_L \left(C_s - C_L \right) = K_G \left(p_G - p_s \right) \tag{32}$$

where p_s is the partial pressure corresponding to the saturation concentration, C_s, and K_L and K_G are, respectively, the overall liquid-film and gas-film coefficients for mass transfer.

To be of use in engineering calculations, the overall coefficients should be dependent on the properties of the liquid and gas and on the flow parameters but independent of the concentration of dissolved gas. From equations 31, 32, and Henry's Law, it can be shown that

$$\frac{1}{K_L} = \frac{1}{\kappa_L} + \frac{1}{h \, \kappa_G} \quad . \tag{33}$$

Thus for any gas-liquid pair that obeys Henry's Law, the overall liquid film coefficient is independent of the gas concentration in the liquid. For a slightly soluble gas that does not react chemically with the liquid, h is large so that equation 33 reduces to

$$K_L \cong \kappa_L \quad . \tag{34}$$

Equation 34 is equivalent to saying that the gas-film resistance is negligible with respect to the liquid-film resistance and that K_L is independent of the concentration of dissolved gas for a slightly soluble gas that obeys Henry's Law. The oxygen-water system is such a gas-liquid pair.

Because mass transfer in the laminar film is by molecular diffusion, and if the concentration gradient across the film is assumed to be linear, then

$$N = D_m \frac{\left(C_s - C_L\right)}{L_f} \tag{35}$$

where L_f is the thickness of the film. By comparing equations 32 and 35, it follows that

$$K_L = \frac{D_m}{L_f} \quad . \tag{36}$$

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In equation 36, the solute and solvent properties are accounted for by the molecular diffusivity, D_m, and the hydrodynamics of the flow by the layer thickness, L_f. For a truly laminar layer to exist on the surface of an open-channel flow, the flow must be quite tranquil. Such flows are seldom encountered in field situations, however, so that equation 36 does not suffice to describe the variation of the reaeration coefficient with flow parameters. The concept of diffusion into laminar patches of infinitesimal area existing for short times on the water surface before being replaced by liquid from the bulk liquid has been used, however, in subsequent models describing the reaeration process.

Renewal models

The renewal models are analogous to those for predicting mass transfer coefficients for fluid flows near solid boundaries. In the renewal models, it is generally assumed that diffusion into a surface layer is purely molecular. The surface layer is sometimes assumed to be of infinite thickness, and sometimes to have a thickness, L_f, which may or may not be randomly distributed about an average thickness, $\overline{L}_f$. Below the layer, the diffusivity in the liquid is assumed to be infinite, the concentration independent of depth. After diffusion into an element of the surface layer has taken place for some period of time, the element is assumed to be replaced by liquid from the bulk flow. The frequency of renewal is governed by an assumed probability density function. The mass transfer coefficients predicted by these models are functions of the molecular diffusivity, an average renewal frequency, and generally an average thickness of the surface layer. The renewal models include (1) the penetration model, (2) the film-penetration model, and (3) the surface renewal-damped eddy diffusivity model.

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Penetration model.--The penetration model was first postulated by Higbie (1935) and later refined by Danckwerts (1951). Both authors visualized the surface of the liquid as being a laminar film, the thickness of which is large with respect to the depth which can be penetrated by molecular diffusion during the life of the film. The film lifetime is the time elapsed between the formation of the film on the surface and its replacement by fresh liquid from the bulk flow. The difference between the Higbie and Danckwerts theories lies in the replacement process visualized by the authors.

Molecular diffusion in a laminar layer is governed by the differential equation

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial y^2} \quad . \tag{37}$$

For an infinitely deep layer the boundary conditions are:

$$
\begin{aligned}
C &= C_L & t &= 0 & y &> 0 \\
C &= C_L & t &> 0 & y &\to \infty \\
C &= C_s & t &> 0 & y &= 0 \quad ,
\end{aligned}
\tag{38}
$$

where C_L is the concentration in the bulk liquid phase, y is the distance from the interface, and t is the time elapsed since the formation of the interface. The solution to equations 37 and 38 is (Carslaw and Jaeger, 1959)

$$C = C_L + \left(C_s - C_L \right) \operatorname{erfc}\left[\frac{y}{2\sqrt{t\, D_m}} \right] , \tag{39}$$

and the rate of transport of solute through the surface is

$$- D_m \left.\frac{\partial C}{\partial y}\right|_{y=0} = \left(C_s - C_L \right) \sqrt{\frac{D_m}{\pi t}} \quad . \tag{40}$$

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Higbie (1935) visualized the surface elements as all being of the same age, and as all being replaced simultaneously on reaching an age t_e. Alternatively, the ages of the differential elements of the laminar surface film can be visualized as being distributed according to the distribution function $\phi(t)$ such that

$$\phi(t) = \begin{cases} \dfrac{1}{t_e} & 0 \leq t \leq t_e \\[2em] 0 & t > t_e \end{cases} \qquad . \qquad (41)$$

The average rate of mass transport, $\overline{N}$, through a unit of surface area for either case is

$$\overline{N} = \frac{1}{t_e} \int_0^{t_e} \left(C_s - C_L \right) \sqrt{\frac{D_m}{\pi t}} \; dt = 2 \left(C_s - C_L \right) \sqrt{\frac{D_m}{\pi t_e}} \qquad . \qquad (42)$$

Because $\overline{N} = K_L \left(C_s - C_L \right)$, one has

$$K_L = 2 \sqrt{\frac{D_m}{\pi t_e}} \qquad . \qquad (43)$$

Danckwerts (1951) assumed that the surface consists of an infinite
number of differential elements of area which have their ages distributed
according to

$$\phi(t) = se^{-st} \quad , \tag{44}$$

where s is the average rate of surface renewal. The average rate of mass
transport through a unit of surface area is then

$$\overline{N} = \int_0^\infty \left(C_s - C_L \right) \sqrt{\frac{D_m}{\pi t}} \; se^{-st} \; dt = \left(C_s - C_L \right) \sqrt{D_m \, s} \quad , \tag{45}$$

so that

$$K_L = \sqrt{D_m \, s} \quad . \tag{46}$$

Neither author attempted to relate either the parameter $1/t_e$ or s
to the mechanics of flow in open channels, but it is clear that they
must represent a parameter related to the average residence time of the
large flow eddies at the surface.

Film-penetration model.--The film-penetration model was developed
by Dobbins (1956) and independently by Toor and Marchello (1958). Certain
modifications have been discussed in the literature (see, for example,
Marchello and Toor, 1963, and Harriott, 1962), but essentially, the film-
penetration theory consists of assuming molecular diffusion into laminar
surface elements of differential area and thickness, L_f, which exist on
top of a turbulent liquid which has uniform solute concentration, C_L.
The ages of the surface elements are assumed to be distributed according
to the distribution function for surface age of Danckwerts (1951) as given
by equation 44.

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The differential equation governing the diffusion process is
equation 37. The boundary conditions for the film-penetration model
are

$$
\begin{aligned}
C &= C_L & t &= 0 & 0 &< y \le L_f \\
C &= C_s & t &\ge 0 & y &= 0 \\
C &= C_L & t &\ge 0 & y &= L_f & .
\end{aligned}
\tag{47}
$$

Dobbins (1956) obtained as the solution to equations 37 and 47

$$
C = C_L + \left(C_s - C_L \right) \sum_{n=0}^{\infty} \left(\mathrm{erf}\ \frac{n+1 - \frac{y}{2L_f}}{\sqrt{\frac{D_m\, t}{L_f^2}}} - \mathrm{erf}\ \frac{n + \frac{y}{2L_f}}{\sqrt{\frac{D_m\, t}{L_f^2}}} \right) ,
\tag{48}
$$

and using the age-distribution function of Danckwerts (1951), he obtained

$$
K_L = \sqrt{D_m\, s}\ \coth \left(\frac{s\, L_f^2}{D_m} \right)^{1/2} .
\tag{49}
$$

When the film-renewal rate, s, becomes very small, equation 49 approaches
the film limit or $K_L = D_m / L_f$, while for $\sqrt{s\, L_f^2 / D_m} > 3.0$, equation 49
gives essentially the penetration limit, or $K_L = \sqrt{D_m\, s}$.

Marchello and Toor (1963) have presented a modification of the film-penetration model in which it is assumed that the surface layer is not replaced, but is instantaneously mixed at times which are distributed according to the age-distribution function of Danckwerts (1951). In the periods between mixings, diffusion is governed by equation 37. They obtained for the mass transfer coefficient

$$K_L = \frac{\sqrt{D_m \, s}}{2} \cdot \frac{\left[1 + \cosh \left(\frac{s \, L_f^2}{D_m} \right)^{1/2} \right]}{\sinh \left(\frac{s \, L_f^2}{D_m} \right)^{1/2}} \quad . \tag{50}$$

For small renewal rates, equation 50 approaches the film model limit, while for large renewal rates it approaches one-half the penetration model prediction for K_L.

Another modification of the film-penetration model has been presented by Harriott (1962). This theory is designed for application to mass transport at fluid-solid interfaces, but it could probably be applied also to open-channel flows, especially in the presence of surfactants. In this theory, it is postulated that diffusion is molecular, according to equation 37, and that renewal occurs not necessarily all the way to the surface, but to some distance y_1 below the surface. In applying this theory, one must solve equation 37 with the boundary conditions

$$
\begin{array}{llll}
C = C_s & y = 0 & t \geq 0 \\
C = C_L & y \to \infty & t \geq 0 \\
C = f(y) & 0 \leq y \leq \infty & t = 0 & .
\end{array}
\tag{51}
$$

The probability density functions used by Harriott (1962) to describe the distributions of the renewal period and of the distance y_1 below the surface to which renewal occurs were of the form

$$
p(f) = \frac{1}{\Gamma(\alpha)\,\beta^\alpha}\, f^{\alpha-1} \exp\,(-f/\beta)
\tag{52}
$$

where f is a dummy variable (signifying y_1 or t), α and β are distribution parameters, and Γ denotes the gamma function. In this model, K_L cannot be obtained analytically, so it must be obtained using numerical techniques. Harriott found that at the penetration model limit, the numerical procedures gave $K_L \propto \sqrt{D_m\,s}$ as expected; however, at what would ordinarily be the film model limit, he found $K_L \propto y_1^{n-1}\, D_m^{1-n/2}\, s^{n/2}$ where $0 \leq n \leq 1$, and where n is highly sensitive to the distribution parameters α and β.

Several methods have been presented for determining the parameters in the Dobbins model in terms of the parameters of the turbulent flow system. Not much has been done along these lines with the Marchello and Toor model or with the Harriott model, however, the concepts used in the case of the Dobbins model should be adaptable to these models as well.

The earliest method for relating the parameters of the Dobbins model to the parameters of open-channel flow was presented by O'Connor and Dobbins (1958). They pointed out that for rivers $\coth\left(\frac{s\ L_f^2}{D_m}\right)^{1/2} \doteq 1$ so that $K_L \doteq \sqrt{D_m\ s}$, and all that needs to be determined in terms of the flow parameters is s, the mean rate of surface renewal. For determining s, river turbulence is divided into two classes, non-isotropic, and essentially isotropic at the water surface. For both types of turbulence, s is defined as the ratio of the vertical turbulent intensity to the mixing length, at the water surface. For a Chezy C less than 17, O'Connor and Dobbins assumed non-isotropic turbulence to exist, and using the definition of the Prandtl mixing length and the log velocity law, they obtained

$$s = \frac{\left(D_m\ g\ S\right)^{1/2}}{\kappa\ H} \quad , \tag{53}$$

where H is the flow depth, S the channel slope, g the gravitational constant, and κ is the slope parameter in von Karman's logarithmic velocity law. Substitution of equation 53 into equation 49, leads to

$$k_L = 480\ \frac{D_m^{1/2}\ S^{1/4}}{H^{1/4}} \quad , \quad \text{or} \quad k_2 = \frac{480\ D_m^{1/2}\ S^{1/4}}{H^{5/4}} \tag{54}$$

where k_L is in feet per day, H in feet, and D_m in feet^2 per day. For a Chezy C greater than 17, isotropic turbulence is assumed to exist. For this case, O'Connor and Dobbins (1958) used measurements made by Kalinske on the Mississippi River which showed that the vertical turbulent intensity was approximately 0.1 U and that the mixing length was approximately 0.1 H, hence

$$s = \frac{0.1\ U}{0.1\ H} = \frac{U}{H} \quad . \tag{55}$$

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Thus

$$k_L = 127\left(\frac{D_m U}{H}\right)^{1/2} , \quad \text{or} \quad k_2 = \frac{127\left(D_m U\right)^{1/2}}{H^{3/2}} \tag{56}$$

where the mean flow velocity U is in fps (feet per second) and all other units are the same as in equation 54. In equations 55 and 56, k_L and k_2 are for use with the base 10.

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Another theory relating the parameters of the Dobbins model to the mean flow parameters was presented by Dobbins (1964b). He postulated that the effective film thickness must be related to the smallest surface eddies into which the gas can penetrate by molecular diffusion before being carried into the flow below. Using Kolmogoroff's limit for the size of the energy-dissipating eddies, he obtained

$$L_f = c_3 \left(\frac{\nu^3}{E_\xi} \right)^{1/4} = c_4 \left(\frac{\nu^3}{E} \right)^{1/4} \tag{57}$$

where c_3 and c_4 are constants, ν is the kinematic viscosity of the liquid, and E_ξ and E are, respectively, the energy dissipated per unit mass of liquid at the surface, and the energy dissipated per unit mass of liquid by the entire flow. Dobbins also postulated that the rate of expenditure of energy required to overcome the surface tension and replace the surface liquid is proportional to the turbulent energy per unit mass of liquid near the surface. Thus

$$s = \frac{c_1 \, \rho \, L_f \, E_\xi}{\sigma} = \frac{c_5}{c_4^3} \, \frac{\rho \, \nu^{3/4} \, E^{3/4}}{\sigma} \tag{58}$$

where c_1 and c_5 are constants, ρ the mass density of the liquid, and σ its surface tension. It can further be shown that

$$s \, L_f^3 = c_5 \, \frac{\rho \, \nu^3}{\sigma} \quad . \tag{59}$$

In equations 57 and 58, c_5 is reportedly dependent only on solute and solvent properties, while c_4 is dependent on the dynamics of the flow system. Dobbins reported c_5 to be 14.3 for the oxygen-water system at 20°C. He obtained

$$c_4 = 0.65 + 15000 \left[\frac{\left(\frac{\nu^3}{E}\right)^{1/4}}{H} \right]^2 \quad , \tag{60}$$

from a plot of experimental results that contains considerable scatter. In the closure to his 1964b paper, Dobbins (1965) presented a prediction equation derived from the same data, but which is more convenient to use than equations 60, 59, and 57 in combination with equation 49. The prediction equation for k_L is

$$k_L = \frac{0.12\ B_F\ A\ E^{3/8}\ \coth\left(\frac{B\ E^{1/8}}{c_4^{1/2}}\right)}{c_4^{3/2}} \quad , \tag{61}$$

where
$$
\left.
\begin{aligned}
B_F &= 1.0 + F^2 \\
c_4 &= 0.9 + F \\
A &= 9.68 + 0.054\ (T-20) \\
B &= 0.976 + 0.0137\ (30-T)^{3/2} \\
E &= 30.0\ S\ U \\
F &= U/\sqrt{g\ H}
\end{aligned}
\right\}
\tag{62}
$$

and where the slope, S, is in feet per thousand feet, T is the temperature in °C, and k_L is in units of feet per day.

In a modification of Dobbins' (1964b) theory, Metzger and Dobbins (1967) used a surface compressional modulus, M_s, in place of the surface tension, σ. Following arguments similar to those used by Dobbins (1964b), they obtained

$$s = \frac{c_1' \, c_2^{3/4} \, (c_3')^3 \, \rho \, \nu^{3/4} \, E^{3/4}}{M_s} \quad , \tag{63}$$

$$L_f = c_4 \left(\frac{\nu^3}{E} \right)^{1/4} \quad , \tag{64}$$

and

$$s \, L_f^3 = c_5' \, \frac{\rho \, \nu^3}{M_s} \quad , \tag{65}$$

where c_2 and c_4 are the same constants as in the Dobbins theory and c_1', c_3', and c_5' are new constants, and where c_5' is independent of the flow dynamics. For distilled water, Metzger and Dobbins (1967) found $\frac{c_5'}{M_s} = 1.3 \, \frac{\sec^2}{\text{gram}}$, and Metzger (1968) found this same value in the presence of 0.5 mg/ℓ of alkyl benzene sulfonate (a surfactant) in water. The significance of having M_s in the denominator of equation 65 rather than σ is that M_s increases in the presence of surface active agents while σ decreases. Thus equation 65 is in qualitative agreement with the observation that surface active agents retard surface renewals.

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The localized mixing model of Marchello and Toor (1963) can be applied not only to the surface layer of an open-channel flow, but also to lower layers within this type of flow, as well as to all layers in other flow types such as pipe flows. When this is done, it can be shown for any layer that

$$\frac{\varepsilon_y}{D_m} = \sqrt{\frac{\beta'}{D_m}} \cdot \frac{1 + \cosh 2\sqrt{\frac{\beta'}{D_m}}}{\sinh 2\sqrt{\frac{\beta'}{D_m}}} - 1 \quad , \tag{66}$$

where ε_y is the eddy diffusivity for mass, and β' is the turbulence parameter for the layer, such that

$$\beta' = s\left(\frac{L_f}{2}\right)^2 \quad . \tag{67}$$

Similarly, after applying the localized mixing model to momentum transfer, Marchello and Toor obtained

$$\frac{\varepsilon_\nu}{\nu} = \sqrt{\frac{\beta'}{\nu}} \frac{1 + \cosh 2\sqrt{\frac{\beta'}{\nu}}}{\sinh 2\sqrt{\frac{\beta'}{\nu}}} - 1 \quad , \tag{68}$$

where ε_ν is the eddy diffusivity for momentum. Thus if one can determine the momentum eddy diffusivity for a particular layer, one can solve equation 68 for β' and determine the eddy diffusivity for mass for the layer from equation 66.

The combination into one model of the film concept of Lewis and Whitman (1924) and the penetration concept of Higbie (1935) and Danckwerts (1951) has, practically speaking, considerable merit in that the combined model can predict accurately reaeration coefficients for natural streams over a much wider range of conditions than can either of the models alone. The film penetration models, however, are idealized in that the diffusion process is visualized as taking place in two separate steps, rather than as being governed by the classical diffusion equation embodying both molecular and turbulent diffusion. The first step is molecular diffusion; the second step is turbulent diffusion or non-gradient diffusion embodied by a renewal or mixing process. This idealization will, of course, lead to difficulties in relating model parameters to flow parameters, and to deviations of the predicted from the true mass transfer coefficients in situations where the flow conditions differ appreciably from those under which the experimental model coefficients were determined. For the Dobbins (1956) model, the O'Connor and Dobbins (1958) method for determining s is perhaps overly simplified, and it requires no experimental coefficients to be evaluated. It is, therefore, a little surprising that this method predicts k_L values for natural streams as well as it does. The Dobbins (1964b) and Metzger and Dobbins (1967) methods are more rational and more sophisticated, and they require the evaluation of two experimental coefficients. Equation 60 used by Dobbins (1964b) to predict c_4 is questionable, because it was obtained from a plot of field data that

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contains considerable scatter. This is, however, apparently of minor importance because if one checks the prediction equation using the data from which equation 60 was evaluated, there is only a small amount of scatter about the line of perfect agreement between predicted and observed k_2 values.

Surface renewal-damped eddy diffusivity model.--The surface renewal-damped eddy diffusivity model was presented by King (1966) who postulated that the mass transport near the surface is due not only to D_m, but also to turbulent diffusion caused by small-scale eddies. The coefficient characterizing the turbulent diffusion caused by the small-scale eddies is the eddy diffusivity for mass, ε_y, which is assumed to be of the form $\varepsilon_y = ay^n$ where a and n are parameters independent of time and y is the distance from the interface. The surface renewals are assumed to be due to the large-scale eddies, and the surface ages are assumed to be distributed according to the distribution function for uniform surface ages (equation 41).

The diffusion equation applicable to the above model is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial y}\left[\left(D_m + ay^n\right)\frac{\partial C}{\partial y}\right] \quad , \tag{69}$$

and the boundary conditions used by King (1966) are

$$
\begin{aligned}
C &= C_L & t &= 0 & y &> 0 \\
C &= C_L & t &> 0 & y &\to \infty \\
C &= C_s & t &> 0 & y &= 0 \quad .
\end{aligned}
\tag{70}
$$

Equation 69 along with the boundary conditions 70 can be solved analytically only in special cases such as for a = 0 and all n, for all a and n = 0, 1, ∞, and for all a and all n with t large. For large t, the solution of equations 69 and 70 (King, 1966) gives

$$\frac{K_L}{a^{1/n}\, D_m^{1-1/n}} = \frac{n}{\pi}\sin\frac{\pi}{n} \quad , \tag{71}$$

where t may be interpreted as the surface age at renewal.

If the surface renewal-damped eddy diffusivity model is to be useful in predicting film coefficients, the parameters a and n in equation 69 as well as an average surface age, $\bar{t}$, must be estimated. From equation 71 it is seen for large surface ages that the exponent n can be estimated from the variation of K_L with molecular diffusivity, if the other factors remain constant. Kozinski and King (1966) concluded that $K_L \propto D_m^{0.75}$ for gas-liquid transfer at large surface ages, thus $n = 4$. From the work of Calderbank and Moo-Young (1961), King (1966) concluded that

$$a = 0.006 \, \frac{E_V \, \rho}{\mu^2} \quad , \tag{72}$$

where E_V is the energy dissipation rate per unit of liquid volume, ρ the mass density of the liquid, and μ the absolute viscosity of the liquid. From figure 3 of King (1966) and from equation 71 for $n = 4$, it is seen that if surface renewal effects control, the surface renewal-damped eddy diffusivity model yields film coefficient predictions of the same order as those measured in large open channels and rivers.

The surface renewal-damped eddy diffusivity model is physically more realistic than previous models because the artifice of a surface layer is avoided. Also the eddy diffusivity is accounted for in the diffusion equation rather than by the surface renewal, so that gradient and nongradient diffusion are more clearly separated. Practically, however, the model is cumbersome in that three parameters must be evaluated and equation 69 must be solved numerically in most cases. If $n = 4$ and a is given by equation 72, King (1966) shows that s should be proportional to $\frac{\rho}{\mu} \left[\frac{E\,H}{\rho} \right]^{2/3}$ for open-channel flows. This has not been checked experimentally.

Kinetic theory

The kinetic theory as developed by Miyamoto (1932) was presented by Krenkel and Orlob (1963). The model is based on the frequencies and velocities of bombardment of the interface by solute molecules from both the liquid and the gas phases. The resulting equation is

$$k_L \propto \frac{1}{1000} \left(\frac{R_G\,T'}{2\pi\,M} \right)^{1/2} \exp\left[-(M/2\,R_G\,T')\,(\mu_0')^2 \right] \qquad (73)$$

where R_G is the ideal gas constant, T' the absolute temperature, M the molecular weight of the gas, and μ_0' is the velocity which a solute molecule must attain normal to the interface to be able to leave the liquid.

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If equation 73 is to account for the turbulent properties of the flow as well as for solute and solvent properties, it must be done with the parameter μ_0'. That μ_0' could account for the turbulence properties of the flow is reasonable, because $\frac{M(\mu_0')^2}{2}$ may be viewed as an activation energy term, and as pointed out by Bird and others (1960, p. 27), the activation energy of liquids is influenced by local values of the shear stress which can in turn be related to local turbulence properties. There does not appear to have been any study either theoretical or experimental in which such relations have been presented.

Another kinetic theory model was presented by Tsivoglou (1967). It too arises from consideration of the difference between the rate of entry and the rate of loss of gas (oxygen) molecules from a surface layer of liquid (water). The loss rate, r_0, is

$$r_0 = b(L_f \, C \, n_s \, A_s) \tag{74}$$

where

C = concentration of gas in the liquid,

L_f = thickness of surface layer from which gas molecules can escape to the atmosphere,

n_s = number of new surface layers exposed per unit of time,

A_s = surface area, and

b = the proportion of available molecules in the surface layer that actually escape.

The entry rate, r_e, which is dependent on the gas concentration in the air above the water, is a constant. It is equal to the loss rate at $C = C_s$, so that

$$r_e = b(L_f \, C_s \, n_s \, A_s) \quad . \tag{75}$$

The time rate of change of the liquid concentration is then

$$\frac{dC}{dt} = \frac{r_e - r_0}{V} = \frac{b \, L_f \, n_s \, A_s}{V} (C_s - C) \quad , \tag{76}$$

so that

$$K_2 = \frac{b \, L_f \, n_s \, A_s}{V} \quad . \tag{77}$$

Because $\frac{A_s}{V} = \frac{1}{H}$, in which V is the volume of the system, and H its depth,

$$K_L = b \, L_f \, n_s \quad . \tag{78}$$

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Equation 78 is mostly of theoretical interest, because at the present time, none of the parameters on the right-hand side can be measured. However, some of the results obtained by Tsivoglou (1967) by manipulation of the equations of this model are of interest. First, because the entry rate is a function only of the gas concentration in the layer above the fluid, Tsivoglou concluded that the factor b varies with temperature according to the relation

$$(b)_{T_2} = (b)_{T_1} \frac{(C_s)_{T_1}}{(C_s)_{T_2}} \quad , \tag{79}$$

where the subscripts indicate two different temperatures. Combining equation 79 with equation 77 yields

$$\frac{K_{2_{T_2}}}{K_{2_{T_1}}} = \frac{C_{s_{T_1}}}{C_{s_{T_2}}} = \theta^{(T_2 - T_1)} \quad , \tag{80}$$

in which θ is a temperature correction coefficient for the mass transfer coefficient. This coefficient will be discussed in greater detail later. At present, the value usually accepted for θ is 1.0241 given by Elmore and West (1961). The values calculated by Tsivoglou for θ from equation 80 for oxygen and water for temperatures from 0° to 30°C range from 1.018 to 1.026. This lends credence to Tsivoglou's model.

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Further support for the model is presented by Tsivoglou (1967). Assuming the average molecular transport within the body of a turbulent liquid to be due to an average concentration gradient between volume elements, and equating the mass transfer at the surface to the average transfer between the volume elements, Tsivoglou showed that for the simultaneous transfer of two gases,

$$\frac{\left(K_2\right)_1}{\left(K_2\right)_2} = \frac{\left(D_m\right)_1}{\left(D_m\right)_2} \quad . \tag{81}$$

When considering the ratio of the mass transfer coefficients of two gases, equation 81 leads to the same conclusion as the film model, namely that the ratio of the mass transfer coefficients of the two gases is directly proportional to the first power of the ratio of their molecular diffusivities.

In further developing his model, Tsivoglou (1967) pointed out that if mass transport through the surface is governed by Einstein's law of diffusion, then

$$\frac{\left(D_m\right)_1}{\left(D_m\right)_2} = \frac{d_2}{d_1} \quad , \tag{82}$$

in which d_1 and d_2 are the molecular diameters of the two gases. From equations 82 and 81

$$\frac{\left(K_2\right)_1}{\left(K_2\right)_2} = \frac{d_2}{d_1} \quad . \tag{83}$$

Tsivoglou and others (1965) and Tsivoglou (1967) completed an extensive series of measurements of the simultaneous transfer of several pairs of gases across a water interface. Two types of apparatus were used, one in which both gases were transferred simultaneously into the water and one in which a second gas was transferred out of the water as oxygen was transferred into it. A range of temperature and turbulence conditions was studied for each pair of gases and each apparatus. On the basis of these measurements, Tsivoglou (1967) concluded that the ratio of the gas transfer coefficients was a constant within the limits of experimental error for the range of temperature and turbulence conditions studied. This supports the model as given in equation 77.

Tsivoglou (1967) suggested that his experimental measurements of the gas transfer ratios for the different pairs of gases together with molecular diameter data from the literature support equation 83. However, a linear regression analysis of the logarithms of the transfer coefficient ratios and the molecular diameter ratios yielded

$$\frac{\left(K_2\right)_1}{\left(K_2\right)_2} = 1.06 \left(\frac{d_2}{d_1}\right)^{1.26} \tag{84}$$

where the 95 percent confidence limits on the exponent are 1.09 and 1.44. There is other experimental evidence suggesting that equation 83 and the argument that D_m can be obtained from Einstein's law of diffusion are not strictly valid. Kozinski and King (1966) found that the exponent on D_m in the relation $k_L \propto D_m^n$ varied from about 0.50 to 0.75 for the stirred tank data of Dobbins (1964a), which is considerably different from the 1.26 indicated by equations 84 and 82.

These apparent discrepancies suggest that Einstein's law of diffusion is not strictly applicable to this situation, but note that these discrepancies do not in any way reflect on the validity of the model as represented by equation 81. The only requirement of the model here is that the gas transfer coefficient ratio be a constant, as was found in a laboratory study by Tsivoglou and others (1965) and Tsivoglou (1967).

Large eddy model

The large eddy model as presented by Fortescue and Pearson (1967) postulates that the mass-transfer properties of a turbulent surface can be modeled by a series of steady, square roll cells. The cells touch the surface of the flow and are convected downstream with the mean velocity at the surface. The roll cells are taken to be Λ on a side, where Λ is the turbulent macroscale of the flow. The velocity pattern within a cell is given by

$$u_e = A_e \, \sin \frac{\pi x}{\Lambda} \, \cos \frac{\pi y}{\Lambda}$$

$$v_e = -A_e \, \cos \frac{\pi x}{\Lambda} \, \sin \frac{\pi y}{\Lambda} \quad . \tag{85}$$

The parameter A_e is a measure of $\overline{E}$, the average kinetic energy of the roll cell, because

$$\overline{E} = \frac{1}{2\Lambda^2} \int_0^\Lambda \int_0^\Lambda (u_e^2 + v_e^2) \, dx \, dy = \frac{1}{4} A_e^2 \quad . \tag{86}$$

The differential equation describing the gas concentration distribution in the large eddy model is

$$u_e \frac{\partial C}{\partial x} + v_e \frac{\partial C}{\partial y} = D_m \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \quad , \tag{87}$$

with boundary conditions

$$
\begin{aligned}
C &= C_s & y &= 0 & 0 &\le x \le \Lambda \\
\frac{\partial C}{\partial x} &= 0 & 0 &\le y \le \Lambda & x &= n\Lambda \\
C &= C_L & y &= \Lambda & 0 &\le x \le \Lambda \quad ,
\end{aligned}
\tag{88}
$$

where n is an integer. Equation 87 with boundary conditions 88 must be solved numerically.

Dimensional analysis of equation 87 along with equation 85 shows that the characteristic parameter describing the large eddy model is P, the Péclet number, where $P = \dfrac{\Lambda\, A_e}{D_m}$. Fortescue and Pearson (1967) reported that for P values "over the range that was relevant", the numerical solution of equations 85, 87, and 88 yields

$$k_L = 1.46\left(\frac{D_m\, \overline{u'}}{\Lambda}\right)^{\frac{1}{2}} \quad , \tag{89}$$

where $\overline{u'}$ is the longitudinal turbulent intensity. Using the O'Connor and Dobbins (1958) relation for $u'/\Lambda = U/H$, Fortescue and Pearson reported that their model gives "rather better" predictions than the Higbie (1935) penetration model (equation 43) with $1/t_e = \overline{u'}/\Lambda = U/H$, for the river data used by O'Connor and Dobbins (1958).

The large eddy model is different in concept from the other models presented in this section, but the concept is as realistic as, for example, the film-penetration concept. An individual cell is a considerably idealized turbulent eddy, and the surface film is a film of eddies, rather than a stagnant film. The model avoids the question of surface age by allowing the age to vary in a set pattern across the top of the cell. It would be interesting to find the effect on the computed film coefficient of assumed distribution functions for varying cell sizes and kinetic energy. A more realistic relation for surface values of $\overline{u'}/\Lambda$ might improve the predictions made by the model.

Turbulent diffusion model

In the turbulent diffusion model, Kishinevsky (1955) postulated for high turbulence levels that the turbulent diffusivity, ε_y, is not damped out at the water surface. He further stated that the turbulent diffusivity at the surface is much larger than the molecular diffusivity, so that

$$k_L = \frac{2}{\sqrt{\pi}} \sqrt{\varepsilon_y s} \quad . \tag{90}$$

An example in which equation 90 can be said to govern is presented by Kishinevsky and Serebryansky (1956). They reported studies in a highly agitated stirred tank in which the measured film coefficients for hydrogen, oxygen, and nitrogen were all roughly the same, despite the fact that the molecular diffusivity of hydrogen is about twice that for oxygen and nitrogen. They also reported, however, that at lower stirring speeds the molecular diffusivity influenced the measured film coefficient. The fact that in open-channel flows the measured values of k_L are a function of temperature indicates that in this type of flow turbulence levels do not reach a magnitude sufficient to make equation 90 applicable.

It is interesting to note that the models discussed predict a range of dependence of k_L on D_m varying from an exponent of one for the film model to zero for the turbulent diffusion model. The film-penetration model predicts an exponent on D_m which varies from 0.5 to 1.0, while the surface renewal-damped eddy diffusivity model can predict an exponent anywhere from 0 to 1.0. Experimental data taken in stirred tanks (Kozinski and King, 1966) indicated that the exponent is in the 0.5 to 0.75 range. Therefore, it would appear that each model (with the possible exception of the film model) is applicable to a limited range of turbulence conditions. However, the surface renewal-damped eddy diffusivity model is the only one which is applicable over the entire range of turbulence conditions.

All the conceptual models for the gas-liquid mass transfer process involve two physical properties of the oxygen-water system. These are the molecular diffusivity and the saturation concentration for oxygen in water. Each of these properties has been studied in considerable detail and the following paragraphs summarize briefly the results of these studies.

The subject of the determination of the molecular diffusivities of dissolved gases in liquids has been reviewed by Himmelblau (1964) and a discussion of the experimental determinations of the molecular diffusivity of oxygen in water has been presented by Duda and Vrentas (1968).

The experimental data for molecular diffusivity at 25°C fall into two groups with one group indicating a value of about 2.5×10^{-5} cm^2 per sec and the second group indicating a value of about 2.0×10^{-5} cm^2 per sec. The larger values in general have been used (Isaacs and Gaudy, 1968; Metzger and Dobbins, 1967; Kozinski and King, 1966; Dobbins, 1964b; O'Connor and Dobbins, 1958). Himmelblau (1964) also believed that the smaller values at 25°C were probably incorrect and Baird and Davidson (1962) believed that the larger values obtained with the wetted sphere procedure were more accurate than the values obtained with the annular jet. On the other hand, Kolthoff and Izutsu (1964) concluded that a modified equation incorporating a second perturbation term should be used in the calculation of oxygen diffusivities from polarographic measurements. This modification resulted in diffusivities of 1.94 and 1.97×10^{-5} cm^2 per sec at 25°C as compared with values of 2.56 and 2.50×10^{-5} cm^2 per sec obtained without the second perturbation term. Duda and Vrentas (1968) concluded from their consideration of the available experimental data that the evidence tended to support the smaller diffusivity values, in agreement with their laminar jet result. It is apparent that controversy exists concerning the correct value for the molecular diffusivity of oxygen in water. Hence, diffusivity data for the oxygen-water system should be used with this consideration in mind.

The saturation concentrations presented in the various editions of Am. Public Health Assoc. (1960; 1965) were accepted and used until 1955 when Truesdale, Downing, and Lowden (1955) obtained results that were significantly different. Since that time, it has been shown (Montgomery and others, 1964) that the results of Truesdale and others (1955) were low because of losses of iodine vapor during the analysis for DO. The reported differences, however, stimulated several other studies of the saturation concentrations and the results of these investigations have been compared by Montgomery and others (1964) and Montgomery (1969). The conclusion was that the values reported in Am. Public Health Assoc. (1965) are slightly high except at low temperatures whereas the more recent results (see Montgomery, 1969, for references) tend to lie above the values obtained by the Committee on Sanitary Engineering Research (1960) at temperatures above 15°C.

The saturation concentration decreases with increasing temperature and decreases with decreasing barometric pressure. The temperature dependence of the saturation concentrations obtained by the Committee on Sanitary Engineering Research (1960) was expressed in terms of a cubic equation. The dependence on barometric pressure, p_B, may be expressed in terms of a simple ratio, or

$$C_{s_2} = C_{s_1} \frac{p_{B_2}}{p_{B_1}} \quad . \tag{91}$$

For elevations above 3000 feet and temperatures above 25°C, corrections for the water vapor pressure should be made (Am. Public Health Assoc., 1965, p. 409).

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Equation 91 demonstrates a fact perhaps not generally recognized. For a temperature of 20°C and a pressure of 760 mm Hg, the saturation concentration is 9.02 mg/ℓ (Committee on Sanitary Engineering Research, 1960). If a concentration of 5.0 mg/ℓ is required for prevention of fish kills, then a range of about 4 mg/ℓ of DO is available for a stream at an elevation of about sea level, for example, along the east coast of the United States. However, for a stream in the Rocky Mountain region at an elevation of about 5000 feet, the saturation concentration is about 7.5 mg/ℓ, and hence a range of only about 2.5 mg/ℓ of DO is available for use for oxidation of wastes. The saturation concentration decreases with increasing chloride concentration in the water. The effect ranges from a decrease of 0.017 mg/ℓ of DO per 100 mg/ℓ of chloride at 0°C to a decrease of 0.008 mg/ℓ of DO per 100 mg/ℓ of chloride at 30°C (Am. Public Health Assoc., 1965, p. 409).

Sewage in the water may affect the DO saturation value. Moore (1938) found that the solubility of oxygen in a domestic sewage was about 95 percent of the solubility in distilled water and Rand (1959) concluded that the solubility of oxygen in sewage was not significantly different from the solubility in pure water.

Semi-empirical Models

The semi-empirical models result from a consideration and combination of the factors that should affect mass transfer at a free surface. These models rely on regression-correlation analysis of experimental data for the establishment of a prediction equation, and for verification of the assumed relations between the mass transfer coefficient and the flow parameters. In general, the steps in the derivation of these models are: (1) from intuition, a knowledge of previous conceptual models, a knowledge of the results of previous empirical studies, or a combination of these, to postulate that the film coefficient k_L (or the reaeration coefficient k_2) is a function of certain of the parameters of the flow; (2) if necessary, to manipulate the assumed relation to obtain a relation for k_L (or k_2) in terms of easily measured mean-flow parameters; and (3) to use regression-correlation analyses to fit experimental data to the assumed relation and to check its validity. The determination of the usefulness of these models must be based on the reliability of the data from which they were derived, on how well they predict mass transfer coefficients for natural streams, and on ease of use. The first two points are discussed in a later section of this paper; the latter, as the models are presented. The models discussed in this section are those presented by Krenkel (1960) and Thackston (1966). The limits on the ranges of data from which the semi-empirical and empirical models were derived are discussed in a later section.

Krenkel model

This model is presented by Krenkel (1960) and Krenkel and Orlob (1963) who reasoned that

$$k_2 \propto \left[\frac{D_i}{\nu} \quad \frac{\varepsilon}{H^2} \right] \quad , \tag{92}$$

where the first term in brackets is characteristic of the rate of absorption at the surface, and the second term is characteristic of the rate of surface renewal. In equation 92, D_i is a combination of molecular and turbulent diffusivity at the surface, and ε is an eddy diffusion coefficient. However, both Krenkel (1960) and Krenkel and Orlob (1963) believed that the reaeration coefficient is better represented by

$$k_2 \propto s \, \exp\left[- E_a / R_G \, T'\right] \tag{93}$$

where $s = \varepsilon/H^2$, E_a is the activation energy for oxygen absorption, R_G is the ideal gas constant, and T' is the absolute temperature. It was decided for use in equations 92 and 93 that the parameter most characteristic of the turbulent diffusion coefficient, ε is D_x, the longitudinal dispersion coefficient of the flow.

Regression analysis by Krenkel and Orlob (1963) of 58 laboratory measurements of k_2 made at depths from 0.08 to 0.20 ft (foot) in a 1-ft wide flume yielded

$$k_2 = 1.418 \exp\left[- E_a / R_G T'\right] \frac{D_x}{H^2} - 0.0069 \quad , \qquad (94)$$

where $E_a = 5875 \frac{cal}{mole}$, $R_G = 1.99 \frac{cal}{mole \, °K}$, T' is the absolute temperature in °K, and the units of k_2 are minutes^{-1}. Because the procedure for measuring D_x is difficult and time consuming, this parameter is not one of the commonly available stream-flow parameters. However, for uniform open-channel flows in the depth range given above, Krenkel (1960) has shown by a regression analysis that D_x can be related to the commonly measured mean flow parameters by

$$D_x = 6.425 \, E^{0.296} \, H^{1.243} \quad , \qquad (95)$$

where D_x is in feet^2 per minute, and $E = U S g$, where U is in fpm (feet per minute), g is in feet per minute^2, and E is the energy dissipated per unit mass of flowing fluid. Alternatively, from a separate regression analysis of the same data, Krenkel (1960) and Krenkel and Orlob (1963) reported that k_2 at 20°C can be determined from

$$(k_2)_{20°} = 1.141 \times 10^{-4} \, E^{0.408} \, H^{-0.66} \qquad (96)$$

where again k_2 is in minutes^{-1}. When equation 96 is to be used for flow at a temperature different than 20°C, adjustment of k_2 must be made using a suitable temperature correction formula (see equation 104).

Experimental differentiation between equations 92 and 93 may be quite difficult if $D_i = D_m$ because for a small temperature range (for example, $\pm 10\,^\circ C$)

$$\frac{D_m}{\nu} \propto \exp\left(- E'/T'\right) \quad , \tag{97}$$

where E' is a combination of the activation energies for molecular diffusion and viscous flow and is independent of temperature. Thus a plot of $\log k_2$ versus $1/T'$ for constant ε/H^2 will show a linear variation whether molecular diffusivity or the activation energy for oxygen absorption controls. It is in fact more likely that D_m (or equation 92) controls because equation 93 in effect states that interfacial resistance controls, while Davies and Rideal (1963) and Sherwood and Pigford (1952) have stated that interfacial resistance is negligible for the absorption of slightly soluble gases.

An important factor to be considered when using equations such as 94 and 95 is that they were developed for flows in straight channels with uniform cross-section, whereas natural streams generally have non-uniform cross-sections and considerable curvature in plan. In such channels, D_x can be considerably greater than the D_x for an equivalent straight channel with uniform cross-section, so equations 94 and 95 might not apply. Equations of the type of 96 might, however, be more valid in natural streams because the rate of energy dissipation includes the effects of non-uniform cross-sections and curvature. Finally, as mentioned above, D_x is difficult to measure or predict whereas equations of the type of 96 use readily measurable mean-flow parameters, so that from this point of view, use of equation 96 would be recommended over the use of equation 94.

Thackston model

This model was presented by Thackston (1966) and Thackston and Krenkel (1969a) who postulated that

$$k_2 \propto \frac{f_1(s)}{f_2(H)} \quad , \tag{98}$$

where s is the average surface renewal rate and H is the flow depth. They further postulated that $f_1(s) \propto \varepsilon_y$, where ε_y is the vertical eddy diffusivity at the water surface, and that $f_2(H) \propto H^2$. They assumed that

$$\varepsilon_y \propto \overline{\varepsilon}_y = \frac{\kappa}{6} H u_* \quad , \tag{99}$$

where $\overline{\varepsilon}_y$ is the average value of the vertical eddy diffusivity, u_* is the shear velocity, $\sqrt{g H S}$, and κ is von Karman's constant. The resulting prediction equation is of the form

$$k_2 = J \frac{u_*}{H} \tag{100}$$

where J is a constant to be determined from regression analysis.

Based on 40 values of k_2 measured by Thackston (1966) in a 2-ft wide flume at flow depths varying from 0.05 to 0.23 ft, a regression analysis yielded

$$k_2 = 0.000215 \frac{u_*}{H} \quad .$$ (101)

More importantly, equation 101 fits rather well to the field data used by O'Connor and Dobbins (1958) and the data collected by Churchill and others (1962). Furthermore, the fit is improved if a Froude number relation is included in the regression analysis. A regression analysis which included this field data plus the flume data of Thackston (1966) yielded

$$k_2 = 0.000125(1 + F^{0.5}) \frac{u_*}{H} \quad ,$$ (102)

where F is the Froude number.

There is some question of the universal applicability of an equation of the type of 102 because when the data of Krenkel (1960) were analyzed in the same fashion as those yielding equation 101, the prediction equation

$$k_2 = 0.000469 \, \frac{u_*}{H} \qquad (103)$$

was obtained. Thackston and Krenkel (1969a) explained this by stating that because Krenkel's 1-ft flume data do not fit field data, and Thackston's 2-ft flume data do, the conditions in the 1-ft flume were not really characteristic of field conditions. It is more likely, however, that this discrepancy indicates that prediction equations of the type of 101 and 102 are not general enough and that some additional parameter such as the width-depth ratio, W/H, should be included in the prediction equation.

Empirical Prediction Equations

The empirical prediction equations result from least squares multiple regression analyses of the variables considered pertinent by the investigator or from dimensional analysis of the mean-flow and gas-liquid parameters. For water and air over the temperature range encountered in the field, it is generally assumed that the temperature dependency of k_2 resulting from the temperature dependence of the molecular diffusivity, kinematic viscosity, surface tension, and other physical properties can be embodied in a single function of the temperature. This dependency is generally removed before the least squares analysis is begun. The empirical temperature correction equation (the form of which can be derived from rate process considerations) is of the form

$$(k_2)_T = (k_2)_{20^\circ} \, (\theta)^{T-20^\circ} \quad , \tag{104}$$

where T is in °C and the θ generally used is the 1.0241 suggested by Elmore and West (1961).

The empirical prediction equations are generally of the form

$$k_2 = \psi(\theta)^{T-20} \, \frac{U^w}{H^j} \quad , \tag{105}$$

where ψ is a constant obtained from a regression analysis of experimental data, and w and j may be chosen in this fashion; or w and j may be chosen for dimensional homogeneity of the prediction equation. Judgment of a particular prediction equation must be based on the quality of the data from which it is derived, and on how well it predicts field reaeration coefficients. The equations discussed in this section are based generally on field-scale data and utilize readily measurable mean-flow parameters for prediction of reaeration coefficients. Presented in the following sections are equations by Streeter and Phelps (1925), Churchill, Elmore, and Buckingham (1962), Owens, Edwards, and Gibbs (1964), Langbein and Durum (1967), Isaacs and Gaudy (1968), and Negulescu and Rojanski (1969).

Streeter-Phelps equations

The pioneering study of reaeration coefficients of large-scale natural streams was presented by Streeter and Phelps (1925). In this study, the classical oxygen sag equation

$$\frac{dD}{dt} = K_1 \, L - K_2 \, D \tag{106}$$

was developed, and used in its integrated form to calculate reaeration coefficients from measured values of the time of travel, upstream and downstream values of the DO deficit and BOD, and the BOD reaction rate constant, K_1.

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The prediction equations were developed from data taken in 1914 and 1915 on the Ohio River between Pittsburgh, Pennsylvania, and Louisville, Kentucky. The study reach was 611 river miles long; it was separated into 11 sub-reaches for experimental measurements. During the study period at the various points in the study reach, the mean monthly values of discharge, depth, and velocity varied, respectively, from 1670 to 309,000 cfs (cubic feet per second), from 16 to 48 feet, and from 0.1 to 4.6 fps. Eighty-six average values of k_2 were reported as corresponding to the monthly averages of the flow parameters existing over the period of measurement on the various sub-reaches.

The prediction equation suggested by Streeter and Phelps (1925) was

$$(k_2)_{20°} = \frac{Z \, U^\eta}{(H')^2} \quad , \tag{107}$$

where H' is the depth above minimum low water stage and k_2 is in days^{-1}. The coefficient Z is a function of what Streeter and Phelps call an irregularity factor, which is defined as the number of changes in channel bottom slope producing a change in elevation greater than 1 ft, expressed on a per-mile basis. For irregularity factors 2.0 to 3.0, $Z = [0.39(10^{1.16}) \, S + 17]$, while for irregularity factors of 3.0 to 5.0, $Z = 1.1 \, S^{2.3}$, where S is the channel water surface slope in feet per mile. The coefficient η is a function of δ, or $\eta = (\delta-0.17)/(\delta-1.17)$, where δ is the mean relative increase in flow velocity per 5 ft increase in gage height.

Because of the need for computing the irregularity factor and the coefficient δ, equation 107 is difficult to use. In addition, because H' is not a true stream flow parameter, it is doubtful if a prediction equation in terms of this parameter can be completely general. Other authors (for example, O'Connor and Dobbins, 1958) have, however, reanalyzed portions of the Streeter-Phelps data to yield prediction equations with a little more generality.

Churchill-Elmore-Buckingham equation

Probably the best field study of the reaeration coefficient is that of Churchill and others (1962). Their measurements were made in stretches below dams where the water released was deficient in DO because of prolonged storage under conditions of thermal stratification, and where generally the BOD was negligible.

The study covered 16 different reaches on 5 rivers. Five hundred and nine individual k_2 determinations were made for 30 different mean-flow situations. The discharge, mean depth, and mean velocity ranged, respectively, from 952 to 17,270 cfs, from 2.12 to 11.41 feet, and from 1.85 to 5.00 fps.

Churchill and others (1962) performed a large number of multiple regression analyses on the pertinent stream flow, gas, and liquid parameters corresponding to the k_2 measurements. None of the prediction equations was found to be statistically any more significant than any of the others, so that the simplest one was suggested by Churchill and others (1962) for general usage. This equation, which has a coefficient of multiple correlation of 0.82, is

$$k_2 = 5.026 \ U^{0.969} \ H^{-1.673} \ (1.0241)^{T-20} \ , \tag{108}$$

where k_2 is in days^{-1}, U in fps, H in feet, and T in °C.

Equation 108 is much more convenient to use than equation 107 because it utilizes only the readily available parameters U, H, and T.

Owens-Edwards-Gibbs equation

Owens and others (1964) reported reaeration coefficient measurements for several English streams. These coefficients were determined using the disturbed equilibrium method of deaeration with sodium sulfite and cobalt catalyst. Use of this procedure eliminates the necessity of considering parameters of the dissolved-oxygen balance that are independent of the dissolved-oxygen concentration.

The study of Owens and others (1964) included measurements on 21 different reaches of 6 streams. They list 32 separate observed values of k_2 for stream discharges, depths, and mean velocities ranging, respectively, from 1.50 to 36.2 cfs, from 0.34 to 2.44 feet, and from 0.13 to 1.83 fps. They also list 6 values of k_2 from Gameson and others (1955) for 2 reaches of a different stream for discharges, depths, and mean velocities within the above ranges.

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Multiple regression analysis of the data by Owens and others (1964) yielded

$$k_2 = 10.90 \ U^{0.73} \ H^{-1.75} \ (1.0241)^{T-20} \ . \tag{109}$$

When Owens and others (1964) included the data of Gameson and others (1955) and that of Churchill and others (1962) in the analysis, the resultant equation was

$$k_2 = 9.41 \ U^{0.67} \ H^{-1.85} \ (1.0241)^{T-20} \ . \tag{110}$$

In these equations k_2 is in days^{-1}, U in fps, H in feet, and T in °C. Equation 110 was obtained from 68 k_2 values with a 300-fold range from about 0.25 to 75 days^{-1}. Again, equations 109 and 110 are quite convenient to use because they utilize only the readily available parameters U, H, and T.

Langbein-Durum equation

Langbein and Durum (1967) combined the river data of O'Connor and Dobbins (1958) and that of Churchill and others (1962) with the laboratory data of Krenkel and Orlob (1963) and that of Streeter, Wright, and Kerr (1936) and obtained the equation

$$(k_2)_{20°} = 3.3 \ \frac{U}{H^{1.33}} \tag{111}$$

where k_2 is in days^{-1}, U in fps, and H in feet. They also considered in a general way the effect of downstream and regional variations of stream discharge on the reaeration coefficient computed from equation 111. It was found that the computed reaeration coefficients decreased in the downstream direction with about the square root of the discharge.

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Isaacs-Gaudy equations

Isaacs and Gaudy (1968) made a study of reaeration in a circular tank with moving walls intended to simulate stream flow conditions. They reported 52 individual k_2 observations for 20 different simulated stream flow conditions. The simulated depth ranged from 0.50 to 1.50 feet, the simulated mean velocity from 0.55 to 1.63 fps.

A multiple regression analysis of the data by Isaacs and Gaudy (1968) yielded exponents of 1.0027 and -1.4859 on mean velocity and depth, respectively, so a second analysis was performed holding these exponents to 1.0 and -1.5. The results of this analysis were

$$k_2 = 3.053 \frac{U}{H^{3/2}} (1.0241)^{T-20} \quad . \tag{112}$$

With 29 of the 30 data points of Churchill and others (1962), Isaacs and Gaudy obtained

$$k_2 = 3.739 \frac{U}{H^{3/2}} (1.0241)^{T-20} \quad , \tag{113}$$

while from Krenkel's (1960) flume data they obtained

$$k_2 = 2.440 \frac{U}{H^{3/2}} (1.0241)^{T-20} \quad , \tag{114}$$

where in equations 112, 113, and 114 k_2 is in days^{-1}, U in fps, and H in feet.

Isaacs and Gaudy (1968) pointed out that the multiplicative constants in equations 112, 113, and 114 can be interpreted as

$$\chi \left(\frac{D_m^{1/2}}{\nu^{1/6} g^{1/6}} \right)_{20°} \quad , \tag{115}$$

where the constant χ is dimensionless.

Equations of the type of 112 through 114 are convenient to use,
and if the constant is expressed as in equation 115, they are dimensionally
homogeneous. There is some question as to whether the data from which
equation 112 is derived truly represents stream-flow conditions (Thackston
and Krenkel, 1969b; Bella, 1969) so that use of this equation for pre-
diction of stream reaeration coefficients is questionable. However,
equation 113 should be applicable to stream flows, at least for the
range of flow parameters over which the measurements were taken because
it is based on field data. The disparity between the constants in
equations 113 and 114 probably indicates the effects of various
non-homogeneities in the data collection and modeling procedures and
also suggests that all the pertinent variables have not been included
in the prediction equations.

Negulescu-Rojanski equations

The equations given by Negulescu and Rojanski (1969) were derived by regression analysis from a series of 18 k_2 and D_x measurements in a 66 ft long by 0.66 ft wide recirculating flume. Not all the data are given, but for that available, the depths range from 0.164 to 0.492 ft and the velocities from 0.656 to 1.903 fps. The equations obtained by Negulescu and Rojanski are

$$k_2 = 4.74 \ \left(\frac{U}{H}\right)^{0.85} \ , \tag{116}$$

and

$$k_2 = 1.423 \ D_x \ \left(\frac{U}{H}\right)^{1.63} \ , \tag{117}$$

where k_2 is in days^{-1}, U/H in seconds^{-1}, and D_x is in feet^2 per day. Comparing values of k_2 predicted by equations 116 and 117 and values from a set of river measurements (which are not reported), Negulescu and Rojanski (1969) concluded that equation 117 is the more accurate.

Again, from the standpoint of convenience in obtaining measured parameters for prediction of k_2 in field streams, equation 116 is the desirable one to use.

EXPERIMENTAL DETERMINATION OF THE REAERATION COEFFICIENT

All the experimental techniques for determining the reaeration coefficient in open-channel flow, except the tracer technique of Tsivoglou (1967) and Tsivoglou and others (1965, 1968), use some integrated form of a DO balance equation, for example, an integrated form of equation 12. The determination of K_2 requires, therefore, that all other parameters in the equation be measured. These parameters are determined using a variety of techniques, all of which depend on the measurement of the amount of oxygen dissolved in a volume of water.

The purpose of this section is to discuss (1) the basic DO measurement techniques; (2) the various techniques for determining K_2; and (3) an analysis of the errors expected from the different techniques for determining the reaeration coefficient.

Measurement of Dissolved Oxygen in Water

The basic method for the determination of DO in water is the Winkler
procedure which was first described in the literature in 1888. (See
Am. Public Health Assoc., 1965, p. 414, for reference.) Since that
time the procedure has been improved by advances in equipment, technique,
and instrumentation and is still the basis for most analytical methods
for the determination of DO in water.

Oxidizing or reducing substances in the sample interfere with the
procedure, however, and various modifications of the basic Winkler
method have been developed. A common interference in waters receiving
sewage and effluents from sewage treatment plants is nitrate nitrogen,
and the Alsterberg modification is used under these conditions. Details
of the procedure are given in Am. Public Health Assoc. (1965) and in
Rainwater and Thatcher (1960). The Alsterberg modification is the
procedure generally used for routine analysis of natural waters.
Details of other modifications of the basic Winkler procedure are given
in Am. Public Health Assoc. (1965) and several of these modifications
are compared by Montgomery, Thom, and Cockburn (1964).

Various instrumental methods for the determination of DO in water
have also been developed. These include, for example, gas exchange,
gas chromatographic, radiometric, voltammetric, and membrane electrode
methods. The procedures, advantages, and disadvantages of these methods
and of titrimetric methods are discussed by Mancy and Jaffe (1966).

Techniques for Determining the Reaeration Coefficient

There are three general techniques for determining the reaeration coefficient of open-channel flow. These are the dissolved-oxygen balance technique, the disturbed equilibrium technique, and the tracer technique. The first two techniques utilize an integrated form of the equation of non-dispersive conservation of mass for a gas dissolved in a liquid (equation 28 with $\bar{\epsilon}_x$ negligibly small). The third technique utilizes an integrated form of this equation for an instantaneous input of tracer material which is convected and dispersed longitudinally by the flow. The basis and procedures of these techniques are discussed in the following paragraphs.

Dissolved-oxygen balance technique

Studies utilizing the DO balance technique are of two types, those in recirculating flumes, and those in natural streams or in non-recirculating flumes. Studies of the first type utilize the non-steady state non-dispersive form of the conservation of mass equation, equation 28 with $\bar{\epsilon}_x = 0$. Those of the second type utilize the steady state, non-dispersive form of this equation, that is, equation 28 with the $\bar{\epsilon}_x$ and the $\partial\bar{C}/\partial t$ terms equal to zero. We know of no techniques which have been applied to the calculation of K_2 in non-steady, dispersive conditions; however, the numerical techniques of Thomann (1963, 1965) and Dresnack and Dobbins (1968) could be modified to compute K_2 from measured variations of DO with time.

The general dissolved-oxygen balance technique for natural streams is based on a more sophisticated version of the equations originally presented by Streeter and Phelps (1925), for example, equations 12 and 13, as presented by Camp (1963). These one-dimensional, steady-state equations are applicable to conditions which meet the assumptions previously given for equations 9 and 10. In addition, longitudinal dispersion is generally assumed to have negligible effects on the longitudinal DO profiles in natural streams.

With these assumptions, the solutions to equations 12 and 13 yield the BOD and DO deficit at a downstream station, $x = x_b$, in terms of the BOD and DO deficit at an upstream station, $x = x_a$. The solutions are

$$L_b = \left[L_a - \frac{m}{2.3(k_1 + k_3)} \right] 10^{-(k_1 + k_3)t} + \frac{m}{2.3(k_1 + k_3)} , \tag{118}$$

and

$$D_b = \frac{k_1}{k_2 - k_1 - k_3} \left[L_a - \frac{m}{2.3(k_1 + k_3)} \right] \left[10^{-(k_1 + k_3)t} - 10^{-k_2 t} \right] +$$

$$\frac{k_1}{k_2} \left[\frac{m}{2.3(k_1 + k_3)} - \frac{p}{2.3\ k_1} \right] \left(1 - 10^{-k_2 t} \right) + D_a\ 10^{-k_2 t} , \tag{119}$$

where the flow time is $t = \dfrac{x_b - x_a}{U}$, the rate constants are to the base ten, and equation 12 has been solved in deficit form.

Equation 119, in its most general form, must be solved for k_2 by trial and error. Before this can be done, however, the other parameters appearing in equation 119 and in equation 118 must be evaluated. The techniques used in evaluating these parameters are discussed briefly in the following paragraphs.

BOD *test and* K_1.--Of the various parameters in a DO balance, the rate constant, K_1, for the oxidation of organic wastes probably has been studied to the greatest extent. The oxidation process is generally considered to be a first order process as represented by equation 1. The two parameters in equation 1, K_1 and L, may be determined from a BOD test. The earliest recorded use of a BOD test was 1870 (Theriault, 1926). Since that time, there have been numerous studies of the BOD test. The literature on the BOD test prior to 1927 has been summarized by Theriault (1927) and a bibliography of the literature on the BOD test since 1927 has been compiled by Hull (1959).

The BOD test consists basically of obtaining two samples of the water containing organic wastes, determining the DO concentration of one of the samples at the beginning of the test, incubating the second sample in darkness at 20°C for a period of time, usually five days, and determining the DO of the second sample at the end of the incubation period. The difference in DO concentrations is the 5-day BOD of the sample.

In practice, however, the procedure is not so simple. To prevent complete depletion of the DO in the test sample, the sample must be properly diluted before the start of the test. The dilution water must be properly prepared and seeded. The type and amount of seed to be used in the dilution water for the particular waste of interest must be determined by experience. If the sample is alkaline or acid or contains residual chlorine or other toxic substances, then the sample must be pre-treated before the start of the test. The complete details of the standard 5-day, 20°C BOD test are given in Am. Public Health Assoc. (1965).

The reaeration technique of Elmore (1955) for BOD determinations has the advantage that dilution water and seeding are not required. This procedure, however, has the disadvantages that the 5-day BOD must be less than 25 mg/ℓ, large sample volumes are required, and considerable attention on the part of the technician is necessary during the initial stages of the test.

A respirometer assembly for BOD determinations has been described by Gannon, Pelton, and Westfield (1965). The sample is placed in a sealed cell with a DO measurement probe and the DO concentration is measured continuously. When the DO concentration decreases to 2 mg/ℓ, the cell is aerated with compressed air. This process is continued for as long as desired. The respirometer has the same advantages as the reaeration technique in that no dilution and seeding are necessary, and has the additional advantage that the original sample is kept intact. The literature on other types of improved techniques for BOD determinations has been reviewed by Gannon and others (1965), and a complete review of respirometric methods has been presented by Montgomery (1967).

The results of a BOD test are usually in the form of BOD or amount of waste oxidized at time t as a function of t. The applicable equation is

$$X_t = L - L \ 10^{-k_1 \ t} \qquad (120)$$

where X_t is the BOD or amount of waste oxidized up to time t and L is the total first stage or carbonaceous BOD of the sample. Because both L and k_1 are unknown, several different techniques have been developed for determining L and k_1 from the results of BOD tests. Among these are the least squares procedure of Reed and Theriault (Theriault, 1927), the log-difference method of Fair (1936), the slope method of Thomas (1937), the moments method of Moore and others (1950), the graphical procedure of Lee (1951), and the ratio methods of Williams (1951) and Sheehy (1960). It is generally agreed that the Reed-Theriault procedure is the most accurate but it also requires the most time for the calculations because it is a trial-and-error procedure. Of the other procedures, the moments method is considered to give the most accurate results for the time consumed (Ludzack and others, 1953; Schroepfer and others, 1960; Gannon, 1966; Zanoni, 1967).

The extensive series of BOD measurements by Streeter and Phelps (1925) suggested that k_1 has a value of 0.1 days^{-1} at 20°C for all types of sewage and organic wastes. Later work, however, has shown that k_1 at 20°C may range from about 0.01 days^{-1} for some industrial wastes and well-oxidized treatment plant effluents to about 0.30 days^{-1} for readily oxidizable wastes (Camp, 1963, p. 247). Schroepfer and others (1960) found that the k_1 values for raw wastewaters and primary settled effluents from treatment plants in the Minneapolis-St. Paul area varied from 0.14 days^{-1} for Sundays and holidays to weekday values of 0.24 days^{-1}. They concluded that k_1 depended greatly on the degree of stabilization of the effluent. Kothandaraman and Ewing (1969) found that k_1 values for the Ohio River downstream of Cincinnati, Ohio, were normally distributed with a mean value of 0.075 days^{-1} and a standard deviation of 0.028 days^{-1}. Camp (1965) also noted considerable daily variation of k_1 values for several stations on the Merrimack River. Thus, it is apparent that k_1 cannot be considered a constant but that k_1 values must be determined for the waste, the reach, and the time of interest.

The k_1 values determined at 20°C in the laboratory are converted to the appropriate river temperature by means of the equation

$$(k_1)_T = (k_1)_{20°} \, \theta^{(T-20)} \tag{121}$$

where θ is the temperature coefficient which has a value of 1.047 for temperatures from 10° to 37°C (Camp, 1963, p. 247). Zanoni (1967) found the same value for θ for a somewhat smaller temperature range (15° to 32°C) with a θ value of 0.985 for temperatures from 32° to 40°C and a θ value of 1.126 for temperatures from 2° to 15°C. He also found that L increased with temperature.

It has become apparent, however, with the widespread use of the laboratory 5-day 20°C BOD test that there are several aspects of the standard BOD bottle test, in addition to the aforementioned problems with dilution and seeding, requiring additional study. These aspects are concerned with how well the diluted and seeded sample incubated in darkness under quiescent conditions in a constant temperature bath approximates the behavior of a slug of water of similar size under dynamic streamflow conditions. For example, the turbulence conditions are obviously different and increased values of k_1 have been found when the BOD bottles were stirred or rotated (Owens and Edwards, 1966; Gannon, 1966). The increased turbulence prevents deposition of suspended material and facilitates the transport of the wastes to the organisms. The large surface-to-volume ratio of the bottle may result in increased growth of organisms on the inside of the bottle, and hence, faster DO consumption than in an unconfined slug of water of the same size (Symons, 1966; Hull, 1969). The bottle test does not consider the possible decrease in the respiration rate of organisms with decreasing DO concentration in the bottle (Owens and Edwards, 1966). When algae are present, the bottle test conducted in darkness could give a high value for the BOD of the sample because of respiration demands of the algae (Owens and Edwards, 1966) whereas in the stream during daylight hours the algae replace the oxygen consumed by their respiration. The 5-day period required for the standard bottle test is also a disadvantage because the conditions in the stream may change considerably while the k_1 value is being determined. Camp (1965) found that the water temperatures varied widely

during the daylight hours on the Merrimack River and concluded that it was pointless to determine the BOD in the laboratory at a constant temperature. Hull (1966, 1969) and Camp (1965) recommend using a dark bottle suspended in the stream at the point at which the sample was obtained. This procedure eliminates delay, the need for a temperature correction, and gives a BOD value for the period of sample incubation. To determine k_1, however, requires BOD values for different times or continuous recording of the DO concentration in the submerged bottle, and one is again faced with the problem of changing conditions in the stream.

Bottom deposits, K_3, and m.--In addition to the biochemical oxidation of organic wastes in the flowing stream, wastes may also be removed from the stream by settling to the bottom. There are three general procedures for the formation of bottom deposits (Velz, 1958): (1) deposits of settleable solids from the wastes; (2) deposits resulting from the flocculation or coagulation of solids within the stream; and (3) biological extraction and accumulation of wastes by growths attached to the bottom of the stream.

The first type of deposit is the result strictly of a sedimentation process. The second type may be considered as resulting from a process analogous to an activated sludge system in which the growth is dispersed throughout the flowing stream. Under certain conditions, the growths flocculate, and the flocs increase in size until sedimentation occurs. The third type of deposit may be considered as resulting from a process analogous to that occurring in a trickling filter. Biological extraction and accumulation of wastes have been studied by Velz and Gannon (1963). The rate of sedimentation is generally assumed to be proportional to the amount of BOD present or

$$\text{rate of sedimentation} = K_3 \, L \; . \tag{122}$$

A velocity of 0.6 fps was considered by Velz (1958) to be the critical velocity at which organic wastes begin to deposit.

Even though the formation of a bottom deposit may result in a reduction of the BOD of the water from which the waste was removed, the deposit may be a sink for DO to other masses of water passing over the deposit. Several processes may be involved:

(1) BOD additions to the overlying water as a result of re-suspension of the bottom deposits. A velocity of from 1.0 to 1.5 fps is considered necessary for re-suspension, the actual velocity necessary being dependent upon the degree of decomposition and compaction of the deposit (Velz, 1958).

(2) Diffusion of the anaerobic decomposition products of the deposit into the overlying water.

(3) Diffusion of DO from the overlying water into the aerobic zone of the deposit.

Fair and others (1941) concluded that the oxygen demand of sludge deposits was controlled by process 2 and that process 3 was relatively unimportant. The relative importance of processes 1 and 2 may be seen qualitatively from an experiment of Edwards and Rolley (1965) in which the DO consumption rate of a mud sample increased approximately six fold when the sample began to scour. Similarly Brown and Clark (1968) reported large decreases in the DO concentrations during dredging operations in a tidal estuary. They also point out that re-suspension of bottom deposits decreases light penetration and consequently the additions of DO by photosynthesis.

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The importance of bottom deposits on dissolved oxygen balances has been demonstrated by several field studies including the work of Velz (1958), Owens and Edwards (1963), and Camp (1965). Velz (1958) discussed the effect of sludge deposits on DO profiles for several situations. Owens and Edwards (1963) found on the River Lark that they obtained very poor agreement between measured and observed DO profiles until the DO demands of the mud were included in the DO balance. Edwards and Owens (1965, figure 1) presented the percent of the total DO consumed by mud as a function of the water depth for BOD and mud consumption values typical of English streams. It can be seen from their graph that for depths of flow less than 1.25 meters the mud consumed more oxygen than was consumed by the biochemical oxidation of the wastes in the water. Camp (1965) found on the Merrimack River that 50 to 80 percent of the BOD removal was by sedimentation. He also noted that most of the BOD removed by sedimentation consisted of solids formed by bioflocculation.

The effects of removal of BOD by sedimentation and addition of BOD to the overlying water by bottom deposits have been included in the DO balances of Dobbins (1964b) and Camp (1963). Dobbins (1964b) describes three situations for which K_3 can be determined if K_1 has been determined from laboratory measurements. The term D_B, which includes the addition of BOD to the water from bottom deposits, in general must be determined by difference from the DO profile equation. This procedure, however, requires an independent estimate of the reaeration coefficient, K_2. Camp (1965) recommends that m, the rate of addition of BOD to the overlying water, be determined from *in situ* measurements by the technique of Fair and others (1941) and Camp (1963, p. 310), and that K_3 be determined from the BOD profile equation after K_1 has been determined from laboratory BOD tests.

In addition to the studies of the overall effect of bottom deposits on the DO and BOD balances, the consumption of DO by muds has been studied in some detail with somewhat contradictory results. For example, Baity (1938) and Fair and others (1941) found that the DO consumption rate, ω, was dependent on the depth, d_M, of the deposit according to

$$\omega = a_1 \, d_M^{0.485} \tag{123}$$

in which a_1 is a constant. On the other hand, Edwards and Rolley (1965) found that the DO consumption rate was independent of the deposit depth for depths greater than 2 cm and McDonnell and Hall (1969) concluded that the consumption rate was essentially independent of the sample depth.

With respect to the dependence of the DO consumption rate on the DO concentration of the overlying water, Baity (1938) found the consumption rate was independent of the DO concentration for the range of 2 to 5 mg/ℓ for deposits 0.5 cm thick. Edwards and Rolley (1965), however, found that the DO consumption rate was dependent on the DO concentration in the overlying water according to

$$\omega = a_2 \, c^{b_1} \tag{124}$$

where b_1 is 0.45 for the muds studied. This relation was valid for DO concentrations in the range from 2 to 8 mg/ℓ but was not satisfactory for muds containing large populations of midge larvae. Similar results were obtained by McDonnell and Hall (1969).

An attempt to correlate the DO consumption rates with various chemical properties of the muds was unsuccessful (Rolley and Owens, 1967). They attempted to correlate five chemical properties with DO consumption rates for both winter and summer samples from 12 English rivers but found no correlation, although a strong correlation was found among all the chemical properties.

Photosynthesis and respiration.--The presence of phytoplankton, benthic algae, and rooted aquatic plants in a stream or river results in the production of oxygen through the process of photosynthesis. The plants combine carbon dioxide and water in the presence of sunlight to produce carbohydrates and oxygen. At the same time, however, the plants require oxygen in their respiration process. In general, the rate of production of oxygen exceeds the rate of consumption during daylight hours whereas consumption is predominant during nighttime hours. This may result in a pronounced diurnal variation of the DO concentration in the stream with the maximum DO concentration occurring in the afternoon and the minimum DO concentration occurring just before dawn.

In the past, the photosynthesis and respiration processes have been of interest only to biologists, who in their studies attempted in a very general way to allow for additions of DO by reaeration. Engineers, on the other hand, with the exception of a few such as Hull (1960), ignored photosynthesis and concentrated their efforts on the reaeration process. When this is done, grossly incorrect values of the reaeration coefficient, K_2, may be obtained if the usual computation procedure is used. For example, Gunnerson and Bailey (1963) found negative values of K_2 for two sampling periods on the Sacramento River. Lynch (1965) also found negative K_2 values for nocturnal sampling periods on the Troughnioga River and he believed that the computed K_2 values for daytime sampling periods would be larger than the true values if a separate factor for photosynthesis were not included in the DO balance. Similarly Camp (1965) concluded that the K_2 values for streams of the type of the Merrimack River were considerably smaller than had been previously thought because of including photosynthetic effects with reaeration.

Opinions as to whether the DO produced by photosynthesis is an asset or a liability to a stream vary widely. Camp (1963) stated that the DO produced by photosynthesis should not be relied upon because there is no assurance that this DO will be available during the critical low flow periods of summer when it is needed most. Similarly Imhoff and Fair (1956) suggest that the DO produced by photosynthesis should not be relied upon in engineering calculations because it is available only during daylight hours and the warmer seasons of the year. On the other hand, Camp (1965) found in a summer study on the Merrimack River that about 67 percent of the DO was furnished by photosynthesis with reaeration relatively unimportant, and he concluded "that reliance must be placed on the photosynthetic production of DO." Merritt, McDonald and Paulson (1968) found on the Iowa River that photosynthesis was a contributing factor in the DO balance and they concluded that "whether or not the photosynthetic effect can be relied upon quantitatively, it remains an important factor of the oxygen balance in streams." Similar photosynthetic effects have been observed in European rivers and this literature has been summarized by Edwards and Owens (1965). Leffel (1968) found on the Chao Phraya River that photosynthetic production of DO was small in comparison with reaeration. Bain (1968) stated that in a deep, turbid stream the photosynthetic production of DO often is not sufficient to offset the respiration demands of the plants, even if the stream is well-mixed. O'Connell and Thomas (1965) pointed out that if the photosynthetic production of DO is by benthic algae or rooted aquatic plants rather than phytoplankton, then photosynthesis is a liability

because the oxygen produced during daylight hours by the attached plants is not in the same mass of water from which oxygen is consumed by night-time respiration. An example of this cited by O'Connell and Thomas is the shallow, rapidly-flowing Truckee River below the outfall of the sewage treatment plant of Reno, Nevada. In a deep, slowly-flowing stream, the response of the stream to a nutrient source is the development of phytoplankton which move with the stream. Hence, the production and consumption of oxygen occur at different points in space but in essentially the same mass of water. In streams with attached plants, the production and consumption of oxygen occur at the same point in space but in different masses of water. Edwards (1962) has suggested that sometimes plant growths may be beneficial even when there is no net gain of DO because the plants produce oxygen during the summer conditions of low flows and high temperatures and remove oxygen during the decay process in winter when high flows and low temperatures exist. Gunnerson (1966) suggests that photosynthesis may be neglected if the time period over which the data are averaged is sufficiently long, for example, longer than one year.

It is apparent from the preceding discussion that considerable controversy exists concerning photosynthesis and respiration in a natural stream. It has been pointed out, however, (Hull, 1966) that the controversy generally is whether the oxygen production by photosynthesis is significant and not whether a term for photosynthesis should be included in the DO balance. Thus Camp (1963), Dobbins (1964b), the Water Pollution Research Laboratory group, O'Connor (1967), and others have included terms for the photosynthetic production of oxygen in their DO balances.

The production of oxygen by plant photosynthesis depends on several factors including the light intensity at the water surface, the optical density of the water, and the weight and distribution of plants in the stream (Ow   and Edwards, 1964). The depth of the stream affects the photosynthetic rate in that the extent of light penetration varies inversely with depth. Photosynthesis is limited to the euphotic zone which is generally assumed to extend to the depth at which the light intensity is one percent of the light intensity at the surface (Owens and Edwards, 1966). The optical density of the water depends on the concentration, type, and size of suspended particles and the color of the water produced by dissolved materials. An example of a situation where the environmental conditions were suitable for a high level of photosynthetic oxygen production but where actual production was limited to a very low level because of the turbidity of the water is the Chao Phya River (Pescod, 1969). The weight and the distribution of the plants affect the net DO production mainly by affecting the total respiration rate. Thus, as the plant density increases, the photo-synthetic production rate remains approximately constant because of self-shading by the plants, although the respiration rate continues to increase (Edwards, 1968).

Several procedures have been developed for the measurement of photosynthetic and respiration effects in natural streams. These include the upstream-downstream method (Odum, 1956; Owens, 1965), the single-curve procedure (Odum, 1956) which is a simplification of the upstream-downstream procedure, and the light- and dark-bottle technique.

In the light- and dark-bottle technique, water samples are collected at a number of verticals in the cross-section and at a number of points at each vertical so that the number of samples is sufficient to yield an accurate value of photosynthesis and respiration for the cross-section. Each sample is divided into three parts: one part is placed in a transparent glass bottle, another part is placed in an opaque bottle so that all light is excluded, and the third part is analyzed for the DO concentration. The light and dark bottles are suspended in the stream at the sampling point for a period of time, usually 24 hours or a multiple thereof. At the end of the desired period, the light- and dark-bottles are analyzed for their DO concentrations. Equations for the light-bottle and dark-bottle DO concentration are, respectively,

$$C_{lf} - C_{li} = P_l - R_l \tag{125}$$

$$C_{di} - C_{df} = R_d \tag{126}$$

where the l and d subscripts refer to light and dark bottles, respectively, i and f subscripts refer to initial and final DO concentrations, R is the gross respiration or BOD, C is DO concentration, and P is the photosynthetic oxygen production. For reasonably short periods of time, $R_l = R_d$ and because $C_{li} = C_{di}$, it follows that

$$C_{lf} - C_{df} = P_l \quad . \tag{127}$$

Hull (1963) believed that the light- and dark-bottle technique probably is more accurate than the standard BOD test and that the technique in general gives conservatively low estimates of the oxygen production by photosynthesis.

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Symons (1966) discussed several problems with the classical light- and dark-bottle technique including unnaturally large surface-to-volume ratios in the bottles, the relatively long time required for the test, the lack of mixing in the bottles, and the necessity for removal of samples from the stream which may result in harm to the algae. He discussed a 3-probe chamber device designed to eliminate these problems. O'Connell and Thomas (1965) also used a chamber device but did not measure DO continuously.

The upstream-downstream method uses measurements of the DO concentrations at the ends of the reach of interest for a 24-hour period. The basis of the procedure is a DO balance of the form (Odum, 1956)

$$Q_0 = P - R + D_0 + A_0 \tag{128}$$

where Q_0 is the rate of change of DO content, P is the gross primary production, R is the respiration rate, D_0 is the rate of reaeration, and A_0 is the rate of addition of dissolved oxygen to the reach by drainage accrual. Each term of equation 128 is on an area basis, for example, g/m^2 hr.

If each term in equation 128 is divided by H, the mean depth of flow, the result is

$$q = p - r + d_0 + a_0 \tag{129}$$

where the terms are now on a concentration basis, for example, mg/ℓ per day.

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The gross primary production, P, is defined as the sum of the net DO plant production and community respiration during the daylight hours. Therefore, it follows if r and d_0 are independent of time and a_0 is negligible or independent of time that (Odum, 1956)

$$P = H \int_{t_1}^{t_2} (q - q_1) \, dt = \frac{F}{A_s} \int_{t_1}^{t_2} (\Delta C - \Delta C_1) \, dt \qquad (130)$$

where F is the volumetric water flow rate, A_s is the surface area of the reach, ΔC is the DO concentration difference between the upstream and downstream stations, and the subscripts 1 and 2 refer, respectively, to the time at which sunrise occurred and the time in the evening at which q or ΔC returned to its sunrise value. When equation 130 is used to determine P, equation 128 must have units of weight per unit of area per day.

In general, the oxygen supplied by reaeration, d_0, is not independent of time because the rate of reaeration depends on the DO deficit. If a reaeration coefficient is available for the reach, then a correction can be applied for each hour in the calculation of the q curve from the DO measurements.

The reaeration coefficient can be calculated from the diurnal DO measurements if r and a_0 are assumed independent of time. From measurements before dawn and in the evening when the p values are zero, it can be shown (Odum, 1956) that

$$K_2 = \frac{q_M - q_E}{D_M - D_E} \qquad (131)$$

where D is now the average DO deficit in the reach, and the M and E subscripts refer to the morning and evening times, respectively. The reaeration coefficient calculated from equation 131 is the K_2 for the average deficit of the reach as compared with an integral K_2 obtained by integrating the deficit over the DO change. The determination of the reaeration coefficient by this procedure will be discussed in greater detail later.

Both equations 130 and 131 assume that r is independent of time and hence independent of the DO concentration level. Opinions differ as to the validity of this assumption. Odum (1956) concluded on the basis of the available information that it was simplest to assume r constant. On the other hand, Edwards and others (1961) concluded that the respiration rate of plants depended on the DO concentration level. Therefore, corrections for the dependence of r on DO concentration may be necessary.

The respiration rate can be determined from the results of an upstream-downstream experiment in the following ways (Odum, 1956). First, if the rate of reaeration is known and A_0 is negligible, then during the hours of darkness, the respiration rate can be calculated from the observed rate of change of dissolved oxygen in the reach. Second, if during the hours of darkness the water is saturated at some time, as usually occurs after sunset, then at that instant, because the reaeration is zero, the respiration rate is equal to the rate of change of DO in the reach, assuming A_0 is negligible.

The single-curve procedure (Odum, 1956) is a simplification of the upstream-downstream procedure in which the diurnal variation of DO concentration at a single station is used in the calculation of P and R. This procedure assumes that the entire reach experiences uniform changes in the DO concentration and hence the curves at the upstream and downstream stations would be identical. Owens (1965) compared the two calculation procedures for two stations on the River Ivel which had nearly identical diurnal DO curves and found that the calculated P and R values were different for the two procedures and also different for the two stations. Edwards and Owens (1962) also found differences between the two procedures.

In addition to the direct effects on the DO balance, plants also exert indirect effects on the DO balance. For example, heavy plant growths can increase the depth of flow and reduce the water velocity which in turn reduces the addition of oxygen by reaeration. At the same time, the reduced velocity increases the deposition of solids. If the plants extend through the surface, then turbulence at the air-water interface may be increased, thereby facilitating the absorption of oxygen by the water. Finally the presence of the plants increases the surface area on which the bacteria can live and oxidize wastes present in the stream.

Other parameters.--Other parameters that are necessary in a DO balance study include the DO concentrations at the upstream and downstream ends of the study reach and the flow time through the reach.

The flow time can be determined from mean velocity measurements
and the distance between the ends of the study reach, or

$$\Delta t = \frac{\Delta x}{U} \quad . \tag{132}$$

Distances may be obtained from topographic maps and mean velocities from
current meters or from stage-discharge ratings and cross-section measure-
ments. Long study reaches are desirable; however, practical considera-
tions such as variations in the channel cross-section, location of sewage
outfalls, and personnel requirements generally limit the length of reach
that can be studied.

The flow time can also be determined from tracer measurements, using either radioactive or fluorescent tracers. The procedure consists of instantaneously injecting a quantity of the tracer far enough upstream of the reach of interest so that the tracer is uniformly mixed in both the lateral and vertical directions before it enters the reach. Procedures for estimating the distances required for complete mixing have been presented by Sayre (1965) and Fischer (1967). The flow time is the time required for the tracer cloud to move through the study reach. In some instances, the peaks of the tracer concentration versus time curves have been used in flow time determinations, however, it is more correct to use the centroids of the curves. The flow time is the difference between the times at which the centroid of the dye cloud passes the downstream and upstream ends of the reach.

The upstream and downstream DO concentrations are determined from samples obtained at the ends of the study reach. One of the procedures previously described is used to determine the DO concentrations of the samples. The samples at the downstream point usually are obtained at a time lag of $\Delta x/U$ after the samples at the upstream point. This is done because DO balance equations generally are written in a coordinate system moving with the mean flow velocity.

The number of samples obtained at each cross-section must be sufficient to define a mean DO concentration for the cross-section. As mentioned previously, gradients of DO in the vertical direction in a flowing stream are generally negligible. The lateral DO distribution depends on many factors including distance from sewage outfalls and stream tributaries, cross-section shape and tortuosity of the channel, and size, shape, and spacing of bed roughness elements. Churchill and others (1962) observed consistent U-shaped DO distributions across the stream channel which they attributed to (a) incomplete mixing of tributary inflows; (b) increased reaeration near the banks because of the longer travel time; and (c) unequal effects across the stream width of photosynthesis and respiration by attached aquatics. Thus the possibility of lateral variations in the DO concentration should be considered.

To determine k_2 in the most general field situations, all the parameters in equation 119 must be evaluated using the methods previously described. In specific reaches, however, some of the factors in equation 119 may be of negligible importance. For example, if p, m, and k_3 are negligible, equation 119 reduces to the classical Streeter-Phelps sag equation, equation 6. Examples of reaches in which p, m, and k_3 were not negligible have been given previously. In the reaches chosen specifically for the study of reaeration by Churchill and others (1962), the BOD, k_3, m, and p parameters were all negligible so that equation 119 reduced to

$$D_b = D_a \ 10^{-k_2 t} \ .$$ (133)

Thus, k_2 could be calculated simply from DO measurements on samples obtained at two points in the reach separated by the flow time, t. In general, however, equation 119 or a similar equation should be the starting point in a DO balance calculation of k_2 for a natural stream, and parameters should be eliminated only after they have been shown to be negligible for the reach and hydraulic conditions of interest.

Calculation of k_2 in a recirculating flume

In a laboratory flume, however, it is possible to control the sources and sinks of DO so that the BOD, k_3, m, and p parameters will in general be zero. With these conditions, the reaeration coefficient can be calculated from equation 133. Flume lengths, however, are limited by space and economical considerations so that the available flow times and the consequent change in DO deficit generally will be very small. Thus the calculated reaeration coefficients will be subject to large errors. This problem can be alleviated by recirculating the water through the flume.

In recirculating flumes, the water is partly deaerated before the start of an experiment, usually using sodium sulfite in the presence of a cobalt catalyst. As the water circulates through the flume, it reaerates at a rate which is dependent on the hydraulic conditions in the flume, and on the characteristics of the flume-return flow system. For steady-state hydraulic conditions, the form of equation 9 generally assumed to be applicable is

$$\frac{\partial D}{\partial t} + U \frac{\partial D}{\partial x} = -2.3 \, k_2 \, D \tag{134}$$

where the DO concentrations have been expressed as deficits. Making the substitutions $x' = x - U t$ and $t' = t$ into equation 134, one obtains

$$\frac{\partial D}{\partial t'} = -2.3 \, k_2 \, D \quad , \tag{135}$$

and integrating equation 135 with $D = D_a$ at $t' = 0$ gives

$$D = D_a \cdot 10^{-k_2 \, t'} \quad , \tag{136}$$

or

$$k_2 = \frac{1}{t'} \{ \log D_a - \log D \} \quad . \tag{137}$$

Equation 137 is identical in form to equation 133, however, in equation 137, because conditions are not steady-state, the flow time t' is a time lag which must elapse between the DO measurements at the two sampling stations, whereas in equation 133, because conditions are steady-state, the DO measurements at the two stations may be made at any time. In a recirculating flume, it is common experimental practice to obtain an average log deficit difference as compared with the single measurement of the difference obtained in a natural stream or a non-recirculating flume. The average log deficit is determined by the procedure illustrated in figure 2. The parallel lines show the variation

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Figure 2.--following here

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with time of the logarithm of the deficit at two points in the flume a distance X apart. Because the water is recirculated, it is possible to obtain several points on each line and thus accurately determine the positions and slopes of the lines.
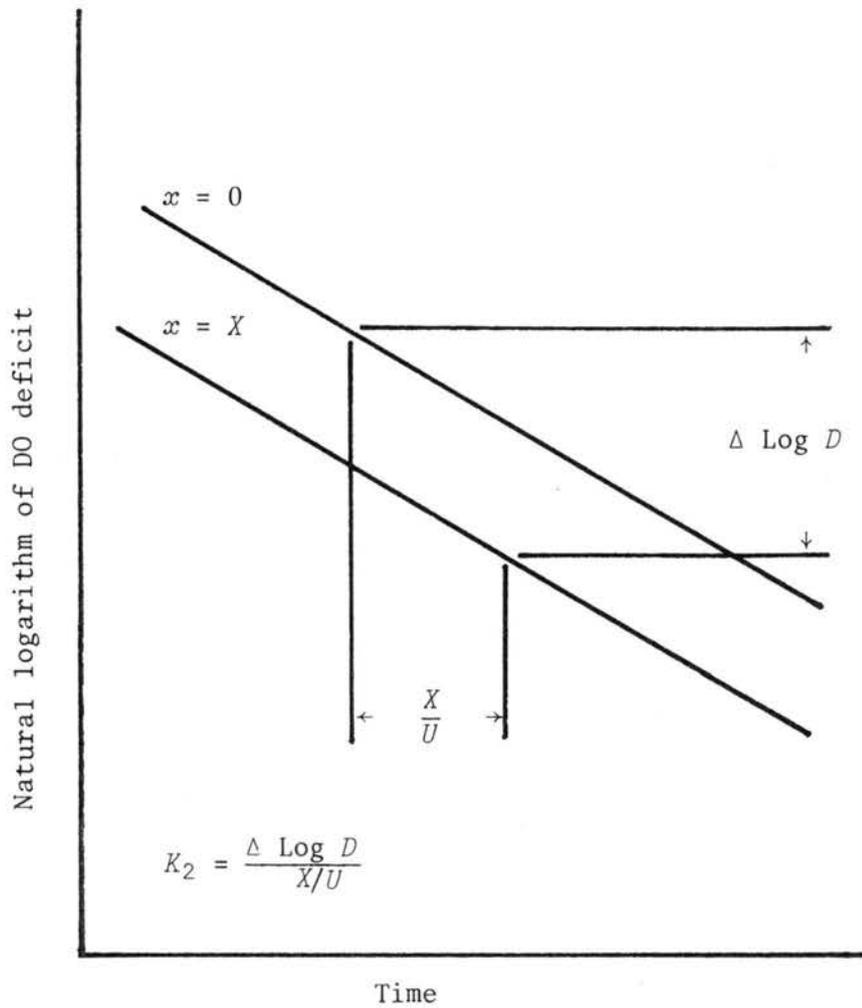
Figure 2.--Computation of the reaeration coefficient, K_2, from recirculating flume data.

Disturbed equilibrium technique

The disturbed equilibrium technique developed by the Water Pollution Research Laboratory (Gameson and Truesdale, 1959) is based on a DO balance described by equation 14. The procedure consists of measuring the DO concentrations at the upstream and downstream ends of the reach of interest at two different levels of DO concentration. The second DO concentration level is obtained usually by adding sodium sulfite and a cobalt catalyst to the stream, although the diurnal variations in DO concentration caused by photosynthesis may be used. If P, R, K_2, U, and C_s are constant for the reach during the period of the experiment and therefore independent of the DO concentration, then by manipulation of equation 14 it was found that

$$K_2 = \frac{1}{t} \ln \frac{C_a - C_a'}{C_b - C_b'} \tag{138}$$

where C_a and C_a' are the upstream DO concentrations at the two levels of concentration, C_b and C_b' are the downstream DO concentrations measured at a time t after the upstream concentrations, and t is the flow time for the reach of interest.

Although the respiration rates of bacteria are independent of the DO concentration for concentrations larger than 1 mg/ℓ (Edwards and others 1961), the respiration rates of plants (Edwards and others, 1961), and of bottom deposits (McDonnell and Hall, 1969; Edwards and Rolley, 1965) are not. Furthermore, photosynthetic DO production can cause large variations in DO concentration with time on a specific day and from day to day. Therefore, when plants are present, Edwards and others (1961) suggested that the experiments be conducted at night when the photosynthetic contributions are negligible. To account for the dependence of the plant respiration on DO concentration, they have showed that

$$K_2 = \frac{1}{H} \; \frac{Q_2 - R' \, Q_1}{\left(C_{s_2} - \overline{C}_2\right) - R'\left(C_{s_1} - \overline{C}_1\right)} \tag{139}$$

where $\overline{C}_1$ and $\overline{C}_2$ are the average DO concentrations for the study reach for the two levels of DO concentration, Q_1 and Q_2 are the average rates of change per unit area of the DO concentration in the reach at each of the two levels of DO concentration, C_{s_2} and C_{s_1} are the DO saturation concentrations at the times of the measurements for the DO concentrations at the two levels, and R' is the ratio of the oxygen consumed by respiration at DO concentration $\overline{C}_2$ to that consumed at DO concentration $\overline{C}_1$. The reaeration coefficient obtained from equation 139 is the K_2 for the average DO deficit in the study reach.

The authors derived from equation 119 an equation that will give an integral reaeration coefficient rather than one based on the average DO deficit for the reach. If equation 119 is written for upstream deficits of D_a and D_a' and the difference taken, the result is

$$K_2 = \frac{1}{t} \ln \left[\frac{(D_a - D_a') + \frac{p-p'}{K_2}}{(D_b - D_b') + \frac{p-p'}{K_2}} \right] \tag{140}$$

where p and p' include the respiration rates of both plants and bottom deposits. In equation 119, the parameter p is the net production of oxygen by photosynthesis. However, the production of DO by photosynthesis is assumed to be constant or zero during the period of the measurement so that the p parameter becomes strictly a respiration term. The derivation of equation 140 also assumes that K_1, K_3, L_a, and m are constant during the period of the measurements. Because K_2 appears on both sides of equation 140, a trial-and-error solution is necessary.

The disturbed equilibrium technique requires measuring the upstream and downstream DO concentrations and the respiration rate in the reach at two different values of the upstream DO deficit. The different values of the upstream deficit may be produced by diurnal variations in photosynthesis-respiration or BOD inflow, or by the addition of sodium sulfite along with a cobalt catalyst. In general, the technique is quite convenient to use, especially if the DO variations are produced by natural conditions in the stream. In this case, however, accurate measurements of the respiration rates p and p' are necessary, quantities which are often not easily obtained. If the deficit is produced by sulfite dosing, where p and p' are small, there is less uncertainty in the measurements of p and p'; however, their variation may still be significant. The amount of sulfite required places limitations on the size of stream that can be dosed and on the length of time that the dose can be applied. Furthermore, it must be assured that the sulfite is completely mixed with the flow and that the reaction has proceeded to completion before the flow enters the study reach. Finally, in either method, the experimenter must assure himself that the effect of the time variations in DO and BOD do not cause serious errors in the computation of the reaeration coefficient.

Tracer technique

Equations 81 and 83 resulting from the kinetic theory model of
Tsivoglou (1967) are the basis of the tracer technique for determination
of the reaeration coefficient. As discussed previously, Tsivoglou (1967)
concluded on the basis of laboratory measurements that the gas transfer
coefficient ratio in equations 81 and 83 was a constant within the
limits of experimental error for the range of temperature and turbulence
conditions studied. Because the ratio is constant, an inert gas that
does not participate in the various biochemical and biological processes
in a stream can be used as a tracer for oxygen. This permits the
determination of a true reaeration coefficient in the presence of pol-
lution and photosynthetic effects, provided the value of the ratio of
gas transfer coefficients is known for the inert gas and oxygen. Thus,
the tracer technique is unique in that it does not require the measure-
ment of any of the parameters in a DO balance. The technique was first
described by Tsivoglou and others (1965), a field application was
described by Tsivoglou and others (1968), and a complete discussion of
the technique was presented by Tsivoglou (1967).

The technique uses an instantaneous injection of three tracers at a point upstream of the reach over which the reaeration coefficient is to be measured. The tracers are a fluorescent dye, the purpose of which is to enable field personnel to follow the movement of the tracers, tritiated water, which is used as a conservative dispersion tracer, and the radioactive tracer gas, krypton-85 which is used to measure the gas transfer capacity of the flow. Samples of stream water are removed from the flow as the dye peak passes the upstream end and again as it passes the downstream end of the reach. The transfer capacity of the flow for the tracer gas is obtained from the relative concentrations of the gas and tritiated water tracers at the two ends of the reach. Tsivoglou (1967) has shown on the basis of an argument involving numbers of krypton and tritium atoms and an exponential expression for gas exchange that

$$\frac{\left(\dfrac{C_G^*}{C_L^*}\right)_b}{\left(\dfrac{C_G^*}{C_L^*}\right)_a} = e^{-K_{2_G} t} \tag{141}$$

where C^* is concentration, t is flow time or $\Delta x / U$ where Δx is the distance between the downstream and upstream stations indicated respectively by the subscripts b and a, the term K_{2_G} is the gas transfer coefficient of the tracer gas, and the G and L subscripts refer respectively to the krypton and tritium tracers.

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The tracer-gas transfer coefficient, K_{2_G}, can be converted to a reaeration coefficient, K_2, by means of the gas transfer ratio determined by Tsivoglou (1967). He found that the average ratio of the rate of krypton desorption to the rate of oxygen absorption was 0.83. Hence

$$K_2 = \frac{K_{2_G}}{0.83} \quad .$$
(142)

The crucial assumption in the tracer technique is that this ratio is a constant, that is, independent of the flow conditions, temperature, and pollutants present.

We developed a theoretical basis for the technique from solutions of the conservation of mass equation for the two tracers. The one-dimensional diffusion equation in a steady-uniform flow for a conservative tracer is

$$\frac{\partial C_L^*}{\partial t} + U \frac{\partial C_L^*}{\partial x} = D_x \frac{\partial^2 C_L^*}{\partial x^2} \quad , \tag{143}$$

where C_L^* is the tracer concentration. The corresponding equation for the gaseous tracer is

$$\frac{\partial C_G^*}{\partial t} + U \frac{\partial C_G^*}{\partial x} = D_x \frac{\partial^2 C_G^*}{\partial x^2} - K_{2_G} C_G^* \quad , \tag{144}$$

where C_G^* is the tracer gas concentration. Implicit in the use of the one-dimensional diffusion equation is the assumption that the tracers are uniformly distributed in the cross-section of the stream. Therefore, the upstream sampling point must be far enough downstream from the injection point so that complete mixing in both the lateral and vertical directions has been achieved.

The solutions to equations 143 and 144 for instantaneous inputs of weight W_L of the liquid and W_G of the gaseous tracer at $x=0$ and $t=0$ have been presented by Camp (1963). For equation 143, the solution is

$$C_L^* = \frac{W_{0_L}}{2\sqrt{\pi\ D_x\ t}}\ e^{-\frac{(x-U t)^2}{4\ D_x\ t}} \tag{145}$$

and for equation 144,

$$C_G^* = \frac{W_{0_G}}{2\sqrt{\pi\ D_x\ t}}\ e^{-\left[\frac{(x-U t)^2}{4\ D_x\ t} + K_{2_G}\ t\right]}, \tag{146}$$

in which $W_{0_L} = W_L/A_x$ and $W_{0_G} = W_G\ A_x$, where A_x is the flow area. For any longitudinal position x at time t, the ratio of the gas concentration to the liquid concentration is

$$\frac{C_G^*}{C_L^*} = \frac{W_{0_G}}{W_{0_L}}\ e^{-K_{2_G}\ t}. \tag{147}$$

If one now takes the ratio of equation 147 for the downstream station at a time $t = \Delta x/U$ to equation 147 for the upstream station at $t=0$, the result is identical to equation 141 given previously by Tsivoglou (1967). Using equations 141 and 142 and the four measured tracer concentrations, the reaeration coefficient K_2 can be computed.

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The arguments used by Tsivoglou (1967) in developing equation 141 require no assumptions regarding vertical and lateral mixing of the tracers. However, the reaeration coefficient obtained from the tracer technique using a point-source injection and samples from the centerline of the channel is representative only of the filament of the stream traversed by the tracers in moving from the injection point to the sampling point. To obtain a K_2 representative of the entire cross-section of a reach, the tracers must be injected sufficiently far upstream so that they are uniformly distributed in the cross-section before entering the reach. Under these conditions, the one-dimensional diffusion equation is applicable, and as shown previously, a theoretical basis exists for the tracer technique equation obtained from intuitive arguments by Tsivoglou (1967).

The assumptions on which the tracer technique is based are listed by Tsivoglou (1967) as follows:

"(1) The tritiated water undergoes only dispersion in the stream, and is not lost from the stream in any significant amount; (2) the dissolved krypton-85 undergoes the same dispersion as the tritiated water, in addition is lost to the atmosphere, and is not otherwise lost in any significant amount; (3) the ratio of gas transfer coefficients for dissolved krypton-85 and oxygen of 0.83 is not significantly affected by temperature, turbulence, or the presence of usual water pollutants, in the range of interest. . . ."

The tritium and krypton tracers were chosen with the first two assumptions in mind and therefore, these assumptions should be valid. The third assumption was verified experimentally, as discussed previously.

The tracer technique has several advantages over the DO balance and disturbed equilibrium techniques for determination of reaeration coefficients. The most obvious advantage is that only the concentrations of two radioactive substances need be determined as compared to all the various parameters that must be measured in the other two techniques. In addition, the nuclear counting techniques are very accurate, and because only ratios of the counts are used, determination of the counting efficiency is not necessary, provided it is the same for the counting of all samples. The possibility exists also of determining with the tracers the discharge and longitudinal dispersion characteristics of the stream at the same time that the reaeration coefficient is measured. This would require additional effort, however, because the complete concentration versus time curve at each cross-section is necessary whereas only the peak concentrations are needed for the reaeration coefficient determination.

There are also disadvantages to the tracer technique. Radiation exposure received by the personnel conducting the study and the public along the stream may be significant. Tsivoglou (1967) reported that radiation exposure could be eliminated with a minimum of trouble for discharges less than 200 cfs. However, for larger flows, more stringent precautions were required because of the larger amounts of tracer necessary. Another disadvantage of using radioactive tracers is that the process for obtaining a license to use radioactive material in a public waterway is quite involved. Finally, the nuclear counting equipment necessary for tritium and krypton is expensive and not field-type equipment, hence samples must be returned to a laboratory for analysis.

Analysis of Errors in Reaeration Coefficient

Calculation Techniques

The determination of the reaeration coefficient by any of the
techniques described previously is subject to many sources of errors.
The most important sources of error are: (1) differences between the
dynamic stream condition and the quiescent condition in the various
bottle techniques developed for measuring the DO balance parameters;
(2) the difficulty and expense of obtaining a sufficient number of
representative samples to describe accurately the stream conditions at
the cross-section of interest; (3) deviations from the assumptions
inherent in the derivation of the DO balance equation; and (4) the
accuracy of the DO measurement procedure used in the various techniques
for determining the DO balance parameters.

A general statistical analysis of the effect of these various
sources of error on the calculation of the reaeration coefficient is
beyond the scope of this report and probably is not feasible with the
present state of our knowledge. However, it is instructive and
important to consider the range of possible errors in the measured DO
balance parameters and the effect of these errors on the DO balance
equation used to calculate the reaeration coefficient.

The purpose of this section is to present a discussion of (1) the sensitivity of the DO balance technique to errors in the measured parameters; (2) the sensitivity of the disturbed equilibrium technique to errors in the measured parameters; (3) possible errors in the tracer technique; and (4) reproducibility of reaeration coefficients measured in flumes.

Accuracy of measured DO balance parameters

The accuracy of the measured value of a DO balance parameter is dependent not only on the accuracy of the DO measurements, but also on the extent to which the measurement conditions under which the measurements are made simulate the conditions in the flow, and, on how representative the samples are of the total flow.

For example, as has already been mentioned, not only is accurate measurement of BOD in bottles difficult due to dilution and seeding problems, but also there is considerable question as to how accurately the behavior of a sample of water incubated under quiescent conditions in a constant temperature bath simulates the behavior of a similar slug of water under dynamic streamflow conditions and varying temperature. There are similar problems with the techniques for determining the rate of oxygen consumption by the benthos, and for determining the rates of photosynthesis and respiration of suspended and attached plants.

Completely aside from the problem of simulating field conditions with measurement techniques is the problem of obtaining representative samples in the field. The uniformity of DO and BOD distribution in a cross-section will depend on a multiplicity of factors, among which the most important are distance from sewage outfalls and stream tributaries, shape of cross-section, tortuosity of channel, and bed roughness size, shape, and spacing. For example, Churchill and others (1962, figures 3 through 9) found a consistent U-shaped DO distribution across the stream channel which they attributed to (1) incomplete mixing into the main stream of flow from upstream tributaries, (2) increased reaeration near the banks due to a longer travel time, and (3) unequal effects across the stream of photosynthesis and respiration by attached aquatics. Considering the large cross-sectional DO variation and the small longitudinal variation in average DO illustrated in these figures, one would expect considerable error in the calculated k_2 if DO were sampled at only one point in the cross-section. Another example of the difficulty of obtaining representative samples for the computation of the DO balance parameters is given by Owens and Edwards (1961) who took extensive samples of attached aquatic plants from several English streams for analysis of the photosynthesis-respiration parameter. In their studies, the standard deviation of the amount of the attached aquatics per unit area averaged 32 percent of the mean. The size of this standard deviation in terms of the mean indicates the difficulty of obtaining a reliable estimate of photosynthesis or respiration without sampling the plants on a large area of the stream bed.

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Because of the difficulty of reproducing the stream environment in the measurement techniques for DO balance parameters, and because of the difficulty and expense of obtaining representative samples, it is apparent that if all parameters in the DO balance equation are significant, then the two conditions discussed above, and not DO measurements per se, limit the accuracy which can be obtained in the calculation of k_2. Because of the present state of uncertainty about these two situations, the accuracy obtainable from DO balance calculations is largely a matter of conjecture. The error analysis techniques used in this section have been designed with this in mind. Reasonable average values for the various DO balance parameters and what the authors consider to be reasonable values of errors are given in this section.

Dissolved oxygen balance technique

Because of the complexity of the general DO balance equation, the number of parameters involved, and the difficulty of reproducing field conditions for replications of k_2 determinations, a rigorous statistical analysis of the effect of errors on the calculated k_2 cannot be performed at the present time. Alternatively, however, one can perform for k_2 a sensitivity analysis similar to that of Kothandaraman and Ewing (1969) on the downstream DO deficit calculated from the DO balance equation. The sensitivity analysis is designed to yield the error in the calculated value of k_2, when the error in another parameter of the DO balance equation is known. When the distribution functions of the errors in the parameters of the DO balance equation are known, a Monte Carlo approach similar to that used by Kothandaraman and Ewing (1969) can be used to determine the distribution function of the calculated k_2 values.

A sensitivity analysis consists of observing the behavior of the output of a system with all except one of its parameters constant. This parameter is varied throughout the range of possible values, and at any given value of the parameter, the sensitivity of the system to the parameter is the change in output per unit change in the parameter. The sensitivity analysis was performed on the general DO balance equation, equation 119, written in the form

$$f(k_2) = \frac{k_1}{k_2 - (k_1 + k_3)} \left[L_a - \frac{m}{2.3(k_1 + k_3)} \right] \left[10^{-(k_1 + k_3)\,t} - 10^{-k_2\,t} \right]$$

$$+ \frac{k_1}{k_2} \left[\frac{m}{2.3(k_1 + k_3)} - \frac{p}{2.3\,k_1} \right] \left[1 - 10^{-k_2\,t} \right] + D_a\, 10^{-k_2\,t} - D_b \ . \quad (148)$$

Equation 148 was solved for k_2 using the Newton-Raphson iterative method (Kunz, 1957) in the form

$$(k_2)_{i+1} = (k_2)_i - \frac{f[(k_2)_i]}{f'[(k_2)_i]} \ , \qquad (149$$

and calculations were stopped when the absolute value of the ratio on the right-hand side of equation 149 was less than 0.001 times the true value of k_2.

The sensitivity analysis consisted of the following steps:

1. Assume a typical set of parameters for use in the DO balance equation, equation 119. This set of parameters is called a BPS (basic parameter set).

2. Substitute the BPS into equation 119, and calculate the corresponding BPS value of D_b.

3. Use equations 148 and 149 to compute the sensitivity of equation 119 to each of the parameters in turn.

4. In some calculations, the classical sensitivity analysis procedure was changed in that several of the parameters were varied simultaneously.

The BPS values are given in table 1. Typical sensitivity analysis

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Table 1.--following here

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plots are given in figures 3 through 8. The ordinates in these figures are expressed as a percent of the BPS value of k_2, and the abscissas are in the dimensions of the parameter that is being varied in the sensitivity analyses. Of the 19 BPS considered in the sensitivity analyses,

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Figures 3,4,5,6,7, and 8.--following here

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six, in general were selected for presentation in figures 3 through 8. Numbers 1, 5, 6, 7, 15, and 16 were selected as being typical of the following field conditions: no. 1, a medium-sized, unpolluted river; no. 5, a medium-sized, heavily-polluted river; no. 6, a large unpolluted river; no. 7, a shallow, swift-flowing stream; no. 15, a medium-size, moderately-polluted river, and no. 16, a medium-sized, unpolluted river in which the effect of ignoring a photosynthetic oxygen production rate of 20 mg/ℓ per day is investigated.

The sedimentation rate constant, k_3, and m, the rate of addition of BOD from bottom deposits, were not considered in figures 3 through 8 because the sensitivity analyses showed that the dependence of k_2 on these parameters was very small. For k_3, the most sensitive example was for BPS no. 5 where k_2 changed only 23 percent of its BPS value for a change of k_3 from 0 to 0.8. For m, the most sensitive example was for BPS no. 10 where k_2 changed only 13 percent as m varied from 0 to 200 mg/ℓ per day.

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Table 1.--*Basic parameter sets used in the sensitivity analyses of the* DO *balance equation*

BPS no.	k_1 days^{-1}	k_2 days^{-1}	k_3 days^{-1}	p mg/ℓ per day	m mg/ℓ per day	D_a mg/ℓ	L_a mg/ℓ	t days	D_b mg/ℓ
1	0.1	1	0	0	0	3	5	0.05	2.73
2	0.1	1	0	0	0	3	0	0.05	2.67
3	0.1	1	0.1	0	0	3	5	0.05	2.73
4	0.1	1	0	1	0	3	5	0.05	2.68
5	0.1	1	0	0	0	3	200	0.05	4.84
6	0.1	0.2	0	0	0	3	5	0.05	2.99
7	0.1	10	0	0	0	3	5	0.05	.98
8	0.1	10	0	0	0	3	200	0.05	2.31
9	0.1	0.2	0	0	0	3	200	0.05	5.20
10	0.1	1	0	0	0	3	200	0.05	4.84
11	0.1	1	0	0	0	5	5	0.05	4.51
12	0.4	1	0	0	0	5	5	0.05	4.67
13	0.4	1	0	0	0	5	50	0.05	6.58
14	0.1	1	0	0	0	3	5	0.05	2.73
15	0.1	1	0	0	0	3	50	0.05	3.21
16	0.1	1	0	20	0	3	5	0.05	1.78
17	0.1	1	0	20	0	3	200	0.05	3.89
18	0.1	1	0	10	0	3	5	0.05	2.26
19	0.1	1	0	5	0	3	5	0.05	2.49
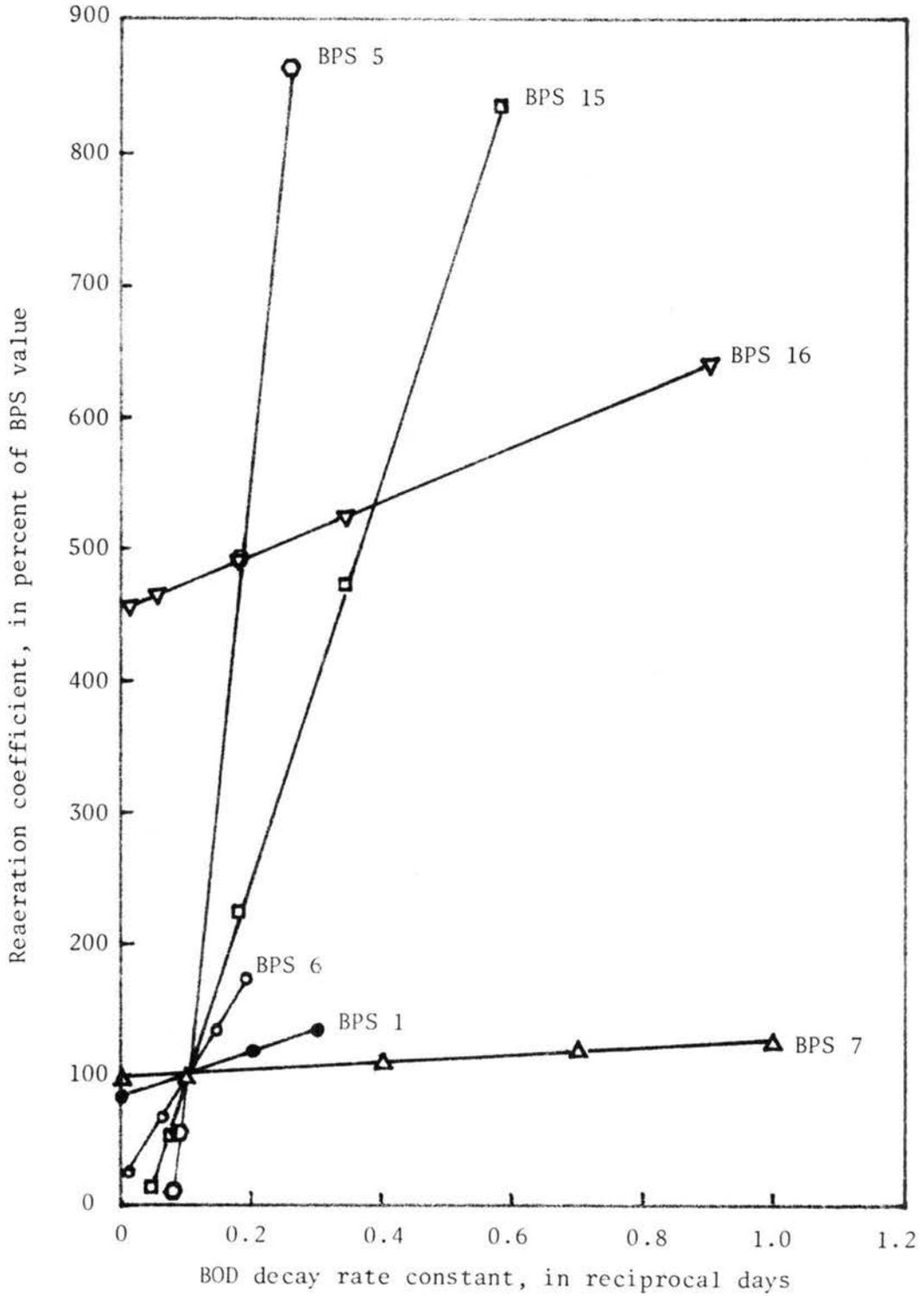
Figure 3.--Sensitivity of reaeration coefficient to rate constant for BOD decay.

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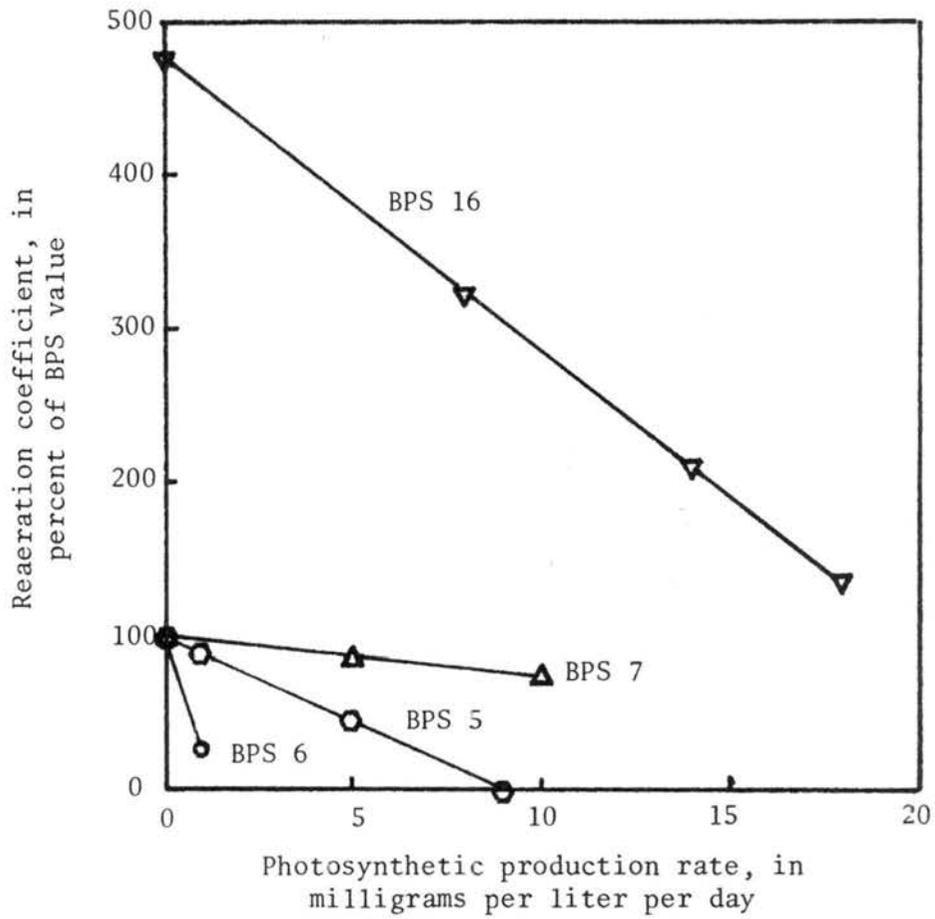
Figure 4.--Sensitivity of reaeration coefficient to photosynthetic production rate.

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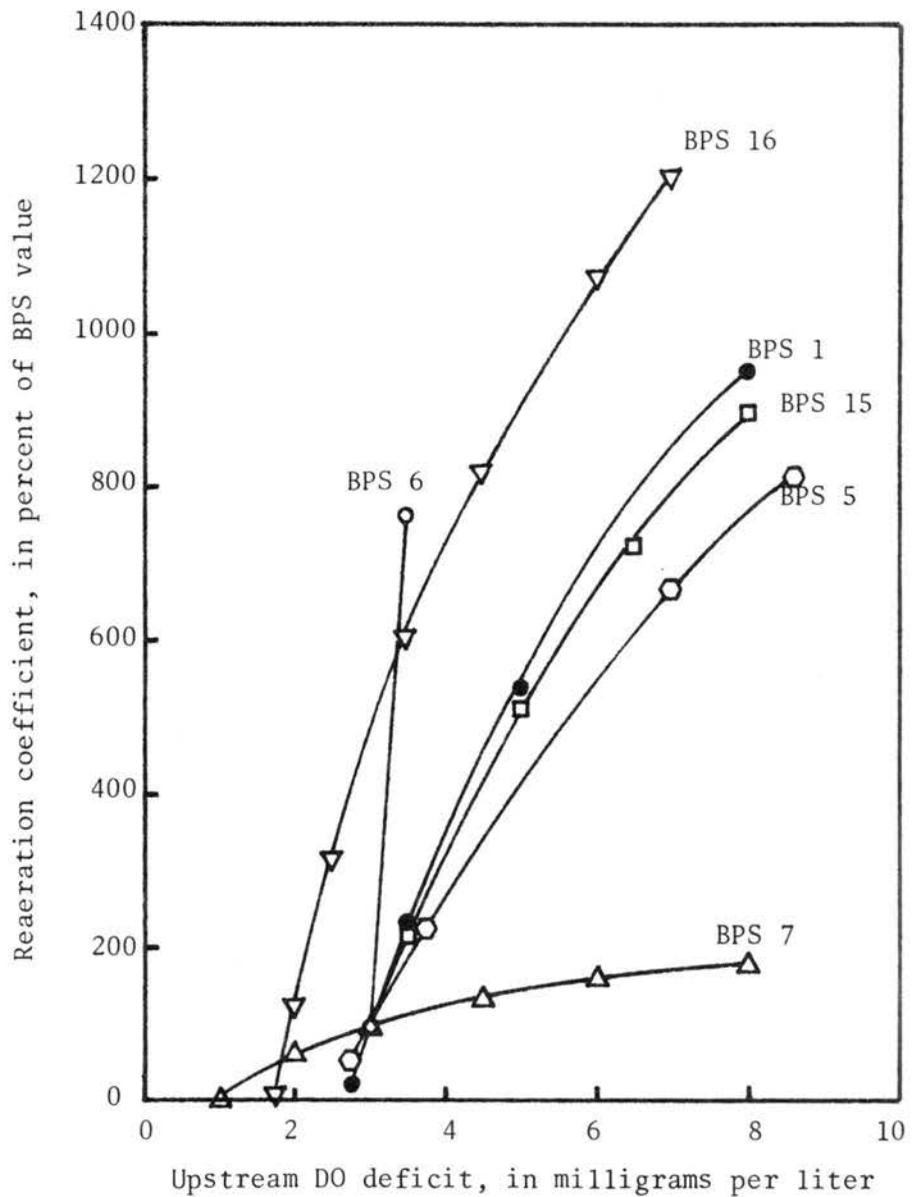
Figure 5.--Sensitivity of reaeration coefficient to
upstream DO deficit.

157
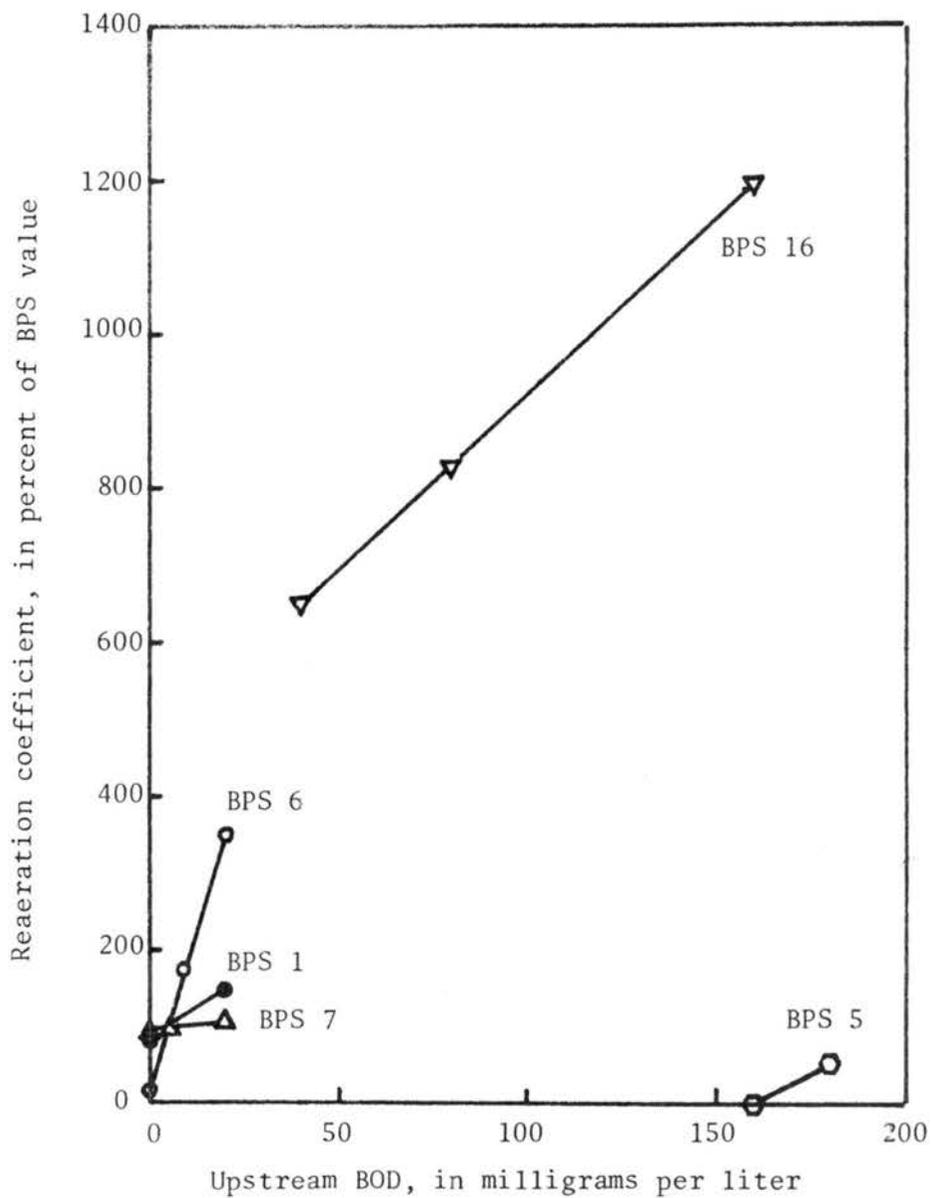
Figure 6.--Sensitivity of reaeration coefficient to
upstream BOD.
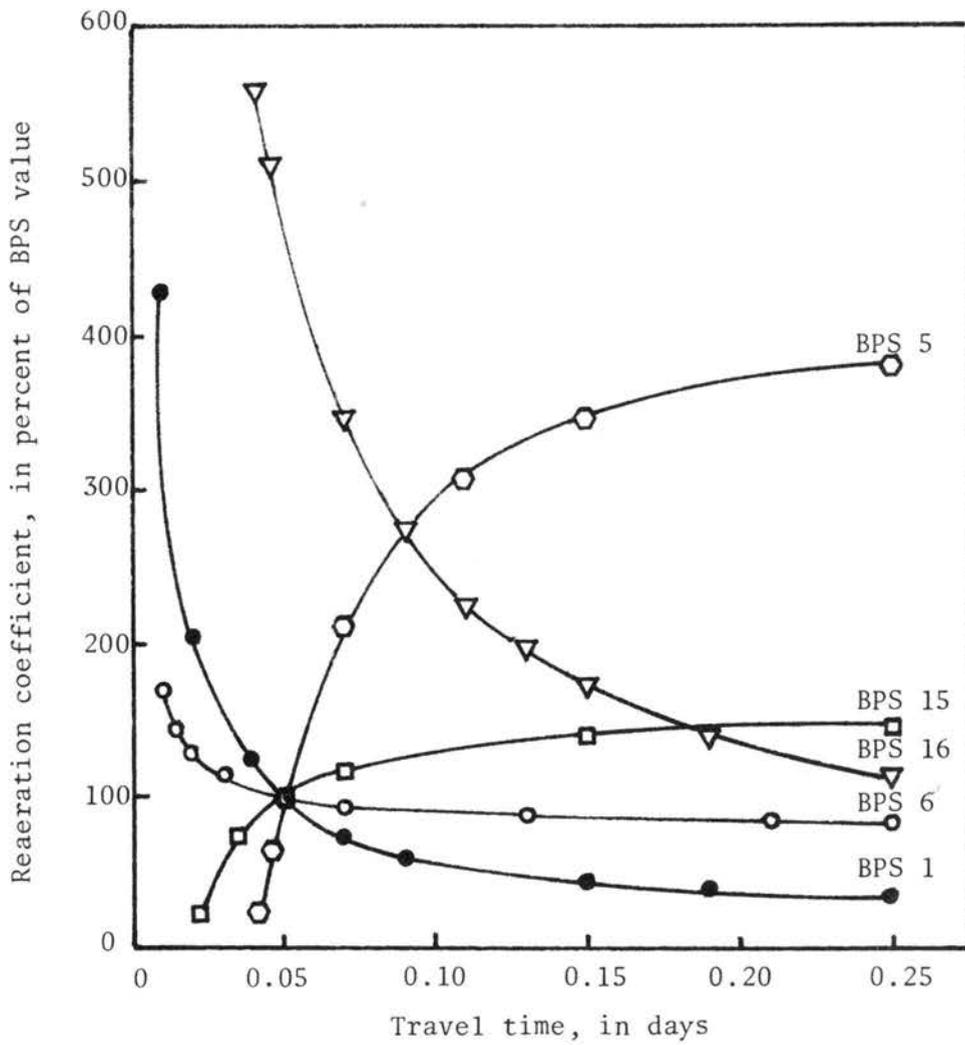
Figure 7.--Sensitivity of reaeration coefficient to travel time.

159
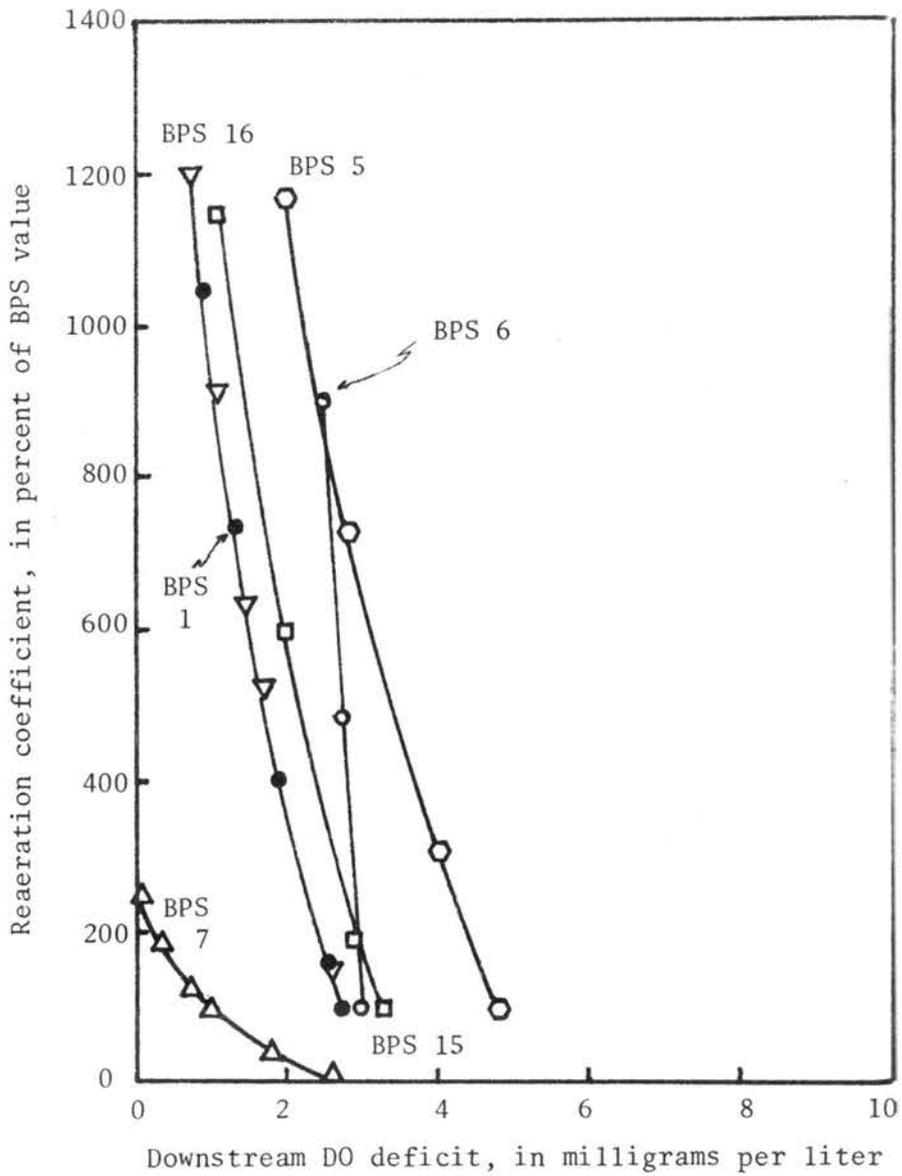
Figure 8.--Sensitivity of reaeration coefficient to
downstream DO deficit.

The results shown on figures 3 through 8 can be clarified using an approximate form of equation 119. Because the exponents in this equation are much less than 1, the exponential terms may be approximated by the first two terms in their Taylor series expansions. In this case, equation 119 reduces to

$$k_2 \approx \frac{1}{2.3}\left[\frac{1}{t}\left(1 - \frac{D_b}{D_a}\right) + \frac{2.3\,k_1\,L_a}{D_a} - \frac{p}{D_a}\right] \quad . \tag{150}$$

The first term in the brackets of equation 150 explains why the sensitivity of k_2 to variations in flow time t decreases as D_b approaches D_a (figure 7). The second and third terms in the brackets explain the linear variation of k_2 in terms of k_1, p, and L_a (figures 3, 4, and 6). The second term in the brackets explains the changes in sensitivity of k_2 to k_1 with changes in L_a. Finally, the absence of k_3 and m from equation 150 explains the lack of sensitivity of the calculated k_2 to these parameters. The solution of equation 150 for k_2 using BPS no. 1 is 0.94 and using set 5, 1.37, thus the approximations in the equation are too great for it to be used for calculation of k_2 directly, but it is valuable for showing quickly the relative seriousness of the errors in the calculated k_2 which can result from errors in the other parameters.

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The extension of the sensitivity analysis to the determination of the error in a reaeration coefficient calculation resulting from an error in a measured parameter requires information on the magnitudes of the errors to be expected in the measured parameters. However, as discussed previously, the different techniques developed for measuring the DO balance parameters are subject to various types of errors and the determination of such errors is difficult. Therefore, we have made for the purpose of an error analysis what we consider to be reasonable assumptions of the RMS (root-mean-square) and maximum errors to be expected in the various measured parameters. These estimates are presented in table 2. The RMS error is the square root of the mean value of the square

Table 2.--following here

of the deviations of the measured parameter from the true value of the parameter.

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Table 2.--*Assumed errors in measurements of* DO *balance parameters*

Parameter	Assumed error	
	Root-mean-square	Maximum
k_1	0.05 days^{-1}	0.30 days^{-1}
k_3	0.10 days^{-1}	0.50 days^{-1}
D_a	0.10 mg/ℓ	1.0 mg/ℓ
D_b	0.10 mg/ℓ	1.0 mg/ℓ
L_a	2.0 mg/ℓ	10 mg/ℓ
p	2.0 mg/ℓ per day	10 mg/ℓ per day
m	5.0 mg/ℓ per day	20 mg/ℓ per day
t	0.002 day	0.005 day

The errors in a calculated k_2 corresponding to the estimated parameter errors given in table 2 are given by the product of the estimated error and the slope of the sensitivity analysis plot. It is apparent from figures 3 through 8 that the slopes of the sensitivity analysis plots depend on the particular BPS considered. Therefore, the minimum, average, and maximum slopes were determined for each parameter so that the entire range of conditions covered by the 19 different BPS would be considered. The slopes are presented in table 3. The minimum,

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Table 3.--following here

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average, and maximum slopes were combined each in turn with the RMS and maximum error estimates from table 2 to give the expected errors in the calculated reaeration coefficient. These errors are presented in table 4. It is apparent that, with the exception of m, errors in all of the parameters may cause considerable error in the calculated k_2 value.

Table 4.--following here

As the value of k_2 decreases, the percent error increases.

Table 3.--*Slopes of the sensitivity analysis plots*

Parameter	Slope		
	Minimum	Average	Maximum
k_1	1.6	10	80
k_3	0.01	0.05	0.50
D_a	1.4 $[\text{mg}/\ell \text{ per day}]^{-1}$	2.0 $[\text{mg}/\ell \text{ per day}]^{-1}$	3.0 $[\text{mg}/\ell \text{ per day}]^{-1}$
D_b	1.6 $[\text{mg}/\ell \text{ per day}]^{-1}$	2.5 $[\text{mg}/\ell \text{ per day}]^{-1}$	6.9 $[\text{mg}/\ell \text{ per day}]^{-1}$
L_a	0.02 $[\text{mg}/\ell \text{ per day}]^{-1}$	0.035 $[\text{mg}/\ell \text{ per day}]^{-1}$	0.08 $[\text{mg}/\ell \text{ per day}]^{-1}$
p	0.11 $(\text{mg}/\ell)^{-1}$	0.20 $(\text{mg}/\ell)^{-1}$	0.30 $(\text{mg}/\ell)^{-1}$
m	$1\times10^{-4} (\text{mg}/\ell)^{-1}$	$5\times10^{-1} (\text{mg}/\ell)^{-1}$	$2\times10^{-3} (\text{mg}/\ell)^{-1}$
t	5.0 days^{-2}	40 days^{-2}	150 days^{-2}

Table 4.--*Errors in the calculated reaeration coefficient resulting from errors in parameter measurement*

Parameter	Error in calculated k_2, in days^{-1}					
	Minimum slope, RMS error	Minimum slope, maximum error	Average slope, RMS error	Average slope, maximum error	Maximum slope, RMS error	Maximum slope, maximum error
k_1	0.08	0.48	0.50	3.0	4.0	24
k_3	0.001	0.005	0.005	0.025	0.05	0.25
D_a	0.14	1.4	0.20	2.0	0.30	3.0
D_b	0.16	1.6	0.25	2.5	0.69	6.9
L_a	0.04	0.20	0.07	0.35	0.16	0.80
p	0.22	1.1	0.40	2.0	0.60	3.0
m	5×10^{-4}	2×10^{-3}	2.5×10^{-3}	0.01	0.01	0.04
t	0.01	0.025	0.08	0.20	0.30	0.75

Figures 5 and 8 show the sensitivity of the calculated k_2 to the upstream and downstream DO deficits, respectively. Because the lines slope in opposite directions, the effect of systematic errors in the procedure used to determine the DO should tend to cancel. This was verified with calculations based on BPS no. 14. The reaeration coefficient was calculated from equations 148 and 149 with a systematic error in the upstream and downstream DO deficits and the results are presented in figure 9. The abscissa is in terms of the systematic error

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Figure 9.--following here

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in DO in percent of the upstream deficit or percent of the deficit range. It is apparent from comparison of figures 9 and 5 or figures 9 and 8 that the effect of the systematic error is much less severe than the effect of a random error of the same magnitude in one of the DO deficits. The use of an incorrect value of the saturation concentration, C_s, in the computation of the DO deficits will have an effect identical to a systematic error in the DO measurement procedure.
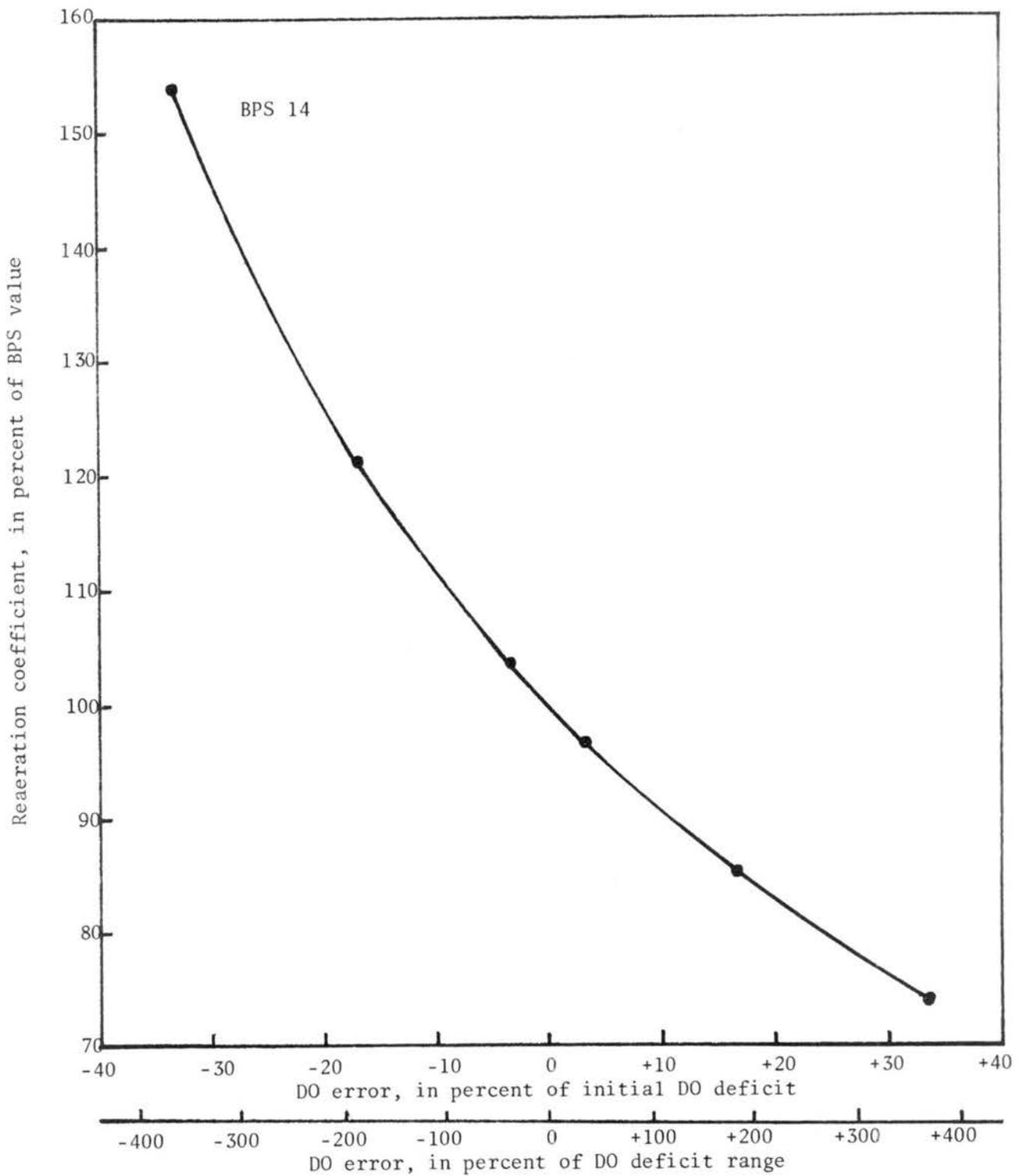
Figure 9.--Effect of a systematic error in the DO measurement
procedure on the calculated reaeration coefficient.

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The effect on the calculated k_2 of ignoring photosynthetic production is shown in figure 10. The downstream DO deficits for BPS nos. 16, 18, and 19 were calculated with the photosynthetic production term in

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Figure 10.--following here

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the equations. Then the k_2 was calculated for the same conditions except that photosynthesis was ignored. The effect is very definite, for example, for a photosynthetic production rate of 2 mg/ℓ per day, the calculated k_2 is 130 percent of the BPS value of 1.0 days^{-1}. Thus, if a term for photosynthetic production is not included in the DO balance equation and this production is significant, the calculated k_2 will be significantly larger than the true value. The effect of photosynthesis was discussed previously by Camp (1965) and Lynch (1965).

The effect on the calculated reaeration coefficient of simultaneous errors in two or more of the parameters has been investigated in this study to a limited extent, and it was found that the overall errors were in general not equal to the sums of the individual errors. Thus each individual error set must be investigated as an entity, however, this is beyond the scope of the present report.
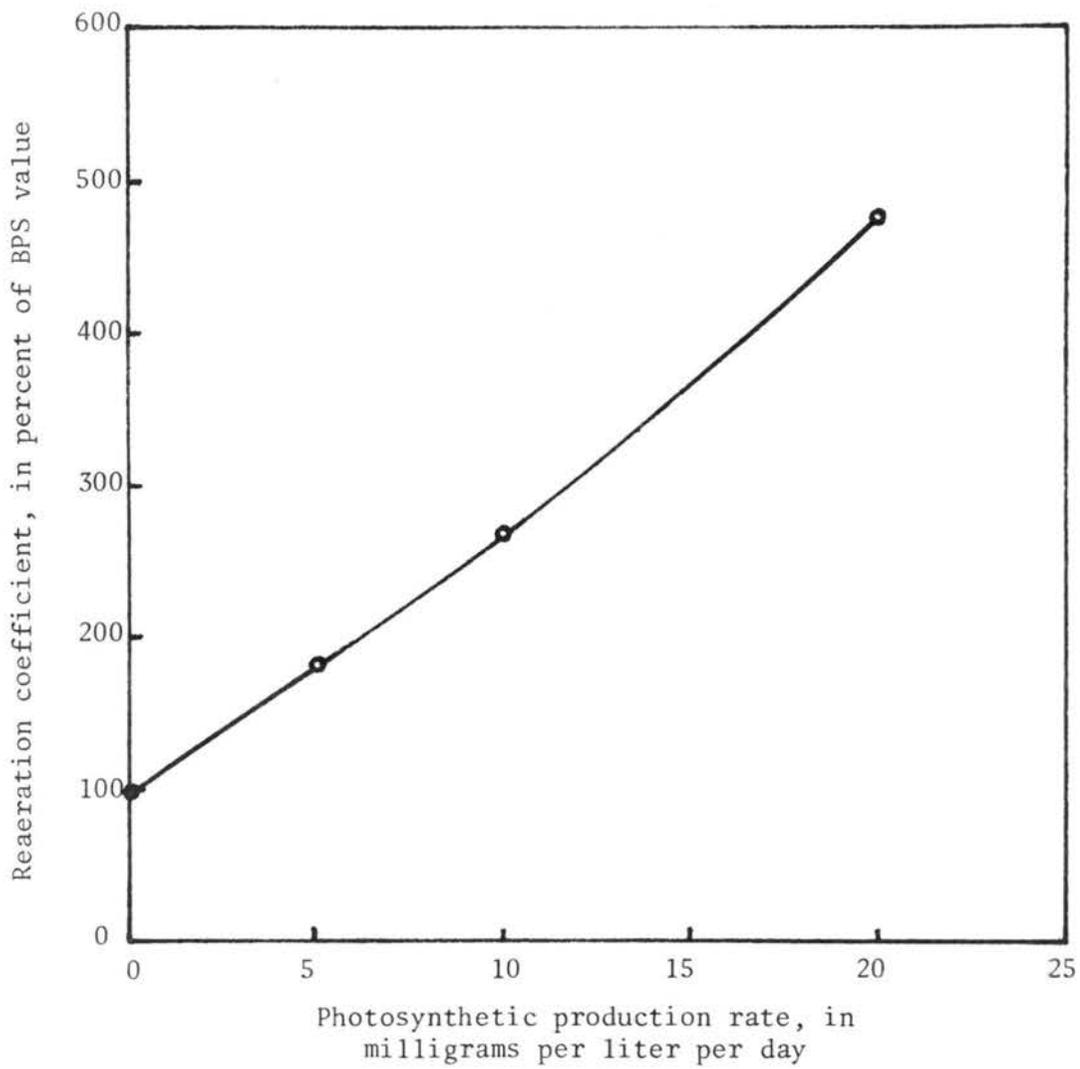
Figure 10.--Effect of ignoring the photosynthetic production rate.

From the results of the sensitivity analysis presented in figures 3 through 10 and table 4, several general conclusions are possible. Because of the limited scope of the sensitivity analysis, estimates of the errors will be of a qualitative nature only. It is expected in the calculation of the reaeration coefficient from equation 119 that:

1. If the BOD levels are small and if attached or floating plants are present in significant quantities, then neglect of the photosynthetic production is probably the largest source of error in the calculation of the reaeration coefficient.

2. If the BOD levels are small and if errors in the upstream and downstream DO deficit are independent, then these errors are probably the second largest source of error in the calculation of the reaeration coefficient.

3. For small to moderate upstream BOD levels, the errors in the calculated k_2 resulting from errors in k_1 and L_a are generally small but significant for $k_2 \leq 1.0$ days^{-1}. For an upstream BOD of greater than about 50 mg/ℓ, the errors in the calculation of k_2 resulting from errors in k_1 are especially significant.

4. The other parameters should cause no significant errors in the calculated k_2 unless $k_2 \leq 0.1$ days^{-1}.

5. By summing the squares of the RMS errors for the average slope column of table 4 and taking the square root, an expected relative RMS error of 65 percent of a true k_2 value of 1.0 days^{-1} is obtained.

6. If errors in the upstream and downstream DO deficits are the result of a systematic error in the DO measurement procedure or of the use of an incorrect DO saturation value, then these errors compensate each other to some extent so that the error in the calculated reaeration coefficient is not as great as it would be if the error had occurred independently in D_a or D_b.

7. The effects of simultaneous errors in two or more parameters are not linearly additive, so that the results of this study cannot be used to determine the effects of more than one parameter error on the calculated k_2 values. Future studies should be directed to determining the sensitivity of the DO balance equation to errors in two or more parameters. The most ideal study would be to use Monte Carlo techniques which would give the distribution function of the reaeration coefficient calculated from the DO balance equation for known distributions of the other parameters.

Disturbed equilibrium technique

A rigorous statistical analysis of the disturbed equilibrium technique is presently impractical for the same reasons that such an analysis is impractical for the DO balance technique. However, a sensitivity analysis was performed, using the same approach as for the DO balance technique. The results of the sensitivity analysis and a comparison of the results of calculating reaeration coefficients from equations 139 and 140 are discussed in the following paragraphs.

The equations used in the sensitivity analysis were equation 140 written in the form

$$f(k_2) = D_b - D'_b + \frac{p-p'}{2.3 \; k_2} - 10^{-k_2 \; t} \left\{ D_a - D'_a + \frac{p-p'}{2.3 \; k_2} \right\} \quad , \qquad (151)$$

and a Newton-Raphson iterative solution as given by equation 149. The BPS values studied are listed in table 5. These were chosen to correspond to the BPS used in the sensitivity analysis of the DO balance technique.

Table 5.--following here

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Table 5.--*Basic parameter sets for the sensitivity analysis of the disturbed equilibrium technique*

BPS no.	k_2 days^{-1}	t days	D_a mg/ℓ	D'_a mg/ℓ	p mg/ℓ per day	p' mg/ℓ per day	D_b mg/ℓ	D'_b mg/ℓ
1	1	0.05	3	5	0	0	2.73	4.51
2	1	0.05	3	5	-1	0	2.73	4.46
3	1	0.05	3	8	0	0	2.73	7.18
4	1	0.05	3	8	-1	0	2.73	7.14
5	.2	0.05	3	5	0	0	2.99	4.94
6	.2	0.05	3	5	-1	0	2.99	4.89
7	10	0.05	3	5	0	0	0.98	1.62
8	10	0.05	3	5	-1	0	0.98	1.59
9	1	0.05	3	5	-1	0	2.73	4.46
10	1	0.05	3	5	-5	0	2.73	4.27
11	1	0.05	3	5	-10	0	2.73	4.04
12	1	0.05	3	8	-5	0	2.73	6.95
13	1	0.05	3	8	-10	0	2.73	6.71

The results of the sensitivity analyses of equation 151 are
presented in figures 11 through 14, in which the ordinates are in terms

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Figures 11,12,13, and 14.--following here

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of percent of the BPS value of the reaeration coefficient, and the
abscissas are in the dimensions of the variable being investigated. In
general, the sensitivity increases as the deficit range decreases.

With the exception of the travel time, two measurements of each
parameter are necessary in the disturbed equilibrium technique. Because
of the additive nature of the variances, we have multiplied by 1.5 the
estimated parameter errors presented previously in table 2 and used in
the sensitivity analysis of the DO balance technique. These estimates
of the parameter errors and the slopes of sensitivity analyses plots for
the disturbed equilibrium technique (figures 11 through 14) are presented
in table 6. The possible errors in the calculated reaeration coefficient

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Table 6.--following here

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obtained from the different combinations of RMS and maximum errors and
minimum, average, and maximum slopes are presented in table 7.

Table 7.--following here
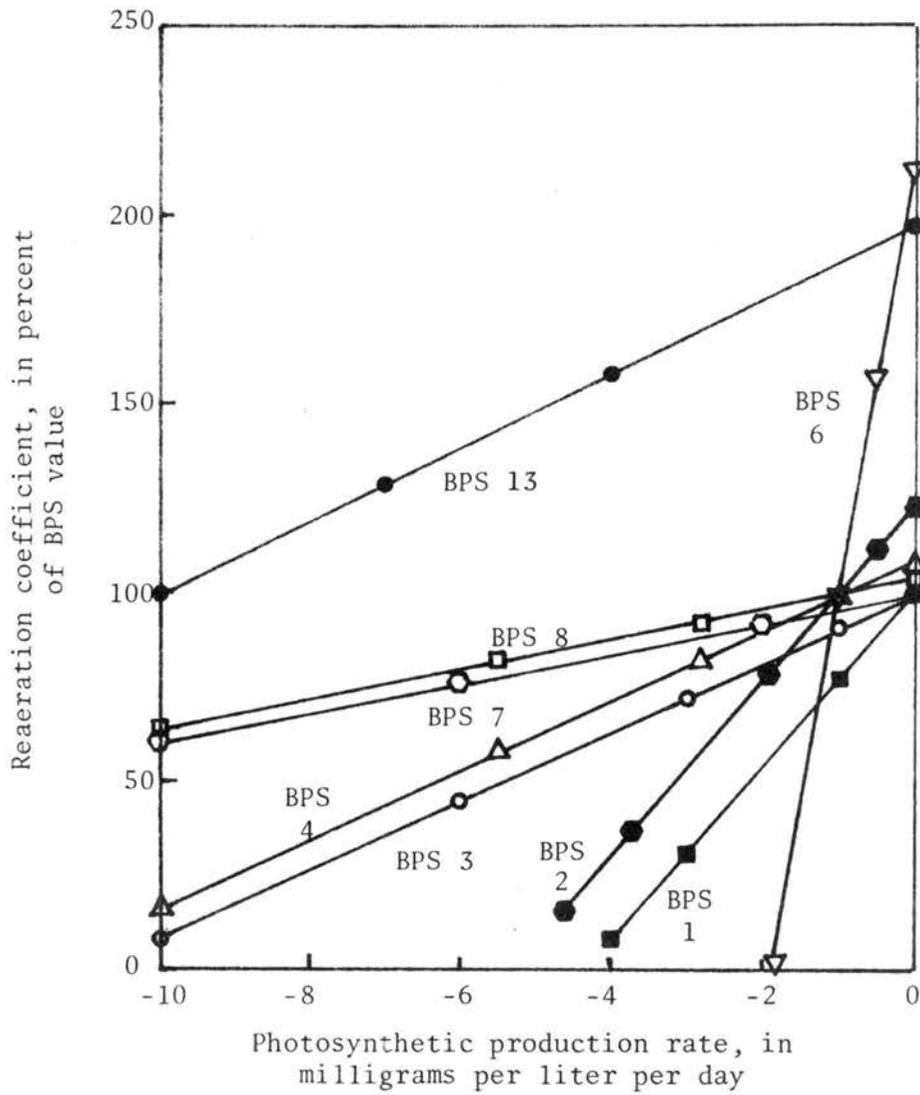
Figure 11.--Sensitivity of reaeration coefficient to
photosynthetic production rate.
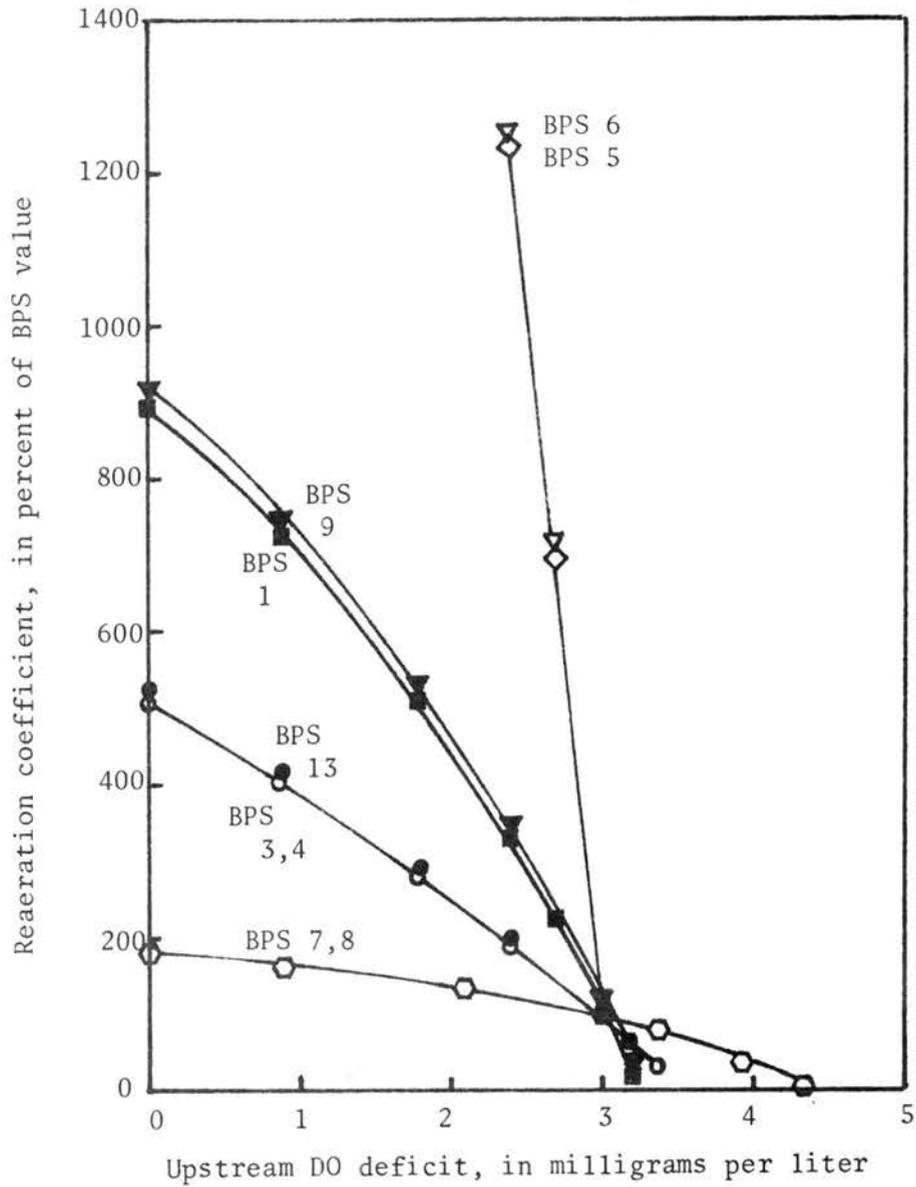
Figure 12. Sensitivity of the reaeration coefficient to the upstream DO deficit.

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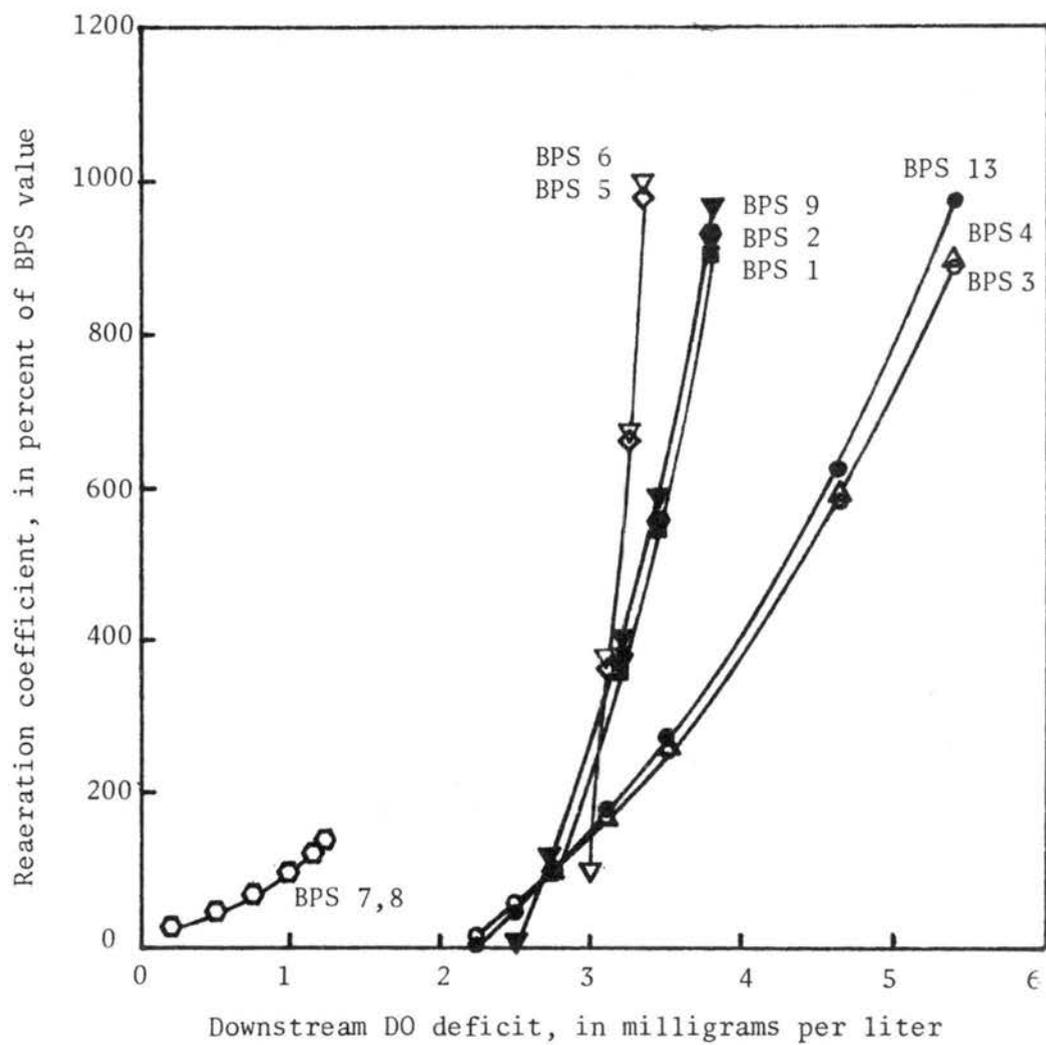
Figure 13.--Sensitivity of the reaeration coefficient to the downstream DO deficit.

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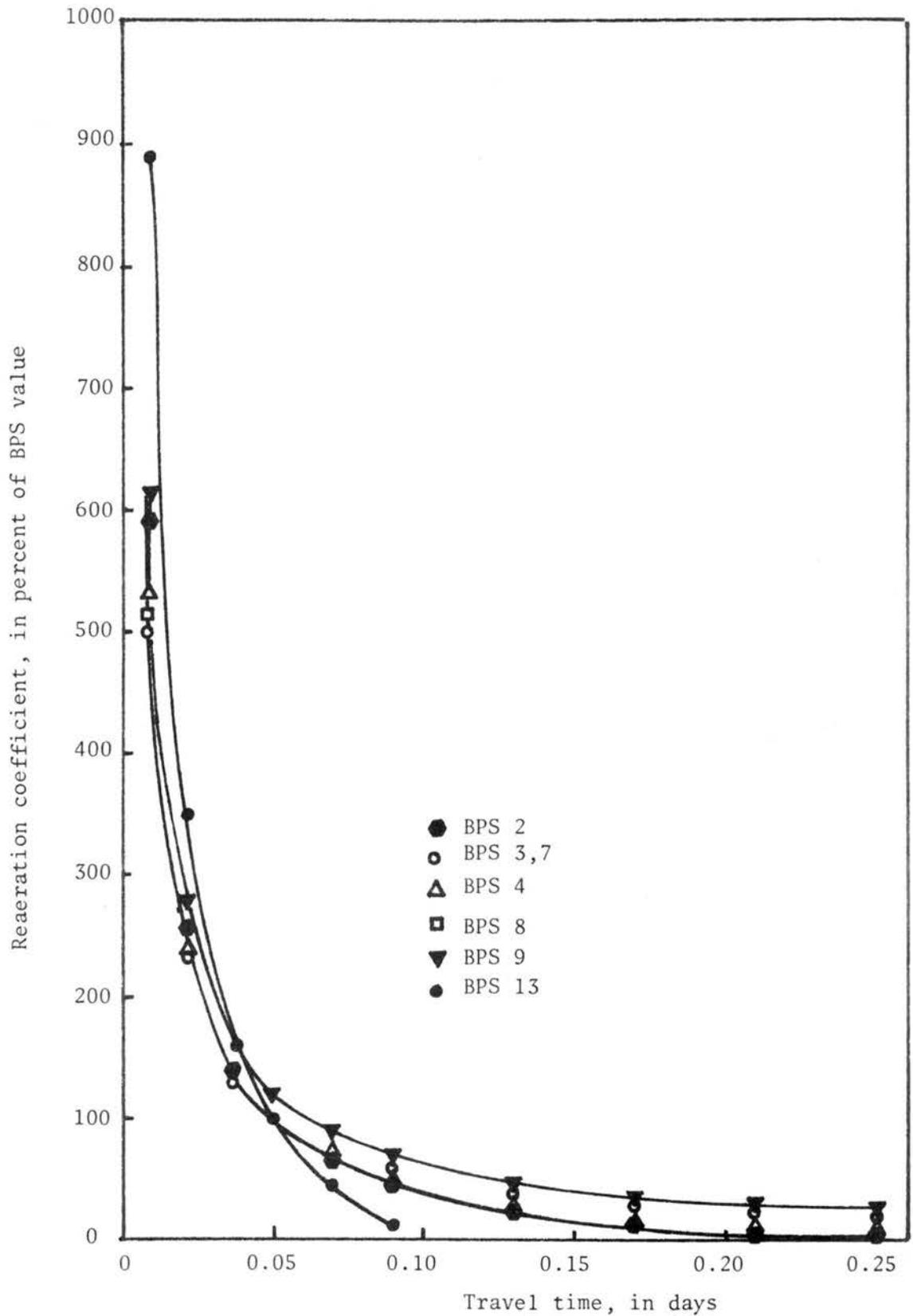
Figure 14.--Sensitivity of the reaeration coefficient to the travel time.

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Table 6.--*Assumed parameter errors and slopes of sensitivity analysis plots for disturbed equilibrium technique*

Parameter	Assumed error		Slope		
	Root-mean-square	Maximum	Minimum	Average	Maximum
p	3.0 mg/ℓ per day	15 mg/ℓ per day	0.09 $(mg/ℓ)^{-1}$	0.20 $(mg/ℓ)^{-1}$	0.40 $(mg/ℓ)^{-1}$
D_a	0.15 mg/ℓ	1.5 mg/ℓ	1.5 $[mg/ℓ\ per\ day]^{-1}$	2.5 $[mg/ℓ\ per\ day]^{-1}$	4.0 $[mg/ℓ\ per\ day]^{-1}$
D_b	0.15 mg/ℓ	1.5 mg/ℓ	2.0 $[mg/ℓ\ per\ day]^{-1}$	6.0 $[mg/ℓ\ per\ day]^{-1}$	14 $[mg/ℓ\ per\ day]^{-1}$
t	0.002 day	0.005 day	2 $days^{-2}$	20 $days^{-2}$	200 $days^{-2}$

Table 7.--*Errors in the calculated reaeration coefficient resulting from errors in parameter measurement, disturbed equilibrium technique*

| Parameter | Error in calculated k_2, in days^{-1} | | | | | |
	Minimum slope, RMS error	Minimum slope, maximum error	Average slope, RMS error	Average slope, maximum error	Maximum slope, RMS error	Maximum slope, maximum error
p	0.27	1.35	0.60	3.0	1.2	6.0
D_a	0.22	2.25	0.38	3.8	0.60	6.0
D_b	0.30	3.0	0.90	9.0	2.1	21
t	0.004	0.01	0.04	0.10	0.40	1.0

Figure 15 shows the effect of ignoring a difference in the respiration rates for the two levels of DO concentration of the disturbed equilibrium technique. Reaeration coefficients were calculated from

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Figure 15.--following here

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equation 151 for various respiration rate differences and then the calculations were repeated with no respiration rate difference. It is apparent from figure 15 that the effect of ignoring the difference between respiration rates is definitely significant. For example, neglecting a respiration rate difference of 1.0 mg/ℓ per day causes about 12 percent error in the calculated reaeration coefficient and the error increases rapidly as the difference in respiration rate increases.
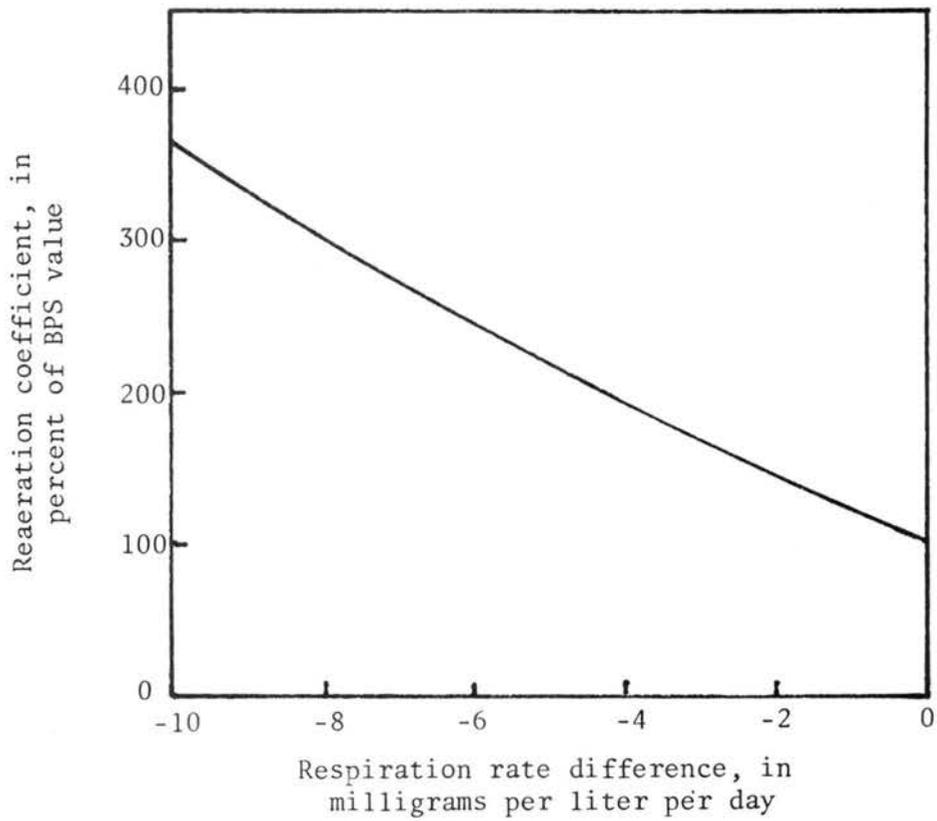
Figure 15.--Effect on the calculated reaeration coefficient
of ignoring a respiration rate difference.

Either equation 139 or 140 can be used to calculate k_2 from measurements by the disturbed-equilibrium technique when the respiration rates are different for the two levels of DO concentration. Equation 140 gives an integral reaeration coefficient whereas equation 139 gives a reaeration coefficient based on the average DO deficit for the reach. Figure 16 shows the variation with respiration rate ratio of k_2 as calculated from

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Figure 16.--following here

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equation 139 for BPS nos. 2, 4, and 13. A comparison of figures 15 and 16 shows that the sensitivity of the reaeration coefficient calculated from equation 140 to the difference in respiration rates is considerably less than the sensitivity of the reaeration coefficient calculated from equation 139 to the respiration rate ratio.

In general, the respiration rate ratio for a disturbed equilibrium technique experiment should not deviate too much from a value of 1.0. From figure 7 of Edwards and others (1961), it is estimated that $R' = 0.85$ for a DO concentration change from 2 to 4 mg/ℓ and $R' = 0.65$ for a change from 2 to 10 mg/ℓ. From figure 16, however, it is apparent that equation 139 cannot give the correct reaeration coefficient of BPS nos. 2, 4, and 13 if $R' > 0.64$. Therefore, because the BPS values were chosen as representative of conditions in natural streams, the use of equation 140 is preferred.
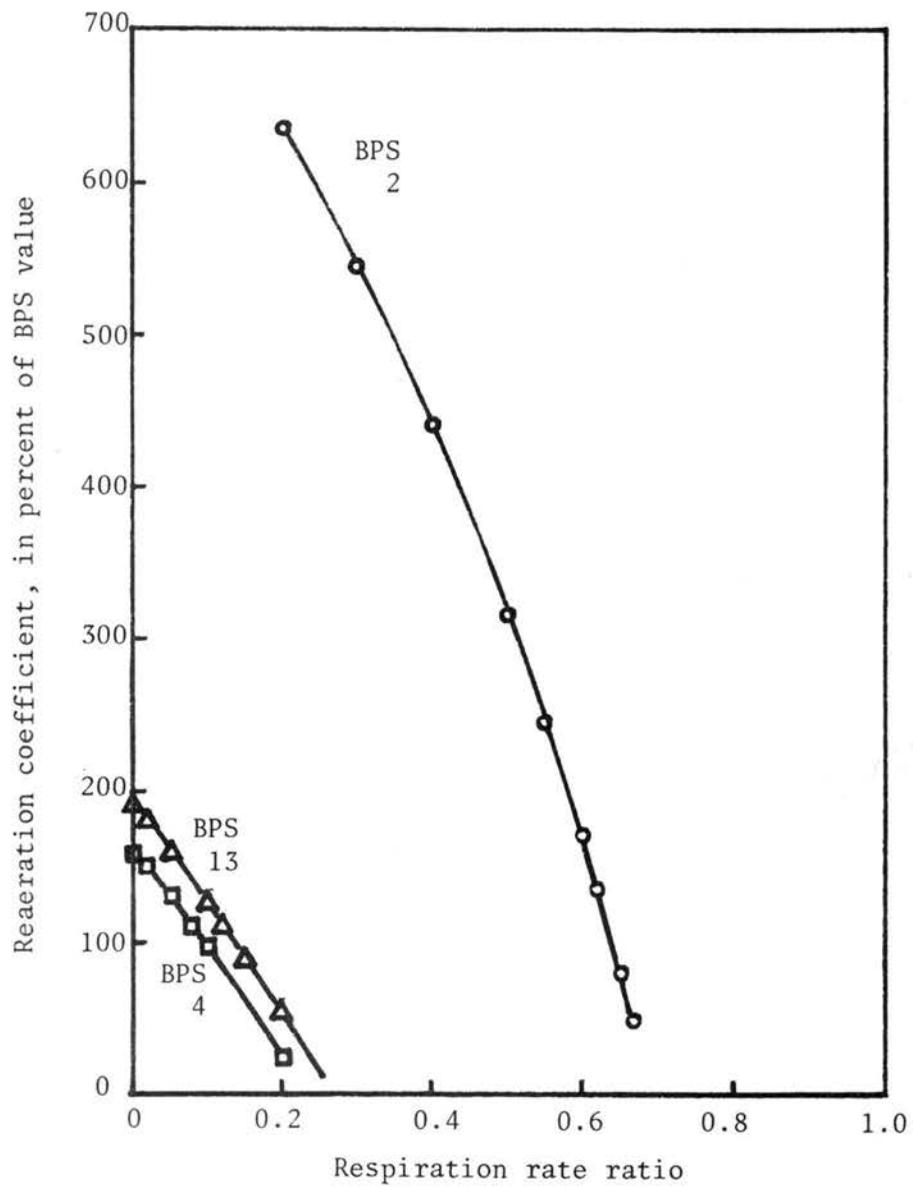
Figure 16.--Variation of the calculated reaeration coefficient with respiration rate ratio.

From the results of the sensitivity analysis presented in figures 11 through 16 and table 7, several general conclusions are possible. These conclusions are of a qualitative nature only because of the limited scope of the sensitivity analysis. It is concluded that

1. Errors in all parameters of the disturbed equilibrium technique are significant in the calculation of the reaeration coefficient. The most significant is the error in the downstream DO deficit followed by errors in the net photosynthetic production parameter, upstream DC deficit, and travel time.

2. Neglecting a respiration rate difference of 1.0 mg/ℓ per day causes about 12 percent error in the calculated reaeration coefficient; therefore, neglecting the effect of DO concentration on the respiration rate may be significant.

3. The use of equation 140 for disturbed equilibrium technique calculations is preferred.

4. The square root of the sum of the squares of the RMS errcrs for the average slope column of table 7 yields an expected relative RMS error of 115 percent for a reaeration coefficient of 1.0 days^{-1}.

Tracer technique

There are two major sources of error that must be considered in an error analysis of the tracer technique. The first is the accuracy of the value of the ratio of the mass transfer coefficient of the tracer gas to that of oxygen. The second is the accuracy of the procedures involved in measuring the mass transfer coefficient of the tracer gas in an actual reaeration coefficient determination.

The value of the mass transfer coefficient ratio can cause errors in the calculated reaeration coefficient in two ways. First, there are errors inherent in the ratio because of errors in the laboratory procedures used to determine the ratio. Second, the conditions of turbulence and temperature and the presence of surfactants and pollutants in the measurement situation may be different from the conditions under which the ratio was determined and this may result in a different ratio value.

The mass transfer coefficient ratio for the krypton-oxygen gas pair was determined under a variety of laboratory conditions by Tsivoglou and others (1965) and by Tsivoglou (1967). The results of these tests are summarized in table 8. Also shown in table 8 are the maximum and minimum

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Table 8.--following here

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reaeration coefficients observed in the two series of tests. A statistical analysis showed that the mean values were not significantly different at the 95 percent level of significance, and weighting the means in inverse proportion to their variances yielded a mean ratio of 0.83. The 95 percent confidence limits for the weighted mean were ±0.034 and the most probable error was 0.011 or about 1.3 percent of the mean ratio. Thus, the value of 0.83 may be regarded as an accurate estimate of the mass transfer coefficient ratio for the krypton-oxygen gas pair.

Table 8.--*Statistical data concerning measured gas transfer coefficient*

Transfer coefficient ratio	Mean	Minimum	Maximum	Median	Standard deviation	Range (K_2) days^{-1}	
						Minimum	Maximum
$\dfrac{K_{2_G}[1]}{K_2}$	0.82	0.76	0.91	0.81	0.04	1.5	12.5
$\dfrac{K_{2_G}[2]}{K_2}$	0.846	0.789	0.909	0.846	0.045	4.4	68.6

[1] Tsivoglou and others (1965).

[2] Tsivoglou (1967).

The effect of different conditions on the ratio was investigated extensively by Tsivoglou and others (1965) and Tsivoglou (1967). They measured mass transfer coefficient ratios in two different experimental systems for seven different gases for transfer both into and out of the water. They also used a range of temperature and turbulence conditions that produced reaeration coefficients comparable to the upper range of reaeration coefficients observed in natural streams. They concluded that the mass transfer coefficient ratio was not influenced significantly by (1) temperature in the range from 10 to 30°C; (2) the degree of turbulent mixing over a wide range of mixing conditions; (3) the presence or absence of a broken water surface; and (4) the direction of gas transfer.

In addition to this experimental evidence, some of the conceptual models discussed previously and a theoretical argument presented by Tsivoglou (1967) suggest that the transfer coefficient ratio is equal to ratio of the molecular diffusivities. Thus, this observation also suggests that the transfer coefficient ratio should be a constant, if differences in the temperature dependences of the diffusivities are neglected.

The accuracy of the procedure used to measure the mass transfer coefficient of the tracer gas in an actual reaeration coefficient determination depends on the accuracy of the nuclear counting techniques, the measurement of the flow time, and sampling errors. The counting technique used by Tsivoglou (1967) involved splitting each sample into three parts and determining the number of counts of each sample for at least two 20 minute periods. Tsivoglou (1967) reported, "This procedure, involving considerable replication and long total counts, provided excellent counting statistics, and a high level of accuracy for river samples whose count rates might be in the neighborhood of only twice the background count rate." Flow time in the tracer technique is determined from measurements of the concentrations of the water-soluble fluorescent dye and hence, should be very accurate. Furthermore, the flow time determined by this procedure should be identical to the flow time for the conservative liquid and gas tracers. Errors resulting from sampling should be small because the only quantity determined from the samples is the ratio of the concentrations of the gas and liquid tracers. Care must be exercised, however, to insure that the gas tracer is not lost from the samples during handling and counting.

It is difficult to estimate the overall accuracy of the tracer technique. A qualitative indication of the reproducibility of k_2 values determined from the tracer technique can be obtained from the work of Tsivoglou (1967) and Tsivoglou and others (1968). This work included two or three repetitions of k_2 measurements for 14 river reaches. The average deviation from the mean for nine reaches was less than ±10 percent, the average deviation was less than ±6 percent for six of the reaches, and the maximum deviation for any reach was ±18.2 percent. Because two days generally elapsed between measurements on a specific reach, some of the variation could have been the result of actual changes in the reaeration coefficient. Thus, on the basis of this limited data, it is expected that errors in reaeration coefficients determined by the tracer technique may be of the order of ±15 percent of the mean.

Laboratory measurements

In the laboratory, it is possible to eliminate most of the sources and sinks in the DO balance so that the complete DO balance, equation 119, reduces to the simple equation 133 for a laboratory flume. Hence laboratory flume measurements of the reaeration coefficient should provide a limit on the reproducibility that can be expected from the DO balance technique in general. Unfortunately, there is not much information in the literature concerning reproducibility of reaeration coefficient measurements in flumes. There is, however, some information available for mixing tank studies, an experimental situation considerably simpler than the flume situation because only one plot of log D versus time is involved. Dobbins (1964a) reported measurements on three different gases at constant turbulence conditions in a mixing tank; in two cases, 4 repetitions were made, and the resulting variances were 3.6 percent and 8.6 percent of the mean. In one case involving 7 repetitions, the variance was 8.5 percent of the mean. Isaacs and Gaudy (1968) reported measurements in a "simulated" stream which in essence was a mixing tank with moving walls, used in an attempt to duplicate velocity conditions in streams. They reported two situations where 5 repetitions were made in which the variance was 6.3 and 6.9 percent of the mean. In five situations where 3 repetitions were used, the variance was from 1.6 to 4.1 percent of the calculated k_2 value. Dobbins' k_2 determinations were based on measurements of the volume of gas absorbed, while Isaacs and Gaudy's were made using the azide modification of the Winkler test. It is interesting to compare

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the average variance of about 5 percent of Isaacs and Gaudy's measure-ments with the 0.1 percent of C_s reproducibility expected in the DO measurements with the Winkler method. This comparison indicates that, as the complexity of the measurement procedure increases, the error increases considerably, so that the variance of flume measurements would be expected to be even larger than 5 percent. Furthermore, the comparison suggests that the accuracy of the DO measurement procedure should not be considered as indicative of the accuracy of the complete determination procedure for the reaeration coefficient.

The difference between the reproducibility of the Winkler method for DO determination and the expected reproducibility of flume measurements shows that other factors are important in the flume measurement procedures. These factors may be errors in reproducing or measuring the hydraulic conditions describing the flow. In addition, another factor not previously considered by researchers is the possibility of a corrosion reaction in the flume system.

Many laboratory flumes are constructed from metals and because metals corrode or react with oxygen to varying degrees, a DO sink may be present that the researcher has not considered. The reaeration coefficient calculated by the procedure illustrated in figure 2 may be incorrect when a corrosion reaction is occurring in the channel. Furthermore, the magnitude of the error has been shown to depend on the relative magnitudes of the reaeration coefficient and the rate constant for the corrosion reaction and also on the initial DO deficit (see appendix A).

Therefore, it is suggested that the first step of any laboratory study of the reaeration coefficient should be the determination of the significance of possible corrosion reactions together with a determination of the reproducibility of the experimental measurements. The reproducibility of the measurement procedure can be determined by replication of the experimental runs, and the significance of possible corrosion reactions can be determined by the procedures outlined in appendix A.

The presence of an oxygen-consuming reaction in the laboratory equipment shows one way in which systematic errors can be introduced into flume measurements of the reaeration coefficient. This might explain one of the puzzling facts present in the literature on reaeration in flumes. This is the inconsistency between prediction equations obtained from data taken in two different but supposedly hydraulically equivalent flumes. The work of Krenkel (1960) and Thackston (1966) illustrates this inconsistency. The flumes used by these investigators were not significantly different hydraulically, except that Krenkel's was 1.0 ft wide, while Thackston's was 2.0 ft wide. The results, however, obtained from their studies over similar ranges of hydraulic variables may be given as (Thackston, 1966)

$$\text{Krenkel} \qquad k_2 = 0.000469 \, \frac{u_*}{H} \qquad\qquad (152)$$

$$\text{Thackston} \qquad k_2 = 0.000215 \, \frac{u_*}{H} \quad . \qquad (153)$$

The constants in the equations differ by a factor of 2.2.

The reasons for the discrepancy between these equations is not known. However, it might be due to the systematic error introduced by an oxygen consuming reaction proceeding in the channel of one or the other of the experimental flumes.

Another possibility for the discrepancy is the failure to include some pertinent hydraulic variable in the equation, for example, the width-depth ratio to account for the different widths. However, Thackston and Krenkel (1969a) say, "It is possible that some sort of wall effect is involved, inasmuch as the values of the width-to-depth ratio were essentially the same in both studies, ..." Additional experimental work is necessary to determine the effect of the width-depth ratio on the reaeration coefficient.

PREDICTION OF THE REAERATION COEFFICIENT

None of the presently available models of the oxygen absorption process in open-channel flows are well enough developed--or have been sufficiently verified--so that they can be used to accurately predict reaeration coefficients from the mean hydraulic parameters. Because of this, it is necessary to rely for the prediction of reaeration coefficients on empirical regression equations based on experimental data. The mean parameters commonly available for use as the independent variables in such equations are width, depth, slope, and velocity. Another parameter which has been used as an independent variable in k_2 prediction equations is the longitudinal dispersion coefficient, D_x, but because of a scarcity of experimental D_x data, this parameter has not been used herein.

The purpose of this section is to (1) present a summary of the known experimental data concerning the reaeration coefficient in open-channel flows, (2) to evaluate the presently available equations for prediction of reaeration coefficients, and (3) to present what we consider to be the most reasonable prediction equations that can be obtained by regression analysis from the available data.

Reaeration Coefficient Data Sets

The reaeration coefficient data sets available in the literature can be judged against two basic criteria. The first of these is accuracy and carefulness with which the basic data were measured and with which the coefficients were calculated. The measurement techniques used must be considered and if the DO balance technique or the disturbed equilibrium technique is used, the effects of all neglected parameters must be evaluated.

The second criterion is the completeness of the data in the set. Specifically, this concerns the number of independent variables reported and the ranges of the independent and dependent variables.

From the point of view of scale, and from the point of view of data collection methods, the reaeration coefficient data fall into two general classes. These classes are data from laboratory flumes, and data from natural streams. The flume data were in general collected at flow depths one to two orders of magnitude lower than the field data, and at slopes one to two orders of magnitude higher. In terms of scaling, the data of Owens and others (1964) to some extent bridge the gap between the rest of the field data and the flume data.

Field data

The best available data were presented by Churchill and others (1962). The DO balance technique was used, for the most part under such idealized conditions, and with such attention to detail, that a high degree of accuracy is expected in the reaeration coefficients. These measurements were made in river reaches downstream of deep-storage impoundments. A DO deficit was present because the water released was low in DO concentrations as a result of prolonged storage under thermally stratified conditions. For the reservoirs studied, the BOD of the water was satisfied during storage, so that it was zero at release time.

Over the study period on each reach, the stream discharge was held constant by keeping the discharge constant at the upstream hydroelectric plant. The discharge was determined from local stream gaging stations, and the mean velocity was determined by dividing the discharge by the average cross-sectional area. The flow time was determined by dividing the length of the test reach by the mean velocity. Because the test reaches were carefully selected for uniformity, and because cross-sections were measured at intervals roughly equivalent to the stream width, the accuracy of this method of determining the flow time is probably consistent with the accuracy of the other steps in the DO balance procedure used for the calculation of k_2.

The Winkler method, with a special end-point determination procedure which produced a standard deviation of only 0.007 mg/ℓ, was used to determine the DO concentrations. The measured DO concentrations showed no variation in the vertical, but for many cross-sections, the lateral DO variation exceeded the variation in DO between the ends of the test reach. This necessitated taking DO samples at several points in the cross-section and using the average of the measurements as the cross-section DO concentration. For most cross-sections, seven samples were used.

In all but seven of the 30 reaches studied, Churchill and others (1962) believed that except for k_2, all of the parameters in the DO balance equation were negligible. In the seven reaches it was felt that correction was necessary for the photosynthesis and respiration of attached plants. The corrections were made using laboratory measurements of the photosynthesis and respiration rates of plants attached to rocks removed from the river bottom. For reasons discussed previously and as pointed out by Hull and Defilippi (1963), this type of correction is dubious, so that these seven values are less reliable than the other values reported. However, the problem was recognized and an attempt was made to compensate for it. In addition, the corrections were for less than 25 percent of the calculated coefficients, which, as will be shown later, is of the order of magnitude of the scatter around the best-fit regression equations obtainable from the field data.

The data obtained by Churchill and others (1962) are listed in table B-1 of appendix B. In terms of the commonly measured mean hydraulic parameters, this data set is considered complete, because all of the variables U, H, S, and W are reported. The ranges of the measured variables are listed in table 9. These data are representative of moderate-sized streams.

Table 9.--following here

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Table 9.--*Ranges of experimental data sets from the literature*

Reference	k_2 days^{-1}		H feet		U feet per second		W feet		$S \times 10^4$ feet per foot	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Churchill and others (1962)	5.558	0.225	11.41	2.12	5.00	1.85	667	90	23.514	1.2571
Owens and others (1964)	49.17	0.31	2.44	0.39	1.83	0.13	39.8	11.0	106.0	1.56
Gameson and others (1955)	57.7	34.3	0.42	0.34	0.73	1.12	5.7	-------	-------	-------
O'Connor and Dobbins (1958) [3]	0.92	0.14	24.2	4.0	4.20	0.19	-------	-------	1.97	0.68
Tsivoglou and others (1967, 1968)	3.373	0.646	3.11	1.16	0.636	0.286	110	58	-------	-------
Thackston (1966)	52.50	5.78	0.232	0.052	2.320	0.365	2.0	-------	201.2	6.5
Krenkel (1960)	115.3	10.63	0.200	0.080	2.140	0.243	1.0	-------	239.9	7.5
Negulescu and Rojanski (1969)	18.70	8.64	0.492	0.164	1.902	0.656	0.66	-------	-------	-------

[3] Streeter and Phelps (1925) data only.

The reaeration coefficient study presented by Owens and others (1964) was performed under conditions much less ideal than those prevailing for the study of Churchill and others (1962). In 11 of the 32 cases presented, it was noted that either considerable weed growth or mild organic pollution was present. In addition, it is not stated whether phytoplankton were present. The presence of plants is an important factor, because the disturbed equilibrium technique was used to calculate the reaeration coefficients and different DO consumption rates of the plants at the two DO levels used in this test could significantly influence the calculated reaeration coefficients.

In the study by Owens and others (1964), the discharge was determined by a dilution technique. The flow time was determined from the time of passage of the centroid of the tracer pulse through the reach. The reliability of the reported depths cannot be determined because the frequency of cross-sectioning is not reported. DO measurements were made using the Alsterberg modification of the Winkler method.

The paper by Owens and others (1964) contains two sets of data. The first set consists of the 32 k_2 values of Owens and others (1964). Eleven of the k_2 values were corrected for oxygen consumption by the bottom mud, or for oxygen consumption by attached plants. This data set does not include the stream width but this parameter can be calculated. The second data set, consisting of 6 k_2 values, was taken from Gameson and others (1955). In this data set, width values may be calculated from the given discharges, depths, and mean velocities, but the slope is not included. The two data sets are given in tables B-2 and B-3 in appendix B, and the ranges of the variables are given in table 9. The hydraulic parameters would be considered typical for steep, shallow streams.

A summary of the pre-1958 field data is presented by O'Connor and Dobbins (1958). The data consist for the most part of that of Streeter and Phelps (1925) which was screened to minimize the effects of algae and sludge deposits and modified so that the reported depth values approximate the true stream depth rather than the distance above mean low water.

The modified Streeter and Phelps (1925) data must be viewed with some caution because it was obtained from a river in which there was organic pollution and probably phytoplankton, and k_2 values were computed from the Streeter-Phelps form of the DO balance equation which ignores all but the suspended and dissolved BOD oxidation term and the surface reaeration. In many of the test reaches the other terms in the DO balance equation probably would have influenced the calculated k_2 values, had they been available for use in a more general form of the DO balance equation.

The data of Streeter and Phelps (1925) as modified by O'Connor and Dobbins (1958) are reproduced in table B-4, appendix B. The ranges of the variables are given in table 9. The data set is incomplete in that width values are not available. The Streeter-Phelps data typify moderate-sized rivers on gentle slopes. In table B-5 of appendix B are listed data collected by O'Connor and Dobbins from sources other than Streeter and Phelps. Stream width is not included in this data set, nor in three cases, is stream slope. Because the sources of the individual data points vary, the ranges of the variables in this data set have not been included in table 9.

The only reaeration coefficient data for streams that have been determined using the tracer technique is that of Tsivoglou and others (1967, 1968). The data are rather limited in scope because the prime purpose of the study was not k_2 determination, but verification of the measurement technique itself.

In the study of Tsivoglou and others (1967, 1968), the travel time was determined from the time of passage of the dye peak between the sampling stations. The stream was cross-sectioned every 1000 feet, but as Tsivoglou states, "The stream was characterized by a series of riffles and pools and an associated considerable range of velocities and depths.", so the average depth measurements are questionable. The nuclear counting techniques used were highly reproducible and sufficient replications were used so that even at low krypton concentrations, the tracer gas to liquid concentration ratio should have been quite accurate. The tracers were introduced into and sampled from the flow at only one point of the stream cross-sections. In light of the results of Churchill and others (1962), this sampling procedure would seem to be questionable if it is desirable to obtain k_2 values which are representative of the entire cross-section. Despite the questionable sampling technique, the reproducibility of calculated k_2 values was good, with a maximum deviation from the mean of 18 percent and with 9 of 14 values having an average deviation from the mean of less than 10 percent.

The experimental data obtained by Tsivoglou and others (1967, 1968) are listed in table B-6, appendix B. The channel slope is not given, and the width value was obtained by dividing the depth-velocity product into 82.5 cfs, the average discharge for the time period. The ranges of the individual variables are listed in table 9.

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Flume data

In all the laboratory studies reported herein, the flumes used were of the recirculating type and the water in the flume was deaerated with sodium sulfite before the start of the experimental measurements.

The flume used by Thackston (1966) was 60 feet long, two feet wide, and three different bottom roughnesses were used. All DO measurements were by the Azide Winkler method, and the travel time measurements were made by means of dissolved sodium chloride as a tracer. The sampling stations in the flume were 42 feet apart; at each station, 10 samples were taken at 2 minute intervals. With at least two of the bottom roughnesses used, it is possible that an oxygen consuming reaction influenced the calculated reaeration coefficients. See appendix A for a discussion of this problem.

The data of Thackston (1966), also reported by Thackston and Krenkel (1969), are given in table B-7, appendix B. The data set is complete, in that all the mean hydraulic parameters commonly measured are available. The ranges in the values of the variables are listed in table 9.

The flume used by Krenkel (1960) was 60 feet long and one foot wide, with the bottom roughness consisting of expanded metal mesh. In terms of experimental methods and techniques and in terms of quality of measurements, the study was comparable to that of Thackston (1966). Again, there is the possibility that oxidation reactions within the flume channel influenced the calculated reaeration coefficients. See appendix A.

The data of Krenkel (1960), which were also used by Krenkel and Orlob (1963), are given in table B-8, appendix B. Again, all the commonly measured mean hydraulic parameters are listed, so the data set is considered to be complete. The ranges in values of the variables are reported in table 9.

The flume used by Negulescu and Rojanski (1969) was 66 feet long and 0.66 feet wide. It had a 40-foot test section, and the bed roughness consisted of 1 mm sand grains cemented to the flume floor. The DO measurements were made using the Winkler method. A 20-minute measuring period was used, with about 10 samples being collected at each sampling station.

Negulescu and Rojanski (1969) tabulated only 8 of the 18 values they determined. These are listed in table B-9, appendix B. Values for slope and temperature were not included in the original reference, so a temperature of 20°C was assumed. The ranges in values of the variables are listed in table 9.

Evaluation of Reaeration Coefficient Prediction Equations

The conceptual models discussed earlier have, in general, not been carried to the point where they can be used by themselves to predict reaeration coefficients from the mean stream parameters of width, depth, slope, and velocity. The most useful reaeration coefficient prediction equations are, therefore, those obtained from the semi-empirical models. These equations have coefficients derived in some fashion from field data, or derived entirely by least squares regression analysis from field data. Of course, such prediction equations should be used with caution in situations for which the mean stream parameters are outside of the range of data from which the prediction equations were derived.

In this section, we will, for the prediction equations available in the literature, evaluate their performance over the entire range of available data. We will also assess on a common basis the performance of the various equations when applied to the data sets from which the equations were derived.

The basis chosen for comparison of the performance of the various prediction equations is the standard error of estimate. For a prediction equation yielding an estimated $(k_2)_e$ for which the calculated reaeration coefficient is $(k_2)_c$, the standard error of estimate, E_S, is

$$E_S = \sqrt{\frac{\sum\limits_{i=1}^{n} [(k_2)_e - (k_2)_c]_i^2}{n}} \quad , \tag{154}$$

where n is the number of k_2 values used. Another definition of the standard error of estimate which is convenient to use in conjunction with least-squares prediction equations derived from the logarithms of of k_2 is

$$E_{SL} = \sqrt{\frac{\sum\limits_{i=1}^{n} [\log_{10} (k_2)_e - \log_{10} (k_2)_c]_i^2}{n}} \quad . \tag{155}$$

The term E_{SL} can be expressed as a percent error, E_P, defined as

$$E_P = 100 \left[1 - 10^{-E_{SL}} \right] \tag{156}$$

where E_P is the percent standard error of estimate in terms of $(k_2)_e$. The term E_P will always be between 0 and 100 percent. When compared to E_S as a percent, it is a conservative estimate (that is, smaller) of the percent error of the prediction equation. It must be emphasized that E_P is not equal to the percent standard error of estimate that would be calculated from the regression of k_2 (rather than the transformed data $\log k_2$).

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In table 10 are reported the quantities E_S and E_P for 13 of the equations discussed previously. For each of the equations, E_S and E_P

Table 10.--following here

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have been computed--first, for the data sets used by the original authors, and second, for all of the data sets discussed in the previous section which are sufficiently complete for use in the particular equation being evaluated. Table 10 also contains, for both groups of data, the number of data points and the ranges of the individual variables.

On the basis of the percent standard error of estimate, the equations which seem to fit best their original data sets are equation 96 with a standard error of estimate of 15 percent and equation 101 with a standard error of estimate of 25 percent. These equations were presented, respectively, by Krenkel (1960) and Thackston (1966). The relatively good fit of these equations is not surprising, because they were obtained from laboratory studies in which it was possible to obtain much better control of the interfering factors and of the hydraulic variables than it was under the field conditions represented by most of the other equations.

Table 10.--*Performance of k_2 prediction equations in terms of standard error of estimate*

Equation number	Reference	Predicted k_2 days^{-1}	Number data points used in original publication	Derivation data range — k_2 days^{-1} Max.	Min.	U feet per second Max.	Min.	H feet Max.	Min.	S feet per foot Max.	Min.	Standard error of estimate E_S days^{-1}	Standard error of estimate E_P percent	Number data points which can be used	Data range used — k_2 days^{-1} Max.	Min.	U feet per second Max.	Min.	H feet Max.	Min.	S feet per foot Max.	Min.	Standard error of estimate E_S days^{-1}	Standard error of estimate E_P percent
54	O'Connor and Dobbins (1958)	$\dfrac{480\,D_m^{1/2}\,S^{1/4}}{H^{5/4}}$ $(C<17)$	13	2.60	0.14	0.73	0.19	8.60	1.90	1.40×10^{-3}	9.50×10^{-5}	0.34	45	38	82.92	0.14	1.37	0.13	33.69	0.06	2.01×10^{-2}	9.50×10^{-5}	33.7	46
56	O'Connor and Dobbins (1958)	$\dfrac{127\left(D_m\,U\right)^{1/2}}{H^{3/2}}$ $(C>17)$	22	4.8	0.14	4.20	0.53	24.20	0.90	3.60×10^{-3}	2.70×10^{-5}	0.42	44	169	115.3	0.14	5.00	0.24	24.20	0.04	2.40×10^{-2}	2.70×10^{-5}	115.0	71
61	Dobbins (1964b)	$\dfrac{0.12\,B_f\,A\,E^{3/8}\coth\left(\frac{B\,E^{1/8}}{C_4^{1/2}}\right)}{H\,C_4^{3/2}}$	123	115.3	0.14	5.00	0.13	24.20	0.08	2.40×10^{-2}	2.70×10^{-5}	7.74	33	207	115.3	0.14	5.00	0.24	24.20	0.04	2.40×10^{-2}	2.70×10^{-5}	21.0	43
89	Fortescue and Pearson (1967)	$429\left(\dfrac{D_m\,U}{H^3}\right)^{1/2}$	38	4.8	0.02	4.20	0.19	37.00	0.90	----------	----------	2.87	70	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	395.2	86
96	Krenkel (1960)	$24.55\,E^{0.408}\,H^{-0.66}$	58	115.3	10.63	2.14	0.13	0.20	0.08	2.40×10^{-2}	7.50×10^{-4}	7.53	15	207	115.3	0.14	5.00	0.24	24.20	0.04	2.40×10^{-2}	2.70×10^{-5}	16.4	51
101	Thackston (1966)	$18.58\,\dfrac{u_*}{H}$	40	82.93	7.66	2.32	3.65	0.23	0.04	2.04×10^{-2}	6.50×10^{-4}	9.96	25	207	115.3	0.14	5.00	0.24	24.20	0.04	2.40×10^{-2}	2.70×10^{-5}	20.6	45
102	Thackston (1966)	$10.80\left[1+F^{0.5}\right]\dfrac{u_*}{H}$	105	82.93	0.14	5.00	0.19	24.20	0.04	2.04×10^{-2}	2.70×10^{-5}	5.90	37	207	115.3	0.14	5.00	0.24	24.20	0.04	2.40×10^{-2}	2.70×10^{-5}	20.0	45
108	Churchill and others (1962)	$5.026\,U^{0.969}\,H^{-1.673}$	30	5.58	0.22	5.00	1.85	11.41	2.12	2.35×10^{-3}	1.26×10^{-4}	0.52	28	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	140.3	73
109	Owens and others (1964)	$10.90\,U^{0.73}\,H^{-1.75}$	32	49.17	0.31	1.83	0.13	2.44	0.39	----------	----------	5.46	35	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	419.8	84
110	Owens and others (1964)	$9.41\,U^{0.67}\,H^{-1.85}$	68	57.7	0.22	5.00	0.13	11.41	0.34	----------	----------	5.00	32	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	474.9	85
113	Isaacs and Gaudy (1968)	$3.739\,\dfrac{U}{H^{3/2}}$	30	5.56	0.22	5.00	1.85	11.41	2.12	----------	----------	0.55	30	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	55.3	63
114	Isaacs and Gaudy (1968)	$2.440\,\dfrac{U}{H^{3/2}}$	58	115.3	0.11	2.14	0.13	0.20	0.08	----------	----------	10.44	29	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	30.8	65
116	Negulescu and Rojanski (1969)	$4.74\left(\dfrac{U}{H}\right)^{0.85}$	23	18.70	0.65	1.90	0.29	3.11	0.16	----------	----------	1.63	29	239	115.3	0.02	5.00	0.13	37.00	0.04	----------	----------	21.2	61

Again on the basis of the percent standard error of estimate, the equations which best fit the entire range of available data are equation 61 with a standard error of estimate of 43 percent, equations 101 and 102 with standard errors of estimate of 45 percent, and equation 54 with a standard error of estimate of 46 percent. Equation 61, given by Dobbins (1964b), was derived from a consideration of two sets of field data and one set of flume data; equation 101, presented by Thackston (1966) was derived from flume data; equation 102, again from Thackston (1966) was derived from flume data, along with two sets of field data; equation 54, presented by O'Connor and Dobbins (1958) was derived without resorting to any experimental data. As might be expected, two of the best-fit equations were derived from data which covered essentially the same range as the data collected in appendix B.

In the 16th column of table 10 it is seen that five of the equations, when applied to the entire available data range, have standard errors of estimate greater than 100 per day. With the exception of equations 56 and 61, these equations were derived from river data and give much too high k_2 predictions at the shallow depths encountered in the flume studies. This illustrates the caution which must be used when applying k_2 prediction equations to situations in which the mean flow parameters are well outside the range of the data from which the prediction equations were obtained. Further caution is indicated when it is realized that none of the values of E_S listed in column 16 are less than 16 per day, a considerable magnitude when compared with the k_2 values of less than 5 per day usually encountered in natural streams.

The reason for the large E_S values of the 16th column of table 10 is further emphasized by reference to figure 17. In this figure, all the equations of table 10 have been plotted for an assumed slope of 0.0001 feet per foot and a mean velocity of 1.0 fps. The square ruled on the graph delimits the range of experimental data used. At the lower edge of the depth range, there is sometimes more than two orders of

Figure 17.--following here

magnitude difference between a given pair of prediction equations. At the lower depth values, the data fall into a range representative of the lower prediction equations on figure 17, so that large standard errors of estimate would be expected for the prediction equations which yield large k_2 values at shallow depths.

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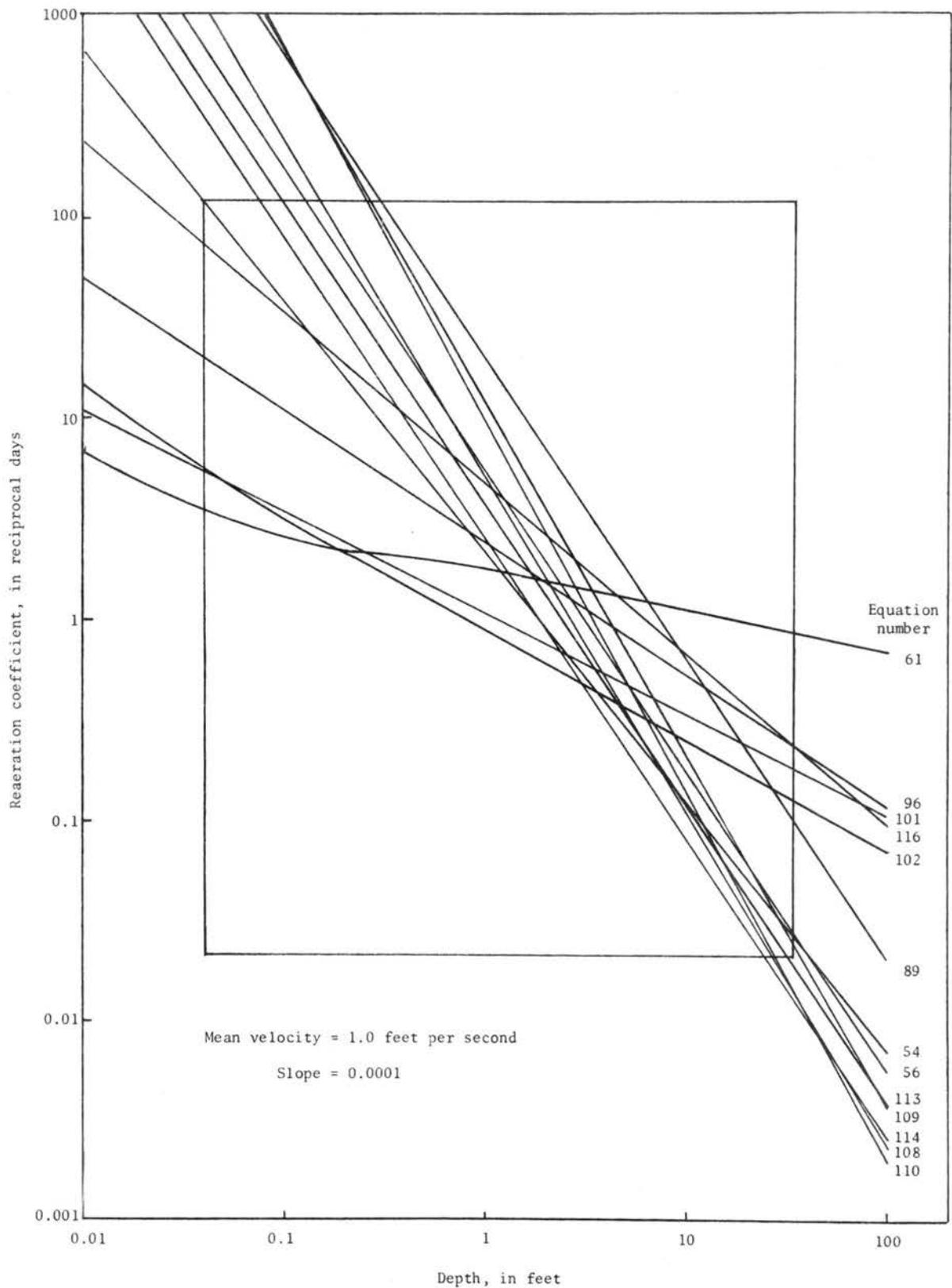
Figure 17.--Reaeration coefficient as a function of depth, from the prediction equations of table 10.

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There are in general two different sets of equations apparent on figure 17--those derived from flume data, which have slopes on the order of -1/2, and those derived from field data, which have slopes on the order of -3/2. It becomes apparent that there is a basic difference between the data sets obtained in the two different situations. If this is so, then the use of equations derived from flume data for the prediction of reaeration coefficients in natural streams is dubious. This matter is discussed further in the following sections.

Development of a Reaeration Coefficient Prediction Equation

As discussed previously, none of the available prediction equations can be considered applicable to the entire range of available data. Assuming the data to be bias-free, there are two possible reasons for this. First, none of the available equations were derived from a wide enough data range, or second, and more likely, there is some basic difference between the two data sets which precludes writing an equation which is applicable to the entire range of data. In this section, these alternatives are investigated using regression analysis procedures. The data used are those discussed previously. The criterion for judging the best equation to use is the standard error of estimate of the prediction equation as obtained from the 62 field and/or 110 flume data sets which contain all the variables U, H, W, and S.

Regression analysis

In general, regression analysis consists of computing the coeffi-
cients for an assumed equation form so that the sum of the squares of
the departures of the experimental data points from the curve given by
the equation is a minimum. For example, if for the data set
$Y_i = G(X_{1i}, X_{2i}, \ldots , X_{ni})$, the linear model

$$Y_{ei} = A_0 + A_1 X_{1i} + A_2 X_{2i} + \ldots + A_n X_{ni} \qquad (157)$$

is used to obtain estimates Y_e of the dependent variable Y, then the A_i,
$i = 0, \ldots n$, are chosen so that the quantity

$$N' E_S^2 = \sum_{i=1}^{N'} [Y_{ei} - Y_i]^2 \qquad (158)$$

is minimized. In equation 158, N' is the number of data sets used.

The best measure of the goodness of fit of a regression equation to a particular data group is the standard error of estimate E_S, as defined by equation 154. A parameter which can be used to determine the relative significance of a particular variable to a given regression equation is the partial correlation coefficient. The partial correlation coefficient is the correlation coefficient between the dependent variable and the chosen independent variable, all other independent variables being held constant. Its value ranges between minus one and plus one, and the larger its magnitude, the more significant is the chosen variable in the regression equation. The standard error of estimate and the partial correlation coefficient are discussed at much greater length in standard statistical methods texts such as Snedecor and Cochran (1967).

The significance of a particular regression coefficient, A_i, may be tested using the fact that the distribution of the quantity

$$R_i = \frac{(A_i - B_i)}{S_{bi}} \tag{159}$$

is "Student"-t distribution with $N' - n$ degrees of freedom. In equation 159, B_i is the population regression coefficient and S_{bi} is the standard error of the regression coefficient A_i. [See Snedecor and Cochran (1967) for more detail.]

In conducting a regression analysis, the limitations of the method must be remembered. First, the model to which the data are fit is preselected so that there is freedom only to adjust the coefficients in the model. If the model is incomplete, a particular variable may appear to be of negligible significance, when in reality it may be highly significant. On the other hand, even though the model is incomplete, prediction equations might be obtained which are entirely satisfactory within the range of data used in deriving them. These equations could, however, yield highly erroneous predictions if applied outside the data range. Second, even though the model is correct, the prediction equation will be incorrect if the data are incorrect or incomplete. Finally, in a regression analysis there are two types of significance which must be considered--physical and statistical. For example, a variable may be highly significant in the physical process yet have little significance in the regression equation because the range of this particular variable was not wide enough in the data group chosen. Furthermore, it is possible to have a high statistical significance in the regression equation and yet to have assumed the wrong physical relation for that particular variable in the model. For these reasons, it is best before beginning a regression analysis to have a reliable physical model available. Unfortunately, as will be emphasized later, there are no such models presently available for the reaeration coefficient in terms of the mean values of the flow parameters which will accurately predict reaeration coefficients for the entire range of available data.

In this report, most of the regression analyses were performed using a general linear model and the logarithms of individual variables. The general model assumed was

$$\log_{10} k_2 = \log_{10} A_0 + A_1 \log_{10} H + A_2 \log_{10} U$$
$$+ A_3 \log_{10} W + A_4 \log_{10} S \qquad (160)$$

which is more commonly expressed

$$k_2 = A_0 H^{A_1} U^{A_2} W^{A_3} S^{A_4} \quad . \qquad (161)$$

In several cases, one or more of the A_i were assumed to be zero and the effect on the standard error of estimate of the prediction equation was investigated. The coefficients were computed using the regression program BMD03R of the University of California, Los Angeles, Health Sciences Computing Facility (Dixon, 1965).

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The results of a linear least squares regression analysis on an equation of the form of 160 are generally slightly different than the results of a least squares regression analysis of an equation in the form of equation 161, because the distribution of the variance of the logarithms of k_2 from equation 160 will be different from the distribution of the variance of k_2 from equation 161. If the analysis is conducted on an equation of the form of 160 and the result is converted to the form of equation 161, the average width of the scatter band about the prediction equation will increase directly in proportion with k_2, whereas if the analysis is conducted directly using equation 161, the scatter band width will be a constant, independent of k_2. In this study, it was decided to use an equation of the type of 160 and to accept deviation from the pure least squares regression analysis procedures because of the relative simplicity of the analytical procedures involved in this type of analysis as compared to a least squares analysis based on equation 161.

A prediction equation of the type of equation 161 was chosen for comparison primarily because this type of k_2 prediction equation has been used frequently in the past. Furthermore, most of the conceptual models available can be reduced, at least for natural streams, to this type of equation. A number of equations of different forms from equation 161 were tried with negligible success in reducing the standard error of estimate.

Results of regression analysis

The available experimental data may be divided into two general groups--first, the data collected in natural streams, and second, the data collected in laboratory flumes. Basic data groups used in the analysis were the data sets for which all of the variables k_2, H, U, W, and S were available. These consisted of the 62 field data sets from Churchill and others (1962) and Owens and others (1964) and the 110 flume data sets from Krenkel (1960) and Thackston (1966). Regression analyses were performed separately and jointly on the two groups of data. Partial results of these regression analyses are listed in table 11.

Table 11.--following here

Table 11 lists several comparable equations obtained from regression analyses of the field and flume data. The flow depth, H, and hydraulic radius, R_H, were used in the field and flume cases, respectively, because in each case this particular variable resulted in a slightly lower standard error of estimate. To show the importance of each of the variables in the various prediction equations, the partial correlation coefficients are given in table 11. The standard error of estimate has been listed both in terms of logarithms and in terms of percent of the predicted k_2 value.

Table 11.--*Results from regression analysis*

	Field								Flume							
Equation $k_2 =$	Partial correlation coefficient					Standard error of estimate		Equation $k_2 =$	Partial correlation coefficient					Standard error of estimate	
	H	U	W	R_H	S	E_{SL}	E_P percent		H	U	W	R_H	S	E_{SL}	E_P percent
$59.40\ \dfrac{U^{0.462}\ S^{0.260}}{H^{1.326}\ W^{0.094}}$	-0.646	0.434	-0.137	------	0.300	0.16388	31.5	$157.20\ \dfrac{U^{0.132}\ S^{0.496}}{R_H^{0.586}\ W^{0.746}}$	------	0.205	-0.770	-0.584	0.816	0.08709	18.2
$36.75\ \dfrac{U^{0.481}\ S^{0.250}}{R_H^{1.413}\ W^{0.029}}$	------	0.437	-0.040	-0.637	0.282	0.16545	31.8	$214.20\ \dfrac{U^{0.130}\ S^{0.494}}{H^{0.497}\ W^{0.825}}$	-0.574	0.201	-0.777	------	0.811	0.08786	18.4
$46.05\ \dfrac{U^{0.413}\ S^{0.273}}{H^{1.408}}$	-0.693	0.418	------	------	0.313	0.16400	31.5	$524.50\ \dfrac{S^{0.650}}{U^{0.126}\ R_H^{0.296}}$	------	-0.135	------	-0.236	0.785	0.13582	26.9
$9.59\ \dfrac{U^{0.674}}{H^{1.865}}$	-0.966	0.832	------	------	-----	0.17120	32.6	$6.24\ \dfrac{U^{0.719}}{R_H^{0.800}}$	------	0.571	------	-0.395	-----	0.21813	39.5
$306.50\ \dfrac{S^{0.608}}{H^{0.783}}$	-0.795	-----	------	------	0.815	0.17895	33.9	$295.30\ \dfrac{S^{0.600}}{R_H^{0.364}}$	------	-----	------	-0.308	0.858	0.13643	27.0
$14.47\ \dfrac{U^{0.721}}{H^{1.735}\ W^{0.118}}$	-0.883	0.809	-0.164	------	-----	0.17033	32.5	$5.00\ \dfrac{U^{0.800}}{R_H^{1.042}\ W^{1.063}}$	------	0.747	-0.730	-0.628	-----	0.14989	29.3
$266.50\ \dfrac{S^{0.600}\ W^{0.028}}{H^{0.829}}$	-0.535	-----	0.039	------	0.783	0.18034	34.0	$245.70\ \dfrac{S^{0.552}}{R_H^{0.506}\ W^{0.702}}$	------	-----	-0.763	-0.566	0.920	0.08857	18.5

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From an analysis of the results presented in table 11, it can be shown that all the prediction equations obtained from the flume data sets are significantly different statistically from the corresponding prediction equations obtained for the field data sets. For example, on comparison of the exponents in the first equation in column nine to those in the second equation in column one, for the variables U, W, R_H, and S, the "Student"-t values (see equation 159) are -5.70, -11.88, 10.42, and 7.18. For 106 degrees of freedom, these values indicate that the exponents in the two equations are different at a significance level less than 0.005. For the fifth equation in column nine and its counterpart for the field case $\left(k_2 = 317.2 \, \dfrac{S^{0.624}}{R_H^{0.750}} \right)$, the "Student"-$t$ values on S and R_H are -0.69 and 3.56. Thus, the exponents on R_H are significantly different at some level less than 0.005, while those on S are different at the 0.25 level. Similar results are obtained for the other equation forms listed. It must be concluded that all the k_2 prediction equations obtained from flume data are significantly different statistically from those obtained from field data.

The difference between the regression equations from the two groups of data is further illustrated in the standard error of estimate. For example, omitting W from the flume prediction equation of column nine, table 11, causes an increase in the standard error of estimate of 8.7 percent, while there is no noticeable effect when this parameter is omitted from the first equation in column one. Furthermore, the largest standard error of estimate occurs for the field equations when the mean velocity, U, is omitted, and for the flume equations when the slope, S, is omitted.

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Finally, the partial correlation coefficients listed in table 11 also indicate a difference between field and flume prediction equations. The field equations have partial correlation coefficients decreasing in the order of H, U, S, and W, with the coefficient for W negligible. On the other hand, the flume equations have partial correlation coefficients decreasing in the order of S, W, R_H, and U.

If a regression analysis is performed on all of the data used in preparing table 11, the resulting prediction equation is

$$k_2 = 721 \frac{S^{0.681}}{U^{0.064} \ W^{0.183} \ R_H^{0.268}} \ , \tag{162}$$

which has a standard error of estimate of logarithms of k_2 of 0.15572 which is equivalent to 30.1 percent. Results of "Student"-t tests comparing the exponents of the variables in equation 162 to the exponents in the two corresponding equations of table 11 are given in table 12.

Table 12.--following here

From table 12, it must be concluded that equation 162 is significantly different at some level less than the 0.005 level from both the corresponding flume and field k_2 prediction equations of table 11. Not only are the flume and field prediction equations significantly different from each other, but also the equation using the combined data is different from both of them.

Table 12.--*Values of "Student"-t for comparison of the exponents in equation 162 to those for the two corresponding field and flume equations of table 12*

Variable	"Student"-t Values	
	Field	Flume
U	-11.49	- 4.06
W	- 3.04	11.12
R_H	16.50	4.58
S	12.00	5.15

Discrepancies similar to those pointed out here between field and flume k_2 prediction equations have been observed in other areas of hydraulic engineering research. For example, in the field of alluvial boundary hydraulics, Maddock (1969) concluded that

"The variability of natural channels cannot be studied in flumes because of constraints placed upon the possible combinations of width, depth, velocity, slope, and load that are inherent in field operations.",

while Colby (1964) stated that

"Flume investigations can provide much helpful information on sediment transportation; but, until scale effects are understood more completely, flume investigations of the discharge of sands are not model studies of the discharge of sands in field streams."

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As another example of the apparent difference between field and flume phenomena, it was attempted to relate to the form of k_2 regression equations the form of the regression equations for the turbulent intensity at one-tenth the flow depth below the water surface. The turbulent intensity, u', is the root-mean-square of the deviations of the velocity fluctuations at a point around the mean value of the velocity at the point. It is equal to the square-root of twice the kinetic energy per unit of mass of the fluid turbulence at the point and thus the near-surface value of u' might reasonably be expected to be related to the reaeration coefficient.

The results of the regression analysis of data obtained from R. S. McQuivey (personal communication, 1970) are listed in table 13. A general model analogous to equation 161 was assumed for the turbulent intensity. Because simultaneous k_2 and u' measurements are not available, it is impossible to arrive at any conclusions about the functional relation, if any, between k_2 and u'.

Table 13.--following here

Table 13.--*Dependence of turbulent intensity on the mean hydraulic parameters*

Equation $u' =$	Partial correlation coefficients					E_{SL}	Number data points	Type of data
	H	U	W	R_H	S			
$0.667 \dfrac{U^{0.121} W^{0.439} S^{0.399}}{H^{0.068}}$	-0.045	0.085	0.302	-----	0.560	0.115	20	flume, rigid
$3.161 \dfrac{H^{0.396} S^{0.503}}{U^{0.090}}$	0.779	-0.068	-----	-----	0.700	0.117	------	flume, rigid
$1.303 \dfrac{U^{0.143} W^{0.798} S^{0.544}}{H^{0.541}}$	-0.390	0.121	0.527	-----	0.590	0.146	------	flume, alluvial
$0.890\, H^{0.158} U^{0.422} S^{0.313}$	0.219	0.315	-----	-----	0.381	0.168	------	flume, alluvial
$23.750\, H^{0.049} U^{0.764} W^{0.757} S^{1.183}$	0.234	0.718	0.490	-----	0.516	0.087	43	field
$0.121\, H^{0.042} U^{1.059} S^{0.090}$	0.176	0.871	-----	-----	0.271	0.098	------	field

On the other hand, in terms of the dependence of u' on S and U, the results of this study are similar to the reaeration study results in that the flume prediction equations show the highest partial correlation with S while the field equations show the highest partial correlation with U. However, the results of this study differ from the results of the reaeration study in that the dependency of u' on W is significant both in the flume and in the field. The results of the "Student"-t tests comparing the exponents on the variables in the two flume situations to those of the field situation of table 13 are listed in table 14. These "Student"-t values show that at least one exponent in each flume equation differs from the corresponding exponent in the field equation at significance levels less than 0.005. It must be concluded that the flume regression equations for the turbulent intensity at one-tenth the flow depth below the water surface are significantly different from the field equation.

Table 14.--following here

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Table 14.--*Results of the "Student"-t test of the exponents in the flume equations and in the field equations of table 13*

Equation	"Student"-t			
	H	U	W	S
Flume, rigid	-0.30	-1.75	-0.89	-5.16
Flume, rigid	0.79	-2.33	----	1.54
Flume, alluvial	-2.13	-2.50	0.15	-4.02
Flume, alluvial	0.79	-2.33	----	1.54

As a final example of the difference between regression equations for flume and field data, consider equations for predicting mean velocity from W, H, and S obtained from the same data as the k_2 prediction equations of table 11. These equations along with the partial correlation coefficients and the standard errors of estimate are listed in table 15.

Table 15.--following here

The partial correlation coefficients and the small change in standard error of estimate on omitting W from the equations indicate considerably less dependency of U than k_2 on this parameter. The partial correlation coefficients further indicate that U in the flume is less dependent on depth than in the field. The difference between the two equations is, however, best illustrated by the "Student"-t test. Comparing the exponents of the third equation to those of the first in column one of table 15, the "Student"-t values for W, R_H, and S are 1.65, -5.02, and -9.94, while for the second and fourth equations, for R_H and S, the "Student"-t values are -8.05 and -10.58. This indicates the two equations are different at some significance level less than 0.005.

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Table 15.--*Prediction equations for mean velocity,
obtained from the data used in table 11*

Equation $U =$	Partial correlation coefficients			E_{SL}	E_P percent	Type of data
	W	R_H	S			
$37.55\ W^{0.187}\ R_H^{1.168}\ S^{0.742}$	0.256	0.676	0.861	0.166	31.8	field
$98.80\ R_H^{1.474}\ S^{0.794}$	-----	0.937	0.891	0.170	32.4	field
$29.82\ W^{0.335}\ R_H^{0.608}\ S^{0.423}$	0.340	0.468	0.755	0.138	27.3	flume
$25.20\ R_H^{0.540}\ S^{0.400}$	-----	0.409	0.721	0.146	28.6	flume

Possible reasons for the difference between the regression equations for flume and field reaeration coefficient data are: (1) differences in the basic physical processes, or misinterpretation of them; (2) statistical quirks; and (3) deficiencies or bias in the available data.

Possible physical differences between the two systems are easy to visualize. For example, the straight-uniform flume flow may have entirely different turbulent transfer properties than the tortuous, non-uniform field stream flows. R. S. McQuivey (personal communication, 1970) indicates that the turbulence profile in a 200-foot long by 8-foot wide flume at depths on the order of one foot does not fully develop at any point in the flume. This indicates some question about the similarity between the turbulent transfer properties near the surface of field and flume flows. In addition, the high partial correlation coefficient between k_2 and W in the flume as compared to u' and U indicates a possible secondary circulation effect on k_2 which is not present in the other phenomena. If such an effect is present, it may not be possible to account for it with simple W/H scaling. As a further example, the comments of Maddock (1969) and Colby (1964) quoted previously could be applied equally as well to reaeration as to sediment transport. That is, the different constraints on the two physical systems might prevent similar mass transfer regimes from developing at the water surface. Finally, the difference between the two sets of equations may be due to a basic misunderstanding of the turbulent mass transfer process near the surface--that is, due to a lack of knowledge of the pertinent scaling parameters, or to the fact that the correct parameters have not been measured.

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There are certain quirks inherent in regression analysis which might cause field and flume regression equations for k_2 to differ. In the first place, the differences in the two systems cause the experimental variables to be selected differently--that is, in the flume slope and discharge vary and determine velocity, whereas in the field depth and discharge vary to determine velocity. This difference in selection of "independent" variables for analysis can be reflected in the regression equations, as can the differences in the adjustments of the so-called independent variables to each other. In the second place, if there is not available a wide enough range of data for each of the independent variables, the significance of the variable may be missed in the regression analysis, or the variable may be represented incorrectly in the regression equation. In this sense, dependency of the flume equations on W is particularly questionable because only two values were available in the literature.

Lastly, if the form of the regression equation chosen is incorrect the equations for the two systems of different scale might be expected to differ radically. This is, in a different sense, a statement of the scaling problem mentioned above.

Finally, no regression equation is better than the data used in its derivation, because if the data contain errors or bias, this will be reflected in the prediction equations. In the field data, especially, the accuracy of the data can be questioned. This is due first to the fact that in none of the studies reported, except possibly that of Churchill and others (1962), have sedimentation, bottom deposits, and photosynthesis been accounted for adequately. In the two sets of flume data, it is felt that there is a possibility of one or both of the data sets being influenced by an oxygen consuming reaction in the flume channel. This would have a tendency to bias the resulting data. (See appendix A.)

It is of interest to compare the equation obtained from the regression analysis of all the field data with those available in the literature. The "Student"-t test was used to compare exponents on various variables of the equations in table 11 with the corresponding exponents from the equations in the literature, and the results are presented in table 16. From table 16 it is seen that all but the two equations of

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Table 16.--following here

Owens and others (1964) have at least one exponent which differs from the exponent in the corresponding field equation at a level less than the 0.005 significance level. Because the second equation of Owens and others (1964) was derived, with the exception of the 6 data sets of Gameson and others (1955), from the same data as the corresponding field regression equation, it is not surprising that the equations do not differ significantly. With the exception of this equation, and the possible exception of the first equation of Owens and others (1964), all the equations of table 16 differ significantly from the corresponding equations derived in this study from the field data.

Table 16.--*Results of the "Student"-t test of exponents in the regression equations of this study and corresponding equations in the literature*

Regression equations (this study) $k_2 =$	Comparable equations in the literature $k_2 =$	"Student"-$t_{0.005}$			E_P percent	Source
		H	U	S		
$46.05 \dfrac{U^{0.413} S^{0.273}}{H^{1.408}}$	$24.55\ (U\,S\,g)^{0.408}\ H^{-0.66}$ $(T=20°C)$	-3.89	0.04	-1.24	31.5	Krenkel (1960)
	$127\ D_m^{1/2}\left(\dfrac{U}{H^3}\right)^{1/2}$ [4/] (Chezy $C > 17$)	-5.60	2.98	-----	32.6	O'Connor and Dobbins (1958)
	$5.026\ U^{0.969}\ H^{-1.673}$ $(T=20°C)$	-2.95	-5.04	-----	----	Churchill and others (1962)
$9.59 \dfrac{U^{0.674}}{H^{1.865}}$	$10.90\ U^{0.73}\ H^{-1.75}$ $(T=20°C)$	-1.77	-0.96	-----	----	Owens and others (1964)
	$9.41\ U^{0.67}\ H^{-1.85}$ $(T=20°C)$	-0.23	-0.07	-----	----	Owens and others (1964)
	$4.74\left(\dfrac{U}{H}\right)^{0.85}$	-15.58	-3.01	-----	----	Negulescu and Rojanski (1969)
$306.50 \dfrac{S^{0.608}}{H^{0.783}}$	$4.80\ D_m^{1/2}\left(\dfrac{S}{H^5}\right)^{1/4}$ (Chezy $C < 17$)	-6.00	-----	6.35	33.9	O'Connor and Dobbins (1958)
	$18.58\ \sqrt{g}\left(\dfrac{S}{H}\right)^{1/2}$	-3.64	-----	1.92	----	Thackston (1966)

[4/] Equations due to Fortescue and Pearson (1967) and Isaacs and Gaudy (1968) are also of this form.

The previous discussion suggests at least two reasons for pursuing the search for a new physical model describing reaeration. The first is the difference observed between the regression equations for the field and flume situations. It would seem that equations describing the physical process of reaeration should be applicable no matter what the scale of the system. The second is the fact that none of the available theoretical models can be related to the regression equation for field data. This is because either the theoretical model is not expressed in terms of the mean hydraulic parameters, or because for the ones which are expressed in this fashion, it has been shown that the exponents in the field regression equation differ significantly from those in the theoretical models. Furthermore, it is possible that the commonly measured mean hydraulic parameters U, H, W, and S are not sufficient to model the phenomenon. It may be that it will be necessary to measure some other parameters such as those characteristic of the near-surface turbulence, or of the velocity in the air above the flow.

Using all the available data and using the standard error of estimate of logarithms as the basis for judgment, it is seen from table 11 that the best prediction equation for reaeration coefficients of natural streams is

$$k_2 = 46.05 \ \frac{U^{0.413} \ S^{0.273}}{H^{1.408}} \ . \tag{163}$$

However, considering the percent variation (table 11), it is seen that the equation

$$k_2 = 9.59 \ \frac{U^{0.674}}{H^{1.865}} \tag{164}$$

has a percent variation only 1.1 percent greater than does equation 163. Considering the difficulty and expense of measuring accurately the slope of a field stream (Yao, 1969), an equation that does not contain the slope is preferred for routine use as a prediction equation for k_2 in natural streams.

In appendix B, it is seen that in addition to the field data used in deriving equation 164, there are other field data which report only U and H. From the 121 sets of field data which contain U and H, the least squares regression equation for k_2 is

$$k_2 = 8.76 \, \frac{U^{0.607}}{H^{1.689}} \quad .$$ (165)

Equation 165 has a standard error of estimate of logs of 0.203 (37.5 percent). The "Student"-t test was used to compare the exponents on U and H; comparing equation 165 to equation 164 (119 degrees of freedom), for U and H, the "Student"-t values are -1.42 and 4.22, while comparing equation 164 to 165 (60 degrees of freedom) gives "Student"-t values of 1.14 and -2.70. Thus equations 164 and 165 have one exponent which differs from its counterpart at a significance level less than 0.005. The standard error of estimate of equation 165 has increased markedly over that of 164. This is probably due to a decrease in overall quality of the data. However, because equation 165 is based on the widest range of field data presently available, it is felt that this equation is the best available for prediction of reaeration coefficients for natural streams.

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EFFECT OF DETERGENTS AND WIND ON THE REAERATION COEFFICIENT

Up to this point, the reaeration process has been considered as occurring under ideal conditions, that is, in relatively pure water with no wind effects. There is evidence in the literature, however, that the presence of sewage and surfactants in the water tends to reduce K_L, the liquid-film coefficient for gas transfer, compared with the pure-water value, whereas winds tend to increase K_L with respect to the value existing for quiescent air conditions. Recall that $K_L = K_2 H$ where K_2 is the reaeration coefficient and H is the mean depth of flow. The results of some of these studies are summarized in the following paragraphs.

Mancy and Okun (1965) discussed two theories concerning the effect of surfactants on the rate of oxygen absorption. On the one hand, they cite four references suggesting that surfactants reduce the absorption rate only by decreasing the hydrodynamic activity at the interface. On the other hand, they cite six references suggesting that surfactants reduce the absorption rate both by increasing the diffusional resistance at the interface and by decreasing the hydrodynamic activity at the interface.

Eckenfelder, Raymond, and Lauria (1956) hypothesize that surfactants would reduce K_L in two ways--first, by increasing the diffusional resistance through a reduction in the surface tension, and second, by decreasing the surface renewal rate through an increase in viscosity. Metzger (1968) studied the absorption of helium and nitrogen under identical mixing conditions in a stirred tank containing 0.5 mg/ℓ of ABS (alkyl benzene sulfonate), a surfactant. He found that the film thickness and surface-renewal parameters of the Dobbins (1956) film-penetration model were larger and smaller, respectively, than the values obtained for the same mixing conditions with distilled water. Downing, Melbourne, and Bruce (1957) studied the effects of household detergents and sewage on oxygen absorption in a stirred tank and in a wave tank. They found that mixed household detergents reduced K_L from the clean-water value by various amounts depending on the concentration of detergent, the initial K_L value, and the way in which the water was agitated. The effects of sewage effluents and settled sewage containing detergents were similar to the effects observed for mixed detergents but the effects of sewage effluents and settled sewage were less when the detergents were not present.

Gameson, Truesdale, and Varley (1956) studied the effect of about 1 mg/ℓ ABS on oxygen absorption by flowing water in a laboratory open channel. They found that the percent reduction in K_L depended on the degree of turbulence, expressed in terms of K_L. The maximum reduction occurred for intermediate K_L values, equivalent to those of lowland English streams. Lower and higher turbulence conditions resulted in smaller percent reductions. Similarly Metzger (1968) and Mancy and Okun (1965) found in stirred-tank studies that the largest reduction in K_L occurred for intermediate mixing intensities.

Gameson, Truesdale, and Downing (1955) added detergents to a small English stream and found that there was no apparent relation between the reduction in K_L and the detergent concentration, in the range from 0.5 to 2 mg/ℓ. The reduction in K_L decreased with increasing K_L for values ranging from about 30 to 120 cm/hr (centimeters per hour). No maximum was observed in the natural streams, apparently because K_L values were all larger than 5 to 10 cm/hr at which the maximum reduction occurred in the laboratory studies.

Ogden, Gibbs, and Gameson (1959) studied the effect of salinity and the combined effect of salinity, detergents, and sewage on the reaeration rate of flowing water in a flume. They found that the percent reduction in K_L was equal to six times the square root of the salinity expressed as grams of salt per 1000 grams of mixture, but that the reductions caused by detergents and sewage did not appear to depend on the presence of salts in the water. Kehr (1938) studied the effect of sewage on reaeration in a laboratory flume and found that the percent reduction increased with the percent of sewage and the flow velocity, however, the maximum velocity considered was only about 0.5 fps.

Lynch and Sawyer (1954) studied the effect on oxygen absorption of 11 synthetic detergents available on the market in 1954. They found with one exception that all reduced the oxygen transfer coefficient, and they pointed out that because these detergents were not bio-degradable, they eventually entered the streams and rivers where they could significantly reduce the reaeration coefficients. However, since 1954, bio-degradable detergents have been developed and these should reduce the effect that detergents have on reaeration coefficients.

Downing and Truesdale (1955) studied the effect of oil films on oxygen absorption in a stirred tank. They found no significant effect until the film thickness exceeded 10^{-4} cm. Thus they concluded that oil films were not a problem because films thicker than 10^{-4} cm were not likely to persist very long in natural streams.

Poon and Campbell (1967) found that the presence of small ccncentrations of biologically inert suspended particles increased the rate of oxygen absorption in an aerator. This is in agreement with the observation of R. S. McQuivey (personal communication, 1970) that suspended sediment increases the intensity of turbulence over that observed in a clear water flow.

Whereas surfactants and sewage generally reduce K_L, the presence of winds and surface disturbances produced by the winds generally increase K_L. Imhoff and Fair (1956, p. 291) discuss wind effects in general terms. They suggested that winds passing over the water surface may double the absorption rate, that wind-induced waves may increase the absorption rate ten times, and whitecaps may, by droplet aeration, increase it 100 times.

Eloubaidy (1969) studied reaeration both with and without wind waves in a laboratory wind-water tunnel. He concluded that the absorption rate was significantly increased when waves developed on the water surface and this increase was considerably more than could be accounted for by the increase in surface area. He presented a prediction equation containing the shear velocity, the kinematic viscosity, and the wind velocity. This equation, however, was verified only with a very limited amount of data.

Downing and Truesdale (1955) studied the effect of surface wind on oxygen absorption in a laboratory ripple tank. They found that there was little change in K_L until a wind velocity between 3.0 and 3.5 meters per second was reached. For larger velocities, K_L increased rapidly. Similar results were obtained in tank experiments by Kanwisher (1963) who found little change in the gas exchange coefficient up to a velocity of about 3 meters per second but a coefficient that increased approximately as the square of the velocity for wind velocities between 3 and 10 meters per second. Downing and Truesdale (1955) also studied the effect of wave height and frequency on K_L. They found that the rate of absorption of oxygen increased almost linearly with increase in wave height, increasing approximately four fold for a four-fold increase in height. For irregular choppy waves of the same frequency, K_L increased less rapidly. They also found that K_L increased with an increase in the frequency of the waves, although there was more scatter in the results. Finally, Juliano (1969) found that absorption rate constants measured in the Sacramento-San Joaquin estuary system varied directly with wind velocity. There was considerable scatter in the relation, however, this was attributed to the fact that wind effects vary greatly from point-to-point in the reach of interest.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From the review of reaeration in open-channel flow presented in previous sections, we have arrived at several general conclusions.

1. The approximations that can be made in the general DO balance equation (see pages 95-127, 147-172) vary radically from situation to situation. Therefore, careful consideration of all the circumstances must be made before any terms of the equation are disregarded.

2. The most general and realistic conceptual model for the reaeration process of open-channel flows is the surface renewal-damped eddy diffusivity model of King (1966). This model merits further development in relating its parameters to the mean flow parameters that are easily measured.

3. In theory, the tracer technique is far superior to the other two techniques commonly used for determining the reaeration coefficient of open-channel flows. In practice, however, the use of radioactive tracers involves problems from the standpoint of obtaining permission for use in natural streams, and from the standpoint of possible hazard to the personnel involved in the study.

4. Sensitivity analysis of the DO balance technique shows that if photosynthetic production is present, its neglect is probably the most serious source of error in the calculation of the reaeration coefficient. Following this in decreasing order of effect are errors in the upstream and downstream DO deficit, k_1, and L_a.

5. Sensitivity analysis of the disturbed equilibrium technique shows that in decreasing order of effect on the calculated k_2, are errors in the downstream DO deficit, net photosynthetic production, upstream DO deficit, and time of travel.

6. The expected root-mean-square error of 15 percent for the tracer technique is much less than the 65 percent error expected from the DO balance technique and the 115 percent error expected from the disturbed equilibrium technique. Thus it would seem well worthwhile to expend further time and effort on developing the tracer technique for use in streams of all sizes.

7. The best available reaeration coefficient data for natural streams is that of Churchill and others (1962). With this data and that of Owens and others (1964), there are 62 field data sets that can be considered complete; that is, they contain all the mean hydraulic parameters commonly measured: velocity, depth, width, and slope.

8. Analysis of available reaeration coefficient data from natural streams and from laboratory flumes indicates that there is a significant difference between the k_2 regression equations obtained from the two groups of data. The most likely reasons for this are (a) an inability to scale correctly the turbulent mass-transfer process at the water surface, (b) statistical quirks involved in regression analysis using the complexly interdependent hydraulic parameters of mean velocity, depth, width, and slope, and (c) experimental bias in one or more of the individual groups of data.

9. For the prediction of k_2 in natural streams, regression analysis indicates that the equation with the smallest standard error of estimate consistent with the ease of obtaining the mean flow parameters is $k_2 = 8.76 \dfrac{U^{0.607}}{H^{1.689}}$, where k_2 is in days^{-1}.

Recommendations

It is evident that a more detailed and reliable theoretical model than is presently available for the transfer of oxygen through the surface of an open-channel flow is needed. The model should account for the effect of impurities in the flow such as sewage, sediment, dissolved solids, and surfactants. It should consider the effect of wind blowing over the water surface, and it should be related directly to hydraulic parameters such as mean velocity, depth, width, slope, and possibly near-surface vertical and/or longitudinal turbulence. The model should, furthermore, scale the interface mass-transfer phenomenon so that field and flume-scale data fit one general equation. This would make possible (with adequate independent verification of the equation) the use of experimental results from laboratory flumes to predict field-scale reaeration coefficients.

For verification of the model in large-scale field streams in which some degree of pollution, photosynthesis, and other interferences may be present, or for obtaining more reliable k_2 values than are presently available, the tracer technique should be modified to avoid the use of the radioactive tracers. This could be done, for example, by using the fluorescent dye as the conservative tracer and gas chromatography for determining the concentration of some inert tracer gas.

If the DO balance technique and the disturbed equilibrium technique are to be used for calculating reaeration coefficients, then conclusions 4 and 5 above indicate that better methods must be found for accounting for photosynthetic production and for the respiration of the suspended and attached aquatic plants. In fact, all of the source-sink terms should be more carefully considered in reaeration coefficient studies than they are presently.

There are other factors concerning DO in streams which require immediate consideration. For example, consider the lateral distribution of DO in a stream cross-section. The measurements of Churchill and others (1962) indicate quite large DO variations in a stream cross-section. The implications of this observation in terms of average DO transferred into the stream and in terms of the cross-section variation of the surface mass transfer coefficient are quite important. A further field for study in terms of lateral DO distribution might be a study of the effect of sewage outfall placement on dispersion, or concentration of pollution by the stream.

There is also further need for study of the probabilistic behavior of DO variations at a particular cross-section. These studies should be aimed at determining the hazard level associated with a particular pollution input at some point upstream of the cross-section of interest.

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APPENDIX A

Effect of a Corrosion Reaction on Reaeration Coefficient

Measurements in a Laboratory Flume

Effect of a Corrosion Reaction on Reaeration Coefficient
Measurements in a Laboratory Flume[1]

A recirculating flume system generally consists of a headbox, a
section of open channel, a tailbox, and a closed return flow conduit.
The system may be conceptualized as a flow loop consisting of an open
channel and a pipe in series. If first order oxidation reactions
proceed in the channel and in the return pipe simultaneously with reaera-
tion in the channel, the characteristic differential equations are:

channel $\quad \dfrac{\partial D_1}{\partial t} + U_1 \dfrac{\partial D_1}{\partial x_1} = - K_2 \, D_1 + b_1 \, C_1 \qquad\qquad$ (A-1)

pipe $\quad \dfrac{\partial D_2}{\partial t} + U_2 \dfrac{\partial D_2}{\partial x_2} = b_2 \, C_2 \qquad\qquad$ (A-2)

where b is the first order rate constant for the oxidation reaction, D
is the dissolved oxygen deficit, C is the dissolved oxygen concentration,
K_2 is the reaeration coefficient, U is the mean water velocity, t is
time, x is longitudinal position, and the 1 and 2 subscripts refer to
the channel and pipe, respectively. These equations assume that the
only source of oxygen is reaeration, the only sink is the oxidation
reaction, and longitudinal dispersion effects are negligible. The
oxidation reaction is assumed to follow the basic law of chemical
kinetics for a first order heterogeneous reaction, that is, the rate of
reaction is proportional to the concentration of the reactant, the
dissolved oxygen.

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[1] Symbols used in Appendix A are given in a list at the end of the appendix.

Note that $D_1 = D_1(x_1,t)$ and $D_2 = D_2(x_2,t)$ and also that $x_1=0$, $x_2=L_2$ designates the beginning of the channel and $x_1=L_1$, $x_2=0$ the end of the channel. The initial and final conditions in the system are:

$$D_1(0,0) = D_2(L_2,0) = D_0 \tag{A-3}$$

$$D_1(0,\infty) = D_2(L_2,\infty) = D_\infty \tag{A-4}$$

where L_2 is the length of the pipe. The solutions to equations A-1 and A-2 (derived by the authors) under these conditions are:

$$D_1(x_1,t) = \frac{b_1 \, C_s}{K_2+b_1} \left[1 - e^{-\frac{(K_2+b_1)\, x_1}{U_1}} \right] + (D_0-D_\infty) \, e^{-\alpha t} \, e^{-(K_2+b_1-\alpha)\frac{x_1}{U_1}}$$

$$+ \, D_\infty \, e^{-\frac{(K_2+b_1)\, x_1}{U_1}} \tag{A-5}$$

and

$$D_2(x_2,t) = C_s \left[1 - e^{-\frac{b_2(x_2-L_2)}{U_2}} \right]$$

$$+ (D_0-D_\infty) \, e^{-\alpha t} \, e^{-\frac{(b_2-\alpha)(x_2-L_2)}{U_2}} + D_\infty \, e^{-\frac{b_2}{U_2}(x_2-L_2)} \tag{A-6}$$

where from

$$D_1(L_1,\infty) = D_2(0,\infty) \tag{A-7}$$

and

$$D_1(L_1,0) = D_2(0,0) \tag{A-8}$$

$$D_\infty = \frac{C_s\left[\left(1 - e^{+\frac{b_2\,L_2}{U_2}}\right) - \frac{b_1}{K_2+b_1}\left(1 - e^{-(K_2+b_1)\frac{L_1}{U_1}}\right)\right]}{e^{-(K_2+b_1)\frac{L_1}{U_1}} - e^{b_2\frac{L_2}{U_2}}} \tag{A-9}$$

and

$$\alpha = \frac{Q}{V}\left[\frac{b_2\,L_2}{U_2} + (K_2+b_1)\frac{L_1}{U_1}\right] \tag{A-10}$$

in which V is the volume of the water in the system, Q is the discharge of the system, C_s is the saturation concentration and L_1 is the length of the channel. Because of the presence of the headbox, tailbox, and pump, the dimensions L_1 and L_2 in a real flume are equivalent dimensions.

Equation A-9 gives the deficit at the station $x_1=0$, $x_2=L_2$ as $t \to \infty$. This non-zero value of the deficit is the value at which the oxygen consumed by the reactions is just replaced by that supplied by surface reaeration. Equation A-5 shows that if there is an oxygen consuming reaction in the channel or return pipe of a flume then because of the first term on the right of that equation and because of the non-zero D_∞ value, the logarithm D versus t relation at a station x_1 will not be a straight line as shown in figure 2 presented previously. Thus the system does not follow the first-order model usually assumed valid for flume systems. Also, if b_1 and/or b_2 are not equal to zero, the curves of logarithm D versus t at two different stations in the channel will not be parallel, as they would be were b_1 and $b_2 = 0$. Furthermore, it is expected, even discounting the curvature of the lines and their deviation from parallel, that the quantity $M = \dfrac{\Delta \ln D}{X/U}$ as determined by the method of figure 2 will be some weighted average of K_2 and b_1, and will not equal the reaeration coefficient, K_2. Examples presented later show that if $b_1=0$, the error due to the curvature and deviation from the parallel is negligible. If $b_1 \neq 0$, equations A-5, A-9, and A-10 can be used to obtain an estimate of the true values of K_2 and b_1 from values of M measured by the procedure of figure 2.

If

$$D_{11}' = D_1'(x_{11}, t) = \frac{b_1}{K_2 + b_1}\left[1 - e^{-(K_2 + b_1)\frac{x_{11}}{U_1}}\right] + D_\infty' \, e^{-(K_2 + b_1)\frac{x_{11}}{U_1}}$$

$$+ (D_0' - D_\infty') \, e^{-\alpha t} \, e^{-(K_2 + b_1 - \alpha)\frac{x_{11}}{U_1}} \tag{A-11}$$

and

$$D_{12}' = D_1'(x_{12}, \, t + \Delta t) = \frac{b_1}{K_2 + b_1}\left[1 - e^{-(K_2 + b_1)\frac{x_{12}}{U_1}}\right] + D_\infty' \, e^{-(K_2 + b_1)\frac{x_{12}}{U_1}}$$

$$+ (D_0' - D_\infty') \, e^{-\alpha(t + \Delta t)} \, e^{-(K_2 + b_1 - \alpha)\frac{x_{12}}{U_1}} \tag{A-12}$$

where in the double subscripts the first subscript, one, indicates the channel and the second, one or two, indicates one of two longitudinal locations in the channel, $\Delta t = \frac{x_{12} - x_{11}}{U_1} = \frac{\Delta x}{U_1}$, and the deficits have been nondimensionalized by dividing by C_s, which is indicated by the primed notation, then from equations A-11 and A-12,

$$D_{12}' - \frac{b_1}{K_2 + b_1} = \left(D_{11}' - \frac{b_1}{K_2 + b_1}\right) e^{-\frac{\Delta x}{U_1}(K_2 + b_1)} \tag{A-13}$$

Equation A-13 may be written

$$D_{12}' = \delta(1 - e^{-\eta}) + D_{11}' \, e^{-\eta} \tag{A-14}$$

where $\eta = \frac{\Delta x}{U_1}(K_2 + b_1)$ and $\delta = \frac{b_1}{K_2 + b_1}$. Because η is small, $e^{-\eta}$ in the first term on the right of equation A-14 is adequately represented by the first two terms in its Taylor series expansion, and equation A-14 becomes

$$D'_{12} = \delta \eta + D'_{11} e^{-\eta} \qquad\qquad (A-15)$$

Taking the natural logarithm of equation A-15, expressing the right
hand side in its power series form, and neglecting all powers of $\delta \eta$
greater than one, it may be shown that

$$\ln D'_{12} \doteq \ln(D'_{11} e^{-\eta}) + \frac{\delta \eta}{D'_{11} e^{-\eta}} \qquad\qquad (A-16)$$

Because $e^{-\eta} \doteq 1$,

$$\Delta \ln D' = \ln D'_{11} - \ln D'_{12} = (K_2 + b_1) \frac{\Delta x}{U_1} \left[1 - \frac{b_1}{D'_{11}(K_2 + b_1)} \right] \quad (A-17)$$

and because $M = \Delta \ln D' \Big/ \dfrac{\Delta x}{U_1}$,

$$K_2 \doteq M + \frac{b_1}{D'_{11}} (1 - D'_{11}) \qquad\qquad (A-18)$$

Equation A-18 states that, assuming one has available DO
deficit measurements of two samples, one from the upstream station, one
from the downstream station at a lag time $\tau = \Delta x/U$ later, then the K_2
value as determined from $M = \Delta \ln D/\tau$ differs from the true value only if
$b_1 \neq 0$. The amount of the deviation of M from K_2 increases as the deficit
at the upstream station decreases. If the method of figure 2 is used,
that is, if M is determined not from two instantaneous point samples,
but from experimental results which were forced to fit two parallel
straight lines, the resulting curve-fitting errors will be added to
those resulting from the non-zero b_1 value.

To determine K_2 and b_1 from experimental data, a plot of $\ln D_1'$ versus t at two different stations, as in figure 2, should be made without forcing the data to fit two parallel straight lines. For two sufficiently different values of D_{11}', one determines M as in figure 2, and computes b_1 and K_2 from two applications of equation A-18. If the data are forced to fit two parallel straight lines, M will be the same for all D_{11}', and it will be impossible to determine b_1 and K_2. Other methods for determining K_2, b_1, and b_2 may be derived from equations A-9, A-10, and A-18. These methods require only a single determination of M, but they involve conducting the experiment until $t \to \infty$ to determine experimentally D_∞. These methods, in addition, require measurements of L_1 and L_2, indeterminate quantities in real flume systems. Thus the procedure outlined at the start of this paragraph appears to be the best one for determining K_2 in a flume system in which a first order oxygen consuming reaction proceeds in the channel in conjunction with reaeration.

Equation A-18 may be rewritten

$$\frac{K_2 - M}{K_2} \doteq \frac{b_1}{K_2} \ \frac{(1 - D'_{11})}{D'_{11}} \tag{A-19}$$

from which it is seen that if b_1 and D'_{11} are constants, the relative error in the measured K_2 increases as K_2 decreases. Thus if b_1 is a constant in a set of flume experiments, the resulting errors will be more severe at the lower end of the experimental K_2 range, with the possibility of severely biasing any resulting least-squares prediction equations. It is suggested that this could be a reason for the widely different values of the multiplicative constants of the regression equations obtained by Thackston and Krenkel (1969a) from the analysis of their data (Thackston, 1966; Krenkel, 1960).

The discussion above suggests a procedure for conducting a series of flume experiments for measuring K_2 which would determine if oxygen consuming reactions are influencing the K_2 measurements. The procedure involves running a special experiment prior to the start of a test series. In this experiment, test conditions are selected which are expected to yield a K_2 value among the lowest in the test series. The experiment is conducted under conditions typical for the entire set, but over a larger DO deficit range than normal, that is, for a long time. If there is no oxygen-consuming reaction in process in the system, the curves logarithm D versus t observed at the two measurement stations will be straight and parallel, and K_2 may be computed by the method of figure 2. If a reaction is in progress in the system, this will be indicated, as t becomes large, by curvature and non-parallelism of the curves logarithm D versus t at the two measuring stations. If the reaction is in the return conduit, b_1 as computed by the method suggested above will be zero, and as will be shown in the examples to follow, again the analysis method of figure 2 will be accurate enough. If $b_1 \neq 0$, K_2 must be calculated by the method given above. The trial experiment described above will point the way for the conduct of the other experiments in the series. If the reaction in the channel is insignificant in the test case, it will most likely also be insignificant in the others. If it were significant, its effects should be considered in the remainder of the experiments.

Examples

The usefulness of the K_2 determination procedure described above is best illustrated by example. The examples which follow utilize, with the exception of the reaction rate constants b_1 and b_2, values of flume and flow parameters which are typical for small laboratory flumes. The values of b_1 and b_2 must necessarily be highly speculative, because available flume data are not sufficient to determine typical values for these parameters. For a mixing tank, however, Tsivoglou and others (1965) reported data which indicate the reaction rate constants in a largely metal system can be on the order of 2×10^{-5} per second. The reaction is most likely due to corrosion of the walls of the system and would be expected to vary widely from one system to another, consequently, slightly larger values for b_1 and b_2 have been chosen for use in the examples described. The relative error in a measured K_2 due to a particular value of b_1 is dependent on the ratio b_1/K_2, so that for the values of b_1 used in the examples, the relative errors will be more or less severe for respectively larger or smaller K_2 values.

In the examples, DO deficits at two sampling stations were calculated using equation A-5 and the parameters listed in table A-1, where α and D_∞ were calculated from equations A-9 and A-10. From the

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Table A-1.--following here

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synthetic flume data, M was calculated for each of the examples by the method of figure 2. Least-squares straight lines were fit to 20-minute increments of the calculated values of the logarithm deficit and t for each of the two sampling stations. The 20-minute sampling period was chosen because this was the period used by both Thackston (1966) and Krenkel (1960). The slopes of the two lines were averaged, and new intercepts were computed for parallel least-squares lines through the two sets of points. The quantity M was then computed from the new intercepts and the average slope. These calculated M values are listed in table A-1. In this procedure, M is not a function of time as it is if the lines are not parallel.

Table A-1.--*Parameters used in calculating the synthetic flume data and the resulting calculated reaeration coefficient*[2]

Example Number	K_2 $\frac{1}{sec} \times 10^4$	b_1 $\frac{1}{sec} \times 10^5$	b_2 $\frac{1}{sec} \times 10^5$	α $\frac{1}{sec} \times 10^4$	D'_0	D'_∞	M $\frac{1}{sec} \times 10^4$
1	8.00	0	8.00	3.50	0.800	0.144	8.00
2	8.00	0	8.00	3.50	0.400	0.144	8.00
3	8.00	4.00	8.00	3.65	0.800	0.179	7.81
4	8.00	4.00	8.00	3.65	0.400	0.179	7.27
5	4.00	4.00	4.00	1.90	0.400	0.211	3.34

[2] Parameters which were the same for all examples are:

$V = 16$ ft^3, $Q = 0.3$ cfs, $U_1 = 1.8$ fps, $U_2 = 1.2$ fps,

$L_1 = 36$ ft, $L_2 = 40$ ft, $x_{11} = 8$ ft at upstream and $x_{12} = 28$ ft at downstream sampling stations.

Figure A-1 shows plots of logarithm D versus t for the upstream sampling stations in examples 3, 4, and 5; the lines are the least-squares fits to the synthetic data points. The curvature due to

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Figure A-1.--following here

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the non-zero D_∞ value is virtually unnoticeable over the 20 minute time period. In fact, if experimental data with its scatter were used, it would probably be impossible to detect the curvature. Thus over a 20 minute experimental time, it is virtually impossible to detect a non-zero D_∞, and thus impossible to conclude whether or not an oxygen consuming reaction proceeds in the system. As can be seen from table A-1, for examples 3, 4, and 5, the deviation of M, the calculated K_2, from the true value is significant. Thus it is possible for oxygen consuming reactions to cause significant errors in calculated K_2 values without their presence being noticed in the experimental results.
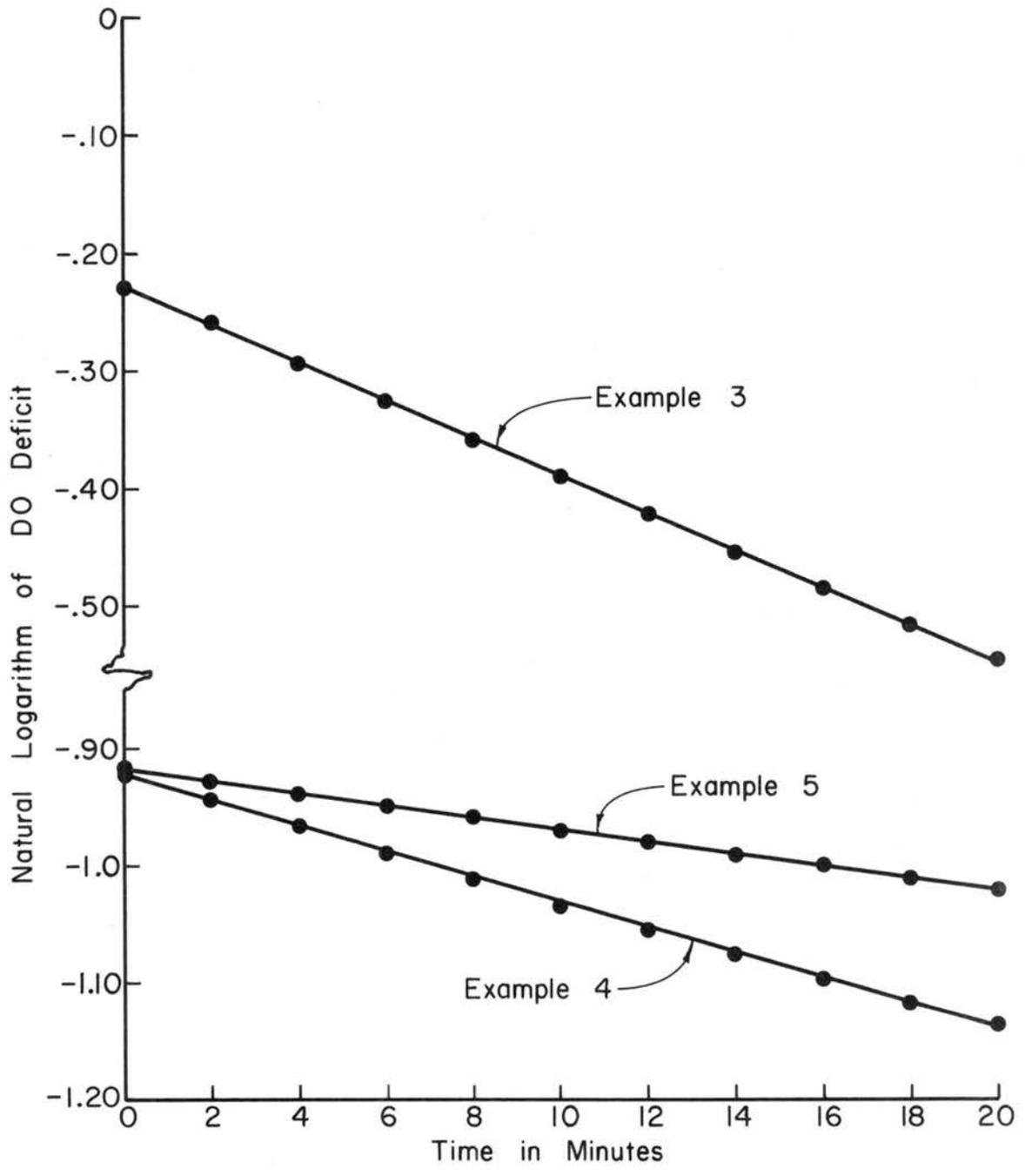
Figure A-1.--Synthetic flume data from the upstream sampling
station.

The values of M for examples 1 and 2 are not significantly different from 8.0×10^{-4} seconds^{-1}. This shows that, at least for short time periods, if b_1 is zero, the deviation of M from the true K_2, due to the curvature induced by a non-zero D_∞ is negligible. Thus, when C_s is known, the K_2 calculation procedure illustrated in figure 2 will contain significant errors only if b_1 is not zero.

The upstream deficit values at $t=0$ minutes for examples 3, 4, and 5, respectively, are 0.676, 0.356, and 0.379. The corresponding values of M calculated from equation A-18 are 7.82, 7.28, and 3.34×10^{-4} seconds^{-1}. These are very nearly equal to the M values calculated by the procedure of figure 2 listed in column 8 of table 1. Even better correspondence between the measured M and the M calculated from equation A-18 is obtained if instantaneous values of the upstream and downstream deficits are used to calculate M. For instance, in example 5 at $t=16$ minutes the upstream deficit is 0.368 and the M value calculated from the deficits is 3.31×10^{-4} seconds^{-1}, while the M calculated from equation A-18 is 3.31×10^{-4} seconds^{-1}. The close correspondence of the M values obtained in the two ways indicates that despite the approximations made in its derivation, equation A-18 provides an accurate means for obtaining K_2 and b_1 from two measured values of M.

The procedure for determining K_2 and b_1 from experimental data is illustrated in figure A-2. Synthetic data parameters shown in figure

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Figure A-2.--following here

A-2 are the same as those for example 4 in table 1. Deficits at the upstream and downstream sampling stations are plotted for two periods: from 0 to 10 minutes and from 50 to 60 minutes. The procedure consists of plotting the natural logarithm of deficit versus time, determining M graphically (as in figure 2) for each of the 10 minute periods, and solving for b_1 and K_2 using equation A-18 and the resulting two sets of D'_{11} and M values. For the example given in figure A-1, D'_{11} and M for the initial 10-minute period are, respectively, 0.376 and 7.20×10^{-4} seconds^{-1}, while for the period from 50 to 60 minutes, they are 0.245 and 6.56×10^{-4} seconds^{-1}. Using equation A-18, the calculated b_1 and K_2 values are, respectively, 4.51×10^{-4} seconds^{-1} and 7.95×10^{-4} seconds^{-1}. The agreement of these values with the b_1 and K_2 values used in generating the synthetic data is quite good, considering that the two M values were determined graphically.
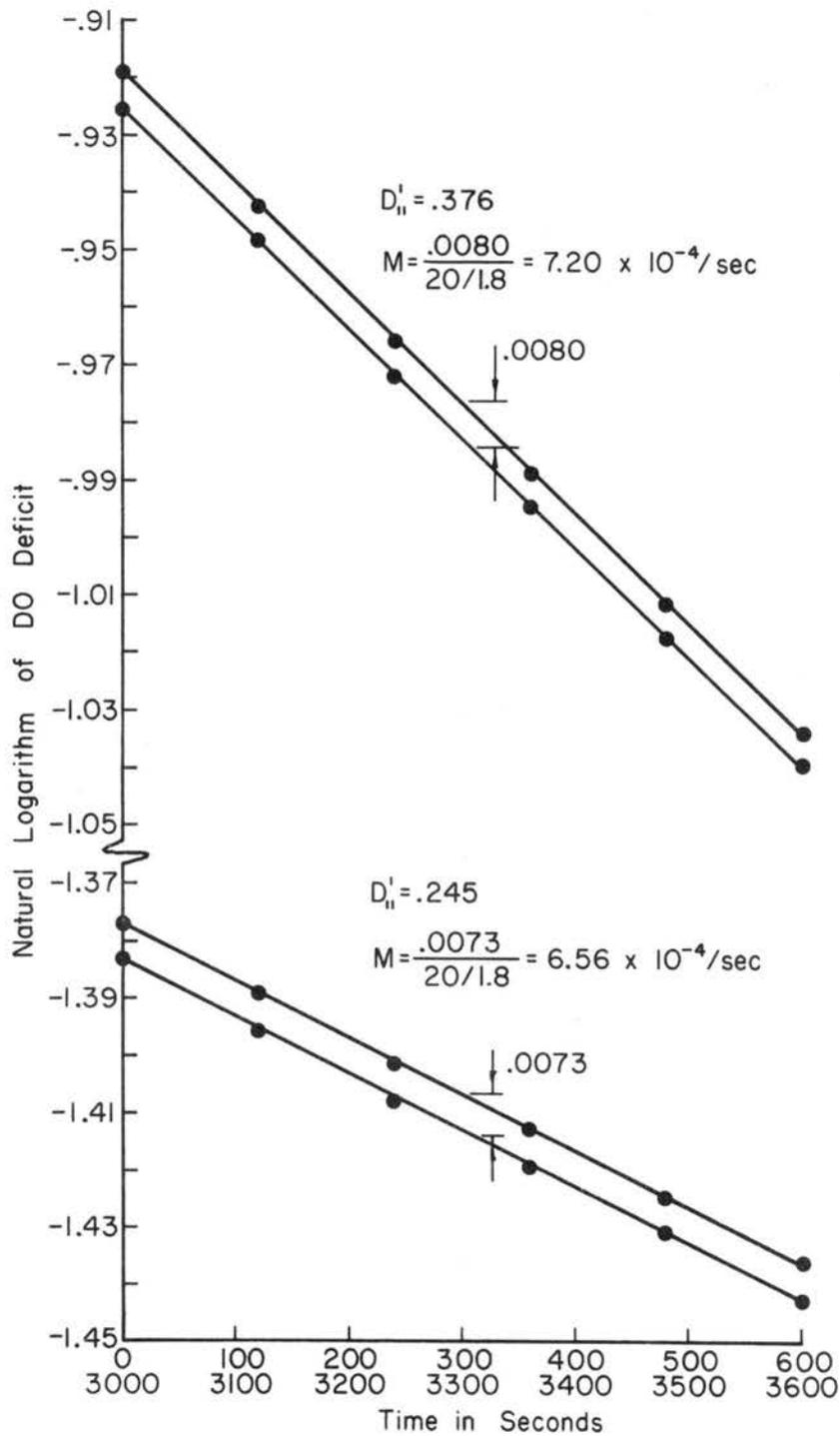
Figure A-2.--Determination of b_1 and K_2 from M values calculated at two different DO deficits.

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If in a flume study there is an error in the value of C_s being used, there will be a corresponding error in all the computed deficits. In such a case, the true deficit D_T is related to the plotted deficit by $D = D_T + d$. The resulting equation for the plotted deficit, assuming no oxygen-consuming reactions in either the channel or the return conduit, is

$$D = d + \left(D_{T_0} - d \right) e^{-\alpha t} \; e^{-(K_2 - \alpha) \frac{x}{U_1}} \quad . \tag{A-21}$$

Equation A-21 is similar to equation A-5, with $b_1 = 0$. It has been shown that in the case of $b_1 = 0$, the error in the K_2 computed using the method of figure 2 is negligible. Thus in a flume study, a negligible error is introduced by using a value of C_s which is incorrect by a small amount Δd. This is in contrast to the nature of errors in analysis of mixing-tank data where K_2 is determined from the slope of a single line (Isaacs and Gaudy, 1968; Tsivoglou and others, 1965).

Symbols - Appendix A

Symbol   *Definition*

b_1 Rate constant for the first-order oxidation reaction in the channel of the flume, in reciprocal seconds.

b_2 Rate constant for the first-order oxidation reaction in the return pipe of the flume, in reciprocal seconds.

C_1 Dissolved oxygen concentration in the water in the channel of the flume, in milligrams per liter.

C_2 Dissolved oxygen concentration in the water in the return pipe of the flume, in milligrams per liter.

C_s Dissolved oxygen concentration at saturation, in milligrams per liter.

D Computed deficit of dissolved oxygen, in milligrams per liter.

D_1 Equivalent to $D_1(x_1, t)$, the dissolved oxygen deficit at longitudinal position x in the channel of the flume at time t, in milligrams per liter. (Subscript 1 indicates the channel of the flume.)

D_2 Equivalent to $D_2(x_2, t)$, the dissolved oxygen deficit at longitudinal position x in the return pipe of the flume at time t, in milligrams per liter. (Subscript 2 indicates the return pipe of the flume.)

D_0 Initial dissolved oxygen deficit in the system at time $t = 0$, in milligrams per liter.

D_∞ Final dissolved oxygen deficit in the system at time $t = \infty$, in milligrams per liter.

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Symbol	Definition

D_0' — Non-dimensional deficit of dissolved oxygen in the system at time $t = 0$, equal to D_0/C_s.

D_∞' — Non-dimensional deficit of dissolved oxygen in the system at time $t = \infty$, equal to D_∞/C_s.

D_T — True deficit of dissolved oxygen, equal to the computed deficit minus an error, or $D - d$, in milligrams per liter.

D_{T_0} — Initial true deficit of dissolved oxygen, equal to the initial computed deficit minus an error, or $D_0 - d$, in milligrams per liter.

D_{11}' — Equivalent to $D_1'(x_{11}, t)$, the non-dimensional deficit of dissolved oxygen in the channel at longitudinal position x_1 at time t. [Deficit non-dimensionalized by dividing by C_s; first subscript in the double subscript (one) indicates the channel of the flume and the second subscript (one) indicates upstream measurement point in the channel.]

D_{12}' — Equivalent to $D_1'(x_{12}, t + \Delta t)$, the non-dimensional deficit of dissolved oxygen in the channel at longitudinal position x_2 at time $t + \Delta t$. [Deficit non-dimensionalized by dividing by C_s; first subscript in the double subscript (one) indicates the channel of the flume and the second subscript (two) indicates downstream measurement point in the channel; Δt is the flow time or $(x_{12} - x_{11})/U_1$ where U_1 is the mean water velocity in the channel.]

d — Error in the saturation concentration of dissolved oxygen, in milligrams per liter.

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Symbol	Definition

K_2 Reaeration coefficient or rate constant for oxygen absorption from the atmosphere, natural logarithm base, in reciprocal days.

L_1 Length of the flume channel, in feet. (Equivalent dimension because of the presence of the headbox and tailbox.)

L_2 Length of the return pipe, in feet. (Equivalent dimension because of the presence of the headbox, tailbox, and pump.)

M Equal to $\Delta \ln D / \frac{X}{U}$ (nomenclature of figure 2 and the main part of the report) or $\Delta \ln D' / \frac{\Delta x}{U_1}$ (nomenclature of appendix A); $X \equiv \Delta x$ = the distance, in feet, between the upstream and downstream measurement points in the flume channel; $U \equiv U_1$ = the mean water velocity, in feet per second, in the flume channel; $\Delta \ln D \equiv \Delta \ln D'$ = the difference in the natural logarithms of the dissolved oxygen deficits at the upstream and downstream measurement points with the downstream measurement lagging the upstream by the flow time, $\Delta x/U_1$. See figure 2.

Q Water discharge, in cubic feet per second.

t Time, in seconds.

U_1 Mean water velocity in the channel of the flume, in feet per second.

U_2 Mean water velocity in the return pipe of the flume, in feet per second.

x_1 Longitudinal position in the channel of the flume, in feet.

Symbol	Definition
x_{11}	Upstream measurement point in the channel of the flume, in feet.
x_{12}	Downstream measurement point in the channel of the flume, in feet.
α	Equal to $\frac{Q}{V}\left[\frac{b_2\, L_2}{U_2} + (K_2 + b_1)\,\frac{L_1}{U_1}\right]$, in reciprocal seconds.
δ	Equal to $b_1/(K_2 + b_1)$.
η	Equal to $\frac{\Delta x}{U_1}\,(K_2 + b_1)$.
τ	Lag time or flow time, equal to $\Delta x/U_1$, in seconds.

APPENDIX B

Collected Data

Table B-1.--*Reaeration coefficients and hydraulic data from Churchill and others (1962).*

k_2[1/] $(day)^{-1}$	H (feet)	U (fps)	S $(\times 10^4)$	W (feet)
2.272	3.27	3.07	10.8502	229
1.440	5.09	3.69	8.6426	242
.981	4.42	2.10	2.7058	344
.496	6.14	2.68	2.9014	358
.743	5.66	2.78	3.6970	376
1.129	7.17	2.64	1.6448	313
.281	11.41	2.92	1.7994	312
3.361	2.12	2.47	14.2342	617
2.794	2.93	3.44	14.5225	635
1.568	4.54	4.65	13.9099	667
.455	9.50	2.94	1.6893	374
.389	6.29	2.51	2.9038	414
.270	7.52	3.15	3.0443	443
.550	7.07	3.30	3.7775	450
.544	5.44	3.11	5.9961	330
.604	8.06	4.28	5.7667	346
1.251	3.88	2.73	6.0706	90
.273	9.28	2.41	1.2571	537
.225	10.19	3.06	1.7789	549
1.881	3.29	2.40	15.5378	520

Table B-1.--*Continued.*

k_2 [1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
.842	4.74	3.46	13.5458	535
.883	5.72	4.02	11.7032	542
.915	6.95	4.52	10.1594	550
.995	4.29	1.85	3.9709	517
.547	6.01	2.75	3.7523	531
.881	7.16	3.23	3.6794	539
.252	8.49	3.71	3.6430	548
5.558	3.42	5.00	23.5142	182
1.712	3.02	3.05	17.4603	124
3.222	2.83	3.51	18.8692	115

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

Table B-2.--*Reaeration coefficients and hydraulic data from Owens and others (1964).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
2.35	1.21	0.14	3.94	28.7
2.06	1.15	.14	3.94	25.8
3.20	1.09	.13	3.94	27.3
2.37	1.50	.37	3.94	27.7
4.57	1.08	.16	4.24	28.1
2.09	.98	.15	4.24	28.2
1.18	1.12	.13	4.24	26.6
3.18	1.46	.38	4.24	27.8
6.18	1.31	.47	11.65	25.0
.90	2.44	.23	8.95	17.9
1.66	2.03	.22	4.08	22.5
.75	1.74	.28	2.69	22.5
2.12	1.47	.37	8.72	20.1
1.41	1.82	.50	1.56	39.8
.31	2.41	.43	1.56	34.9
31.80	.72	1.37	106.00	21.9
24.53	.87	1.19	84.00	20.9
24.57	.85	1.07	61.00	23.7
25.59	.40	.44	92.00	15.3
28.34	.40	.56	61.50	12.1
22.80	.39	.63	60.50	11.0

Table B-2.--*Continued.*

k_2[1/] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
49.17	.60	1.83	92.00	16.1
30.77	.69	1.81	61.50	14.2
18.46	1.00	1.54	60.50	11.5
21.05	.82	1.07	101.60	21.8
16.06	.78	1.27	83.00	19.3
12.04	.64	.46	61.20	17.3
20.32	.48	.60	65.70	17.7
18.90	.72	1.16	61.20	20.7
20.25	.66	1.31	65.70	20.0
17.09	.67	1.30	65.70	19.9
19.16	.69	1.25	65.70	20.0

[1/] Adjusted to $(k_2)_{20^\circ}$, using equation 104.

Table B-3.--*Reaeration coefficients and hydraulic data from Gameson and others (1955).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	W (feet)
57.7	0.41	1.04	5.7
48.7	.41	1.12	5.3
55.6	.42	.99	5.6
46.2	.42	1.02	5.4
34.3	.42	.73	6.0
35.2	.34	.74	6.0

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

Table B-4.--*Reaeration coefficients and hydraulic data from O'Connor and Dobbins (1958) (Streeter and Phelps, 1925).*

k_2 [1]/ (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)
0.45	9.2	2.32	0.68
.23	8.8	1.98	.68
.15	9.3	2.18	.68
.34	6.5	1.41	.68
.17	7.0	.59	1.97
.26	5.8	.32	1.97
.20	5.3	.22	1.97
.14	4.8	.19	1.97
.19	6.4	.43	1.23
.37	4.0	.23	1.23
.22	8.6	.40	.95
.71	7.6	.40	.95
.15	7.1	.22	.95
.20	5.5	.51	1.67
.26	13.8	2.50	1.97
.22	15.0	4.20	1.23
.31	8.6	1.36	1.23
.21	7.2	.86	1.23
.23	6.6	.53	1.23
.86	14.3	3.68	.95
.92	9.3	1.01	.95

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Table B-4.--*Continued*.

k_2 [1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)
.45	9.0	.62	.95
.19	18.7	3.72	1.67
.24	8.8	1.48	1.67
.17	8.2	1.18	1.67
.19	7.2	.91	1.67
.16	7.3	.96	1.67
.14	24.2	3.90	.68

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

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Table B-5.--*Reaeration coefficients and hydraulic data from O'Connor and Dobbins (1958) (various sources).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)
5.80	0.9	0.97	36.
3.07	1.9	.55	14.
1.22	4.0	.73	4.9
.92	3.1	.65	6.9
.23	9.2	1.37	.27
.28	9.0	1.57	.27
.30	8.9	1.63	.27
.048	12.	.32	-
.018	32.	.50	-
.026	37.	.88	-

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

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Table B-6.--*Reaeration coefficients and hydraulic data from Tsivoglou and others (1967, 1968).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	W (feet)
1.273	1.16	0.636	73.7
1.142	1.94	.419	101.5
.977	2.09	.359	110.0
.646	3.11	.458	57.9
1.653	.167	.570	86.7
.872	2.36	.346	101.0
1.251	1.99	.335	123.8
1.170	2.26	.436	83.72
1.261	2.83	.286	101.9
3.373	2.30	.563	63.7
1.163	1.95	.529	80.
1.491	2.42	.441	77.3
2.344	2.13	.539	71.9
1.420	2.06	.425	94.2
.977	1.66	.457	108.8

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

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Table B-7.--*Reaeration coefficients and hydraulic variables from Thackston (1966).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
18.72	0.125	1.323	59.6	2.0
20.75	.109	1.449	89.4	2.0
25.45	.124	1.878	116.1	2.0
34.85	.092	1.707	144.6	2.0
40.6	.098	1.858	162.3	2.0
44.9	.122	2.320	178.5	2.0
52.5	.117	2.029	141.8	2.0
24.35	.170	2.079	84.3	2.0
19.57	.112	1.225	55.7	2.0
18.38	.104	.994	43.0	2.0
21.1	.107	.921	38.0	2.0
15.39	.094	.802	23.6	2.0
16.69	.107	.940	42.3	2.0
9.98	.113	.773	24.5	2.0
13.19	.099	.776	28.2	2.0
26.15	.065	.754	57.1	2.0
39.55	.065	1.116	112.4	2.0
40.55	.063	.961	89.4	2.0
43.8	.072	1.069	89.7	2.0
31.90	.052	.678	67.4	2.0
39.45	.078	.848	52.4	2.0

Table B-7.--*Continued.*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
16.74	.082	.802	43.8	2.0
16.32	.085	.365	31.5	2.0
36.45	.070	.389	60.0	2.0
14.62	.101	.645	65.9	2.0
21.95	.119	.865	79.4	2.0
25.87	.146	1.100	79.1	2.0
24.25	.082	.636	107.6	2.0
24.72	.129	1.110	107.4	2.0
64.05	.057	.558	201.2	2.0
10.88	.141	.476	14.4	2.0
11.38	.175	.955	42.6	2.0
5.78	.232	.484	6.5	2.0
44.55	.154	1.471	133.2	2.0
31.55	.150	1.743	203.8	2.0
39.3	.189	2.015	168.8	2.0
23.80	.089	1.333	24.1	2.0
18.45	.067	.978	17.4	2.0
28.80	.037	.592	18.2	2.0
14.36	.080	.843	10.3	2.0
29.80	.078	.767	44.1	2.0
19.08	.111	.900	32.4	2.0
22.45	.096	.764	32.4	2.0

Table B-7.--*Continued.*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
24.30	.121	.968	32.4	2.0
23.35	.088	.738	32.4	2.0
16.82	.083	.688	32.4	2.0
22.45	.073	.595	32.4	2.0
32.08	.082	.666	32.4	2.0
19.32	.085	.855	46.5	2.0
18.82	.080	.782	40.6	2.0
25.55	.072	.753	40.6	2.0
18.60	.148	.741	30.9	2.0

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

Table B-8.--*Reaeration coefficients and hydraulic variables from Krenkel (1960).*

$k_2\underline{1/}$ (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
34.37	0.0802	0.473	44.38	1.0
69.91	.0823	.739	100.0	1.0
37.26	.0820	.385	28.25	1.0
24.66	.0824	.295	15.75	1.0
64.32	.0861	.788	100.	1.0
82.39	.0852	.897	145.88	1.0
99.38	.0857	1.020	162.86	1.0
50.93	.0844	.634	70.33	1.0
75.93	.0871	.823	106.75	1.0
40.06	.0894	.461	32.	1.0
104.3	.0930	1.330	239.9	1.0
115.3	.0901	1.205	212.5	1.0
34.51	.0878	.553	44.	1.0
26.57	.0932	.364	17.5	1.0
100.7	.0876	1.024	158.75	1.0
111.7	.0882	1.063	177.75	1.0
59.22	.0964	.859	93.75	1.0
78.99	.0971	1.020	127.5	1.0
77.25	.0974	1.150	164	1.0
40.80	.0974	.605	45.25	1.0
91.04	.0963	1.185	137.5	1.0
67.25	.1091	1.200	137.5	1.0

Table B-8.--*Continued*.

$k_2 \frac{1}{}$ (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
29.11	.1115	.662	411.8	1.0
66.73	.0993	.898	91.56	1.0
14.31	.1001	.243	08.	1.0
49.39	.1048	.793	63.44	1.0
102.5	.1045	1.272	175.	1.0
114.9	.1090	1.590	236.	1.0
109.2	.1043	1.438	212.6	1.0
43.70	.1232	.830	51.75	1.0
62.70	.1182	.967	76.25	1.0
71.81	.1161	1.085	104.	1.0
64.31	.1189	1.108	100.45	1.0
96.17	.1360	1.590	156.25	1.0
19.65	.1416	.539	17.5	1.0
32.64	.1422	.733	31.75	1.0
41.50	.1415	.904	49.25	1.0
95.67	.1427	1.450	118.25	1.0
82.67	.1410	1.510	138.5	1.0
13.26	.1447	.359	7.75	1.0
53.02	.1463	1.180	77.25	1.0
69.10	.1451	1.340	106.	1.0
53.23	.1478	1.030	59.	1.0
96.13	.1521	1.810	180.	1.0

Table B-8.--*Continued*.

k_2 [1] (day)$^{-1}$	H (feet)	U (fps)	S ($\times 10^4$)	W (feet)
97.18	.1507	2.030	212.6	1.0
108.7	.1481	2.140	234.3	1.0
13.04	.1650	.408	7.5	1.0
38.05	.1651	1.050	49.5	1.0
52.01	.1650	1.350	78.5	1.0
53.31	.1662	1.560	105.75	1.0
32.32	.1651	.828	33.25	1.0
10.63	.2014	.441	7.5	1.0
16.46	.1983	.743	18.	1.0
39.18	.1985	1.186	49.25	1.0
28.85	.1989	1.020	32.75	1.0
37.62	.1995	1.315	59.	1.0
42.99	.1968	1.478	77.	1.0
50.54	.1989	1.790	113.6	1.0

[1] Adjusted to $(k_2)_{20°}$, using equation 104.

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Table B-9.--*Reaeration coefficients and hydraulic data from Negulescu and Rojanski (1969).*

k_2[1] (day)$^{-1}$	H (feet)	U (fps)	W (feet)
15.90	0.492	1.902	0.66
11.50	.492	1.640	.66
17.25	.164	.951	.66
18.70	.164	.853	.66
8.64	.492	1.050	.66
11.50	.492	.656	.66
8.64	.492	.886	.66
14.45	.361	1.082	.66

[1] Adjusted to $(k_2)_{20°}$, using equation 104.