BOD/DO KINETICS

BOD in Wastewaters

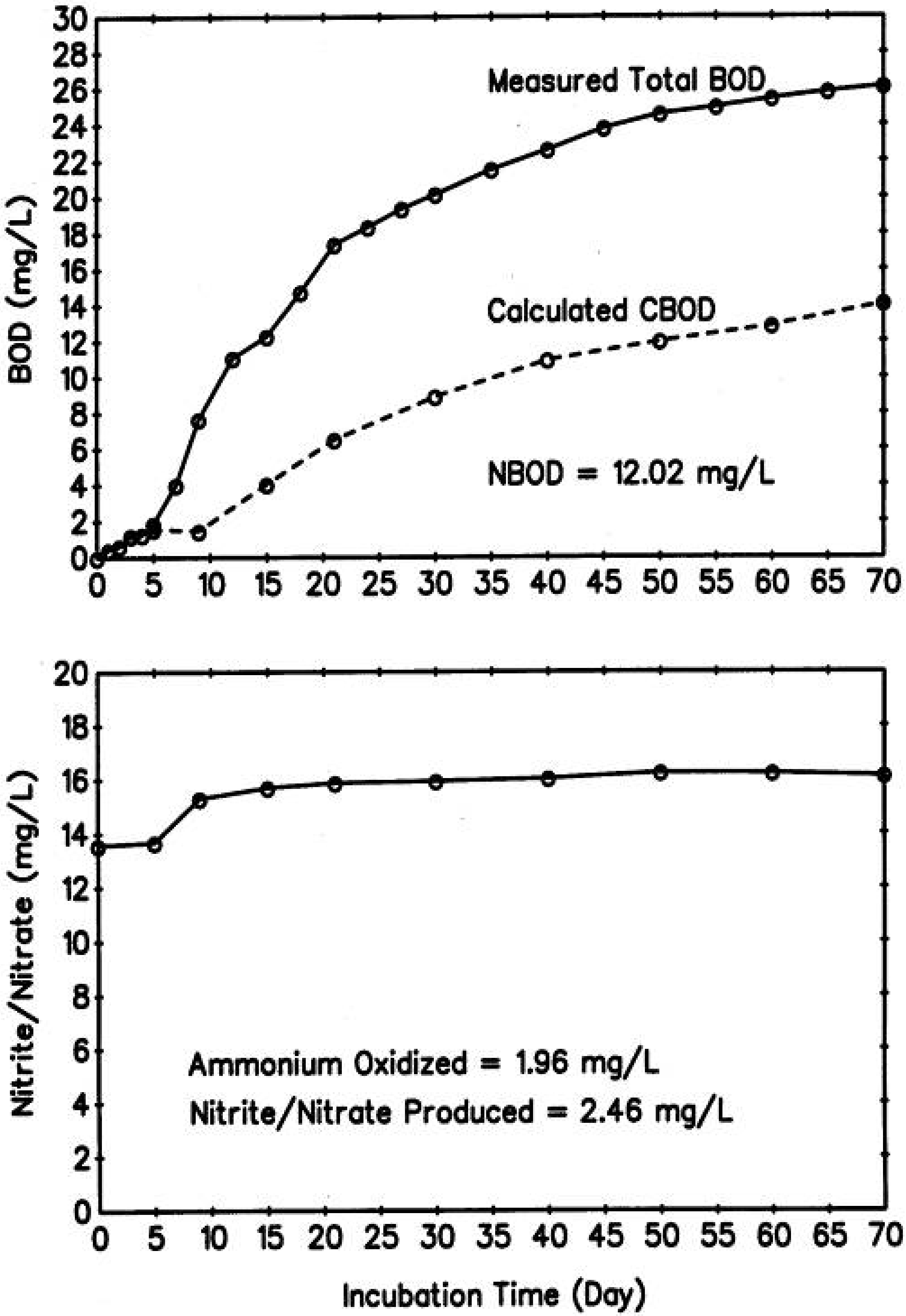
Table 1. Metro Plant Effluent Concentrations (mg/L)[1]

Parameter	Primary Treatment	Secondary Treatment	Secondary with Nitrification
CBOD	101	40.89	20.28
$CBOD_u$ / $CBOD_5$	1	2.5	-
Organic Nitrogen	10.2	3.27	3.09
Ammonia Nitrogen	11.68	14.95	0.8
Nitrite/Nitrate	0.3	0.09	12.63
Total Nitrogen	22.2	18.31	16.51
Organic Phosphorus	5.5	0.89	0.19
Ortho-P	8	2.77	2.53
Total Phosphorus	13.5	3.65	2.73
In-stream k_d (day^{-1})	0.35	0.25	0.073

1. from Lung (2001)

CBOD Measurements

The laboratory protocol to quantify the $CBOD_u$ of wastewaters has improved significantly in recent years. The current practice of determining $CBOD_u$ does not call for the use of nitrification suppressors (NCASI, 1982). Instead, the total amount of oxygen consumption is recorded along with concurrent measurements of ammonium, nitrite, and nitrate concentrations, insuring an accurate mass balance of the nitrogen components. The CBOD is then derived by subtracting the amount of oxygen used in the nitrification process from the measured total oxygen consumption. Using this protocol, Haffely (1997) has obtained excellent long-term BOD test results for the Metro Plant final effluent (see attached figure) and ambient water samples from the Upper Mississippi River. Results from the Metro Plant show that the $CBOD_u$ is about 14 mg/L. The nitrogenous BOD (NBOD) is about 12 mg/L, equivalent to an ammonium concentration of 2.63 mg/L (= 12/4.57), and close to the nitrite/nitrate production of 2.46 mg/L. The test also tracks the amount of ammonium consumed and finds that to be 1.96 mg/L, indicating that a small amount of organic nitrogen was converted to ammonium, which in turn is oxidized to form nitrate. The time series plots in the figure show that the majority of ammonium oxidation (or nitrate production) takes place between days 5 and 10. In general, the mass balance between ammonium, nitrite/nitrate, and NBOD is maintained during the long-term BOD test for the Metro Plant final effluent.



Measured Total BOD
Calculated CBOD
NBOD = 12.02 mg/L
BOD (mg/L)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70
Ammonium Oxidized = 1.96 mg/L
Nitrite/Nitrate Produced = 2.46 mg/L
Nitrite/Nitrate (mg/L)
0 2 4 6 8 10 12 14 16 18 20
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70
Incubation Time (Day)

Leo et al. (1984) compiled data from 144 municipal wastewater treatment plants to assess the effluent characteristics. Table 2 shows the BOD_5, $CBOD_5$, and ammonia concentrations in wastewaters ranging from primary effluent to secondary effluent with nitrification and filters.

Table 2. Mean Effluent Cons (mg/L) at Municipal Plants[1]

Treatment Type	No. of Plants[2]	BOD_5	$CBOD_5$	NH_3
Primary	2	101	-	-
Trickling Filter	13	41.2	-	16.6
Secondary	38	19.1	10.3	8.9
Secondary with Nitrification	10	11.5	4.8	1
Secondary with Phosphorus Removal	9	16.2	14.6	7.9
Secondary with P-Removal & Nitrification	3	13.6	-	0.9
Secondary with Nitrification & Filters	3	3.9	-	4.8

1. from Leo et al. (1984)

2. Number of plants with BOD_5 data, in some cases number with $CBOD_5$ or NH_3 data may be less

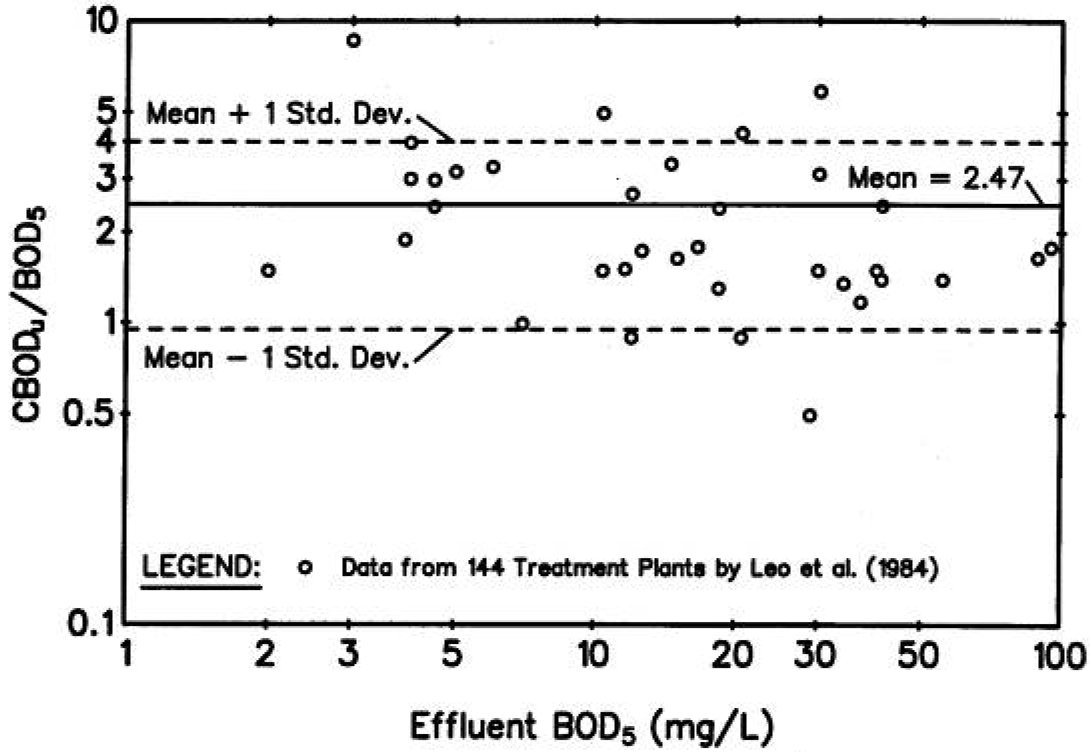
$CBOD_u$ to $CBOD_5$ Ratio in Wastewater

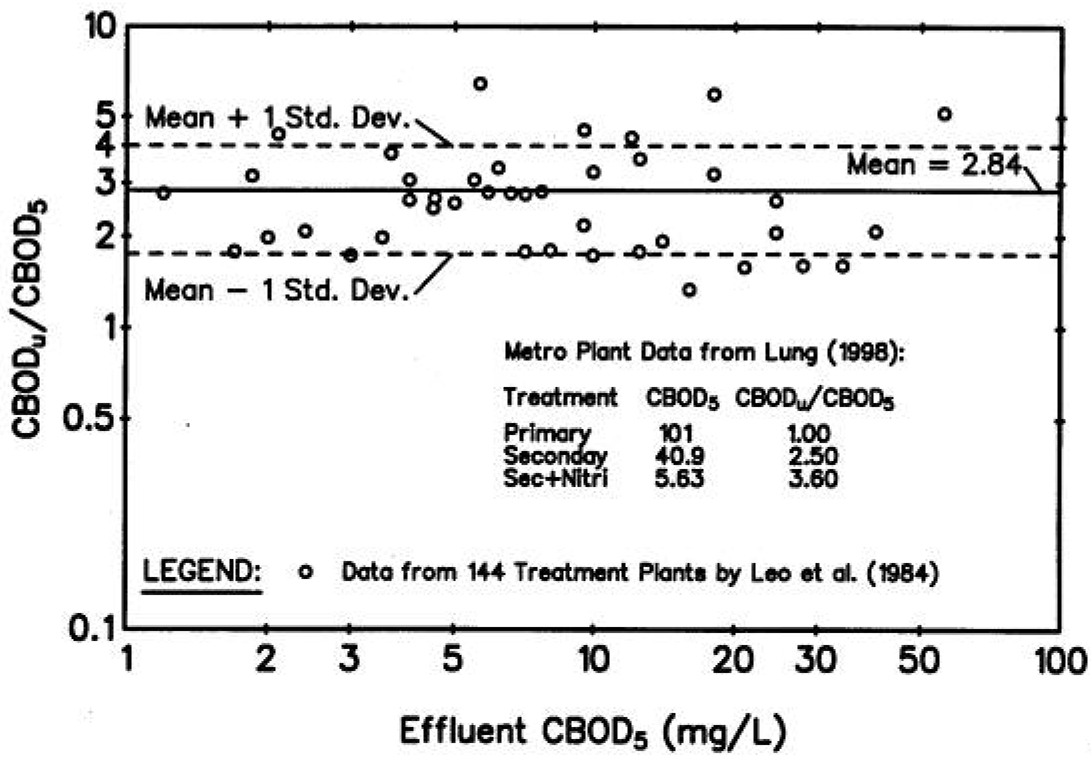
While NPDES permits are written in terms of 5-day CBOD ($CBOD_5$) concentrations, water quality models use ultimate CBOD ($CBOD_u$) in their calculations. So the model calculated wasteloads (in $CBOD_u$) must be converted to $CBOD_5$ values for use in the permit, thereby requiring a ratio of $CBOD_u$ to $CBOD_5$. This ratio is strongly dependent on the wastewater characteristics via the following equation:

$$\frac{CBOD_u}{CBOD_5} = \frac{1}{1 - e^{-(k_1)(5)}}$$

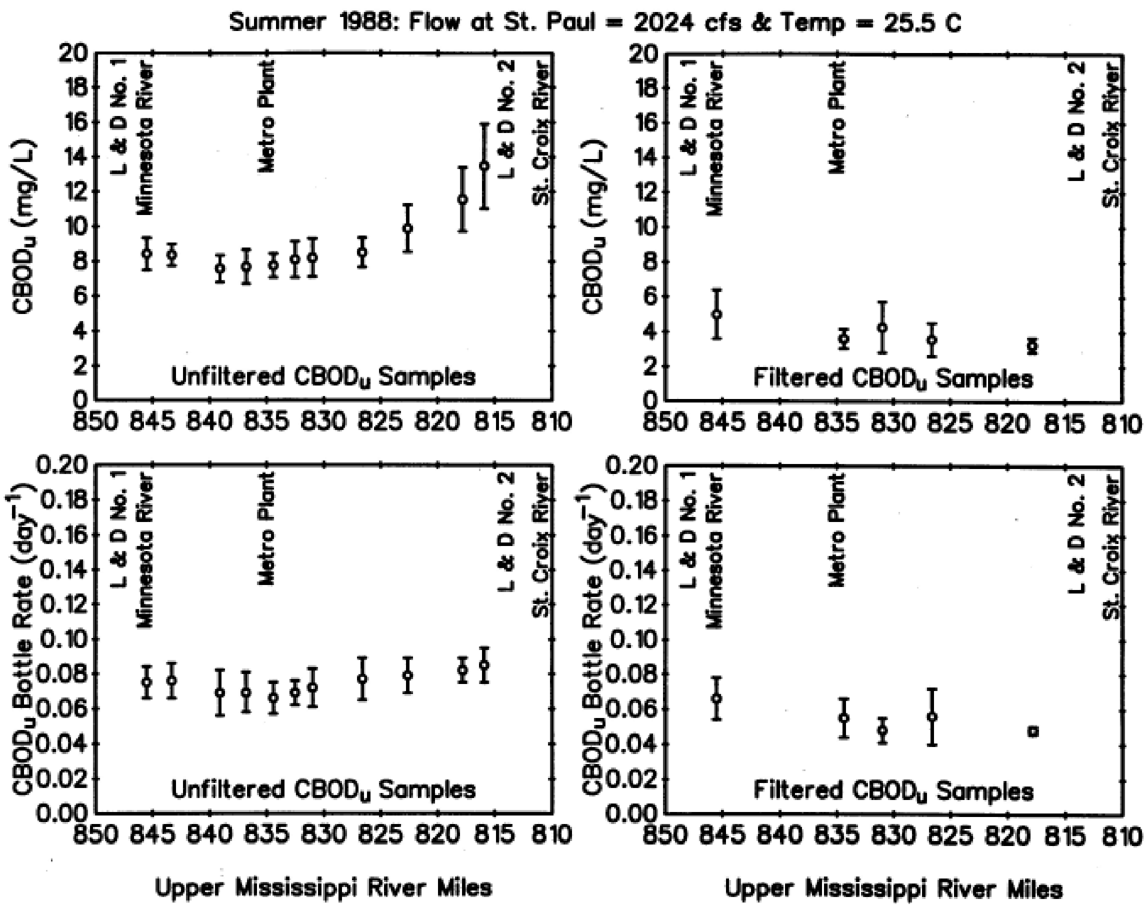
The above equation suggests that increased wastewater treatment (i.e., a lower k_1) tends to stabilize the wastewater, resulting in a higher $CBOD_u$ to $CBOD_5$ ratio. Such a change reflects not only the reduced impact of the effluent CBOD on the k_d rate, but also indicates the presence of highly refractory material in the well treated effluent (Lung, 1996). Table 1 shows that this ratio for the Metro Plant effluent increases from 1.0 for the primary effluent to 2.50 for the secondary effluent. Results from the long-term CBOD test of the recent Metro Plant wastewater, a secondary effluent with nitrification, yield a bottle rate of 0.065

day^{-1} (see Figure 4-2), associated with a $CBOD_u$ to $CBOD_5$ ratio of 3.60 and significantly higher than 1.0 and 2.50.





$CBOD_u$ to $CBOD_5$ Ratio and CBOD Deoxygenation Rate in Receiving Water

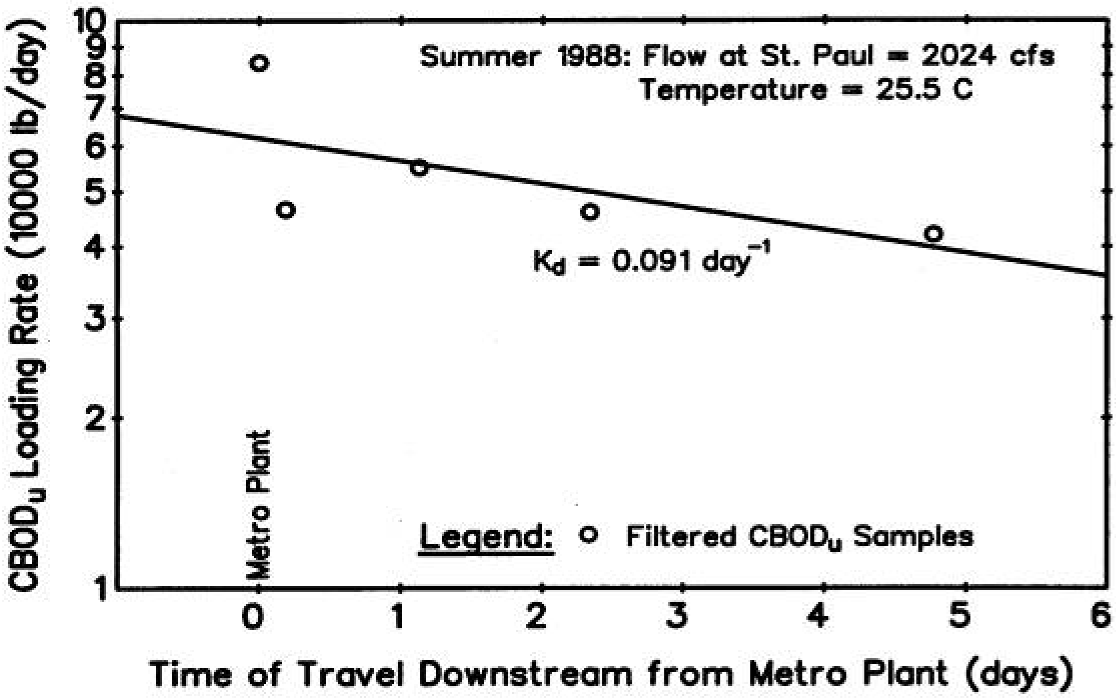


Deriving Deoxygenation Rate in Rivers

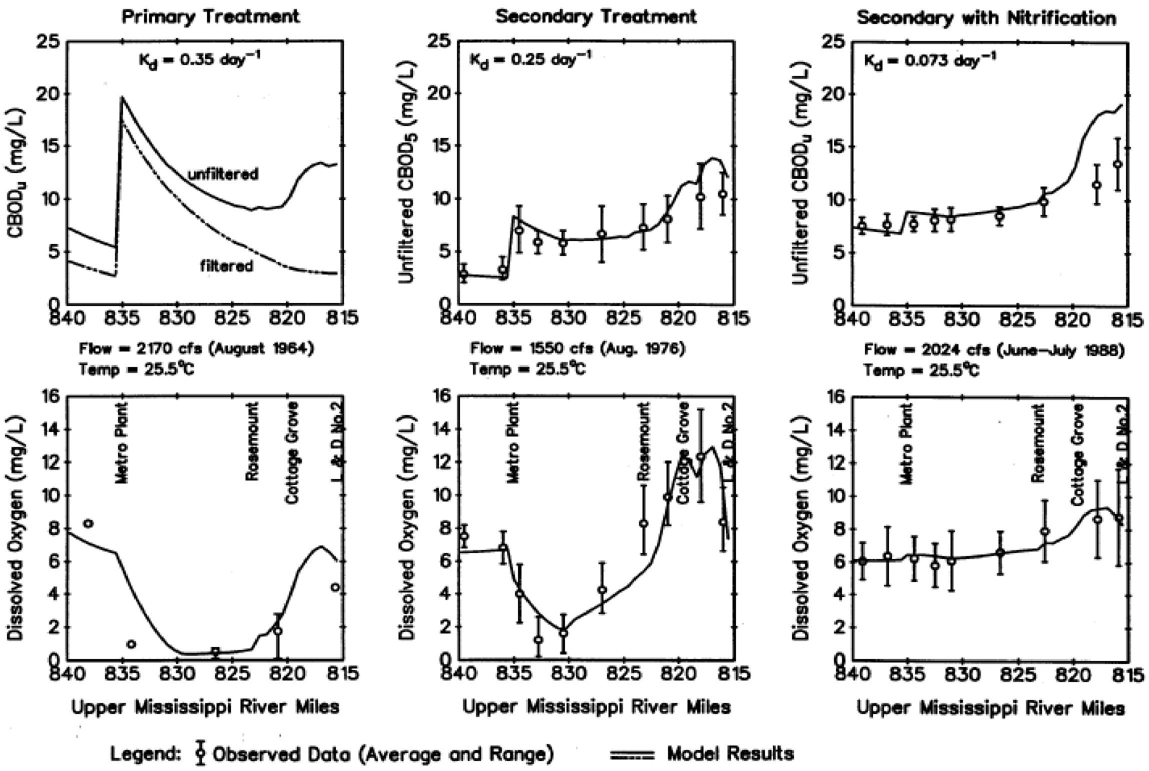
The deoxygenation of CBOD in the receiving water is generally characterized by first-order kinetics:

$$C = C_o e^{-k_d \frac{x}{U}}$$

where C_o is the completely mixed CBOD concentration following the waste input; k_d is the in-stream deoxygenation rate (day^{-1}), x is distance downstream, and U is average stream velocity. Note that x/U is called travel time (day). By measuring the filtered CBOD concentrations in the receiving water, one can determine the in-stream k_d rate by fitting the data points to the exponential decay in above equation. To account for the dilution effect, the $CBOD_u$ at each station is expressed in loading rate (pounds per day), and the filtered $CBOD_u$ data are then fitted by a straight-line in a regression analysis. The slope of the straight-line yields an in-stream deoxygenation rate, k_d, of 0.073 day $^{-1}$ from the semi-log plot of loading rate vs. travel time along the Upper Mississippi River following the Metro Plant input (see figure below).

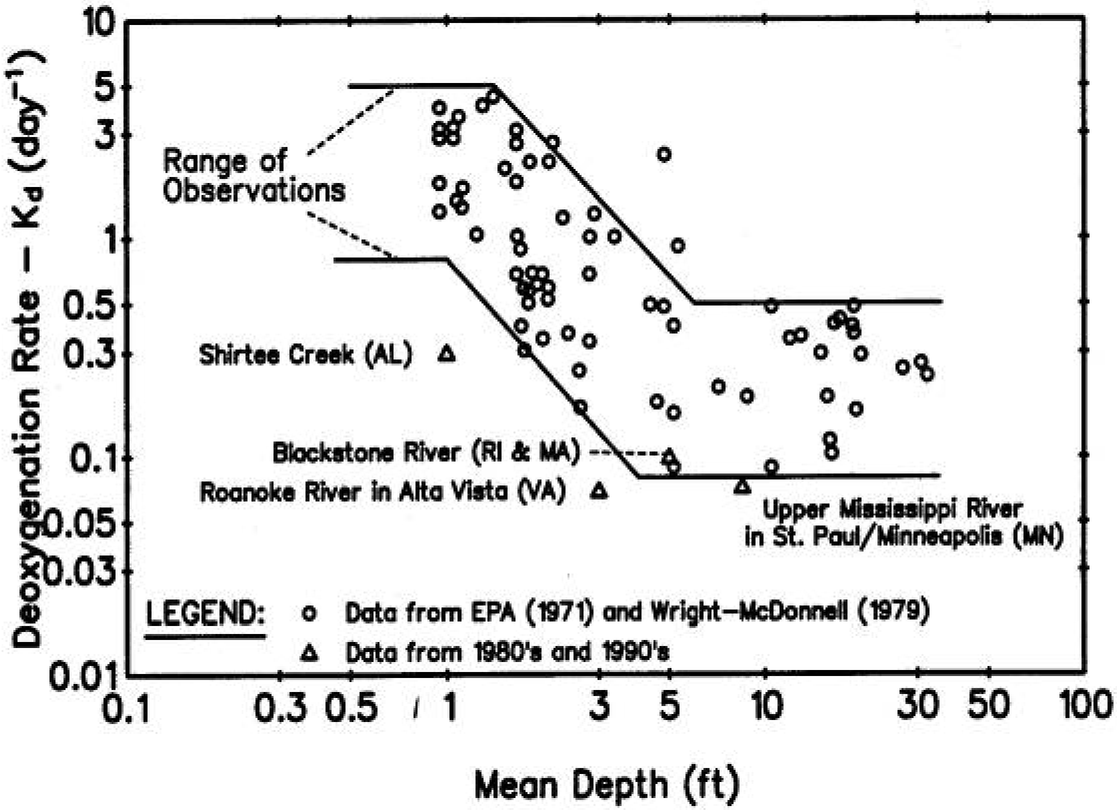


Change of In-stream CBOD Deoxygenation Rate with Treatment Level – The Metro Plant



Developing Preliminary CBOD Deoxygenation Rate in Receiving Water

A review of the historical data and information from recent studies



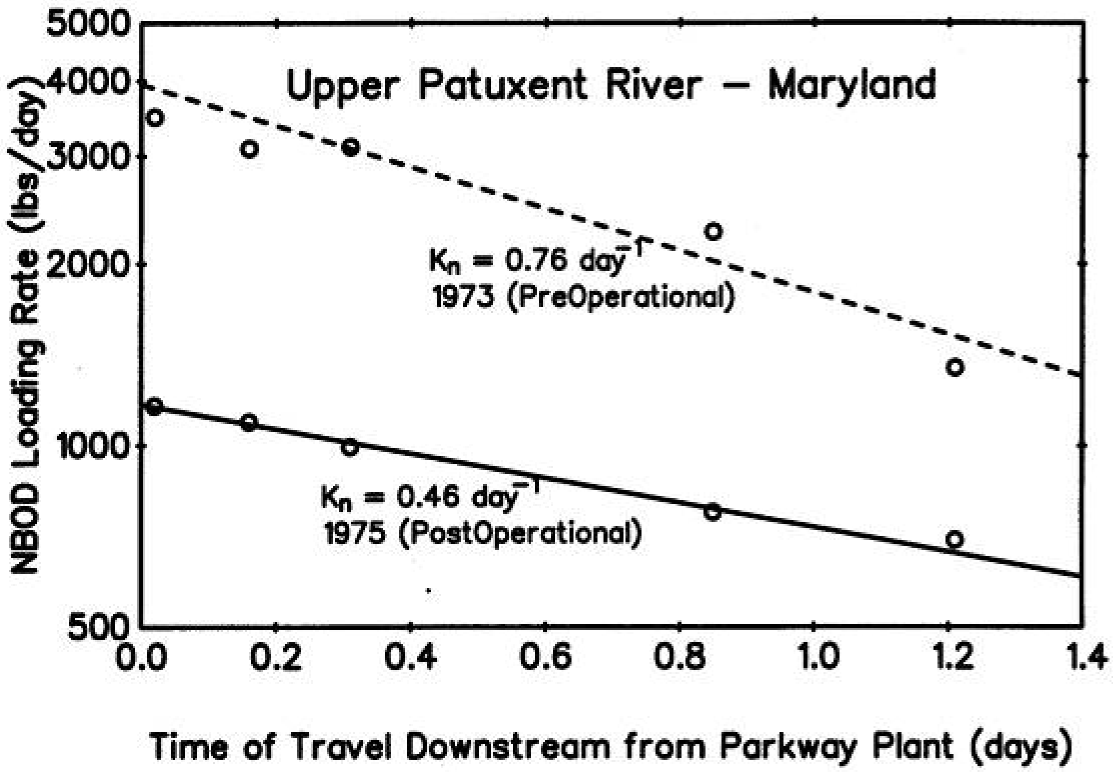
This discussion strongly suggests that field data are crucial in determining the CBOD deoxygenation rate in the receiving water (Lung, 1993). In situations where no field data is available, the EPA guidance manual (EPA, 1995) recommends the use of a plot of k_d vs. river depth (see above figure). Note that the range of observations is derived from 1970's data and earlier when many wastewater treatment plants had only primary treatment. Data from 1980's and 1990's are shown for the Shirtee Creek in Alabama, the Blackstone River in Massachusetts, the Roanoke River in Alta Vista, Virginia, and the Upper Mississippi River in St. Paul and Minneapolis, Minnesota. These four data points are below the lower bound of the historical observations, suggesting that improved wastewater treatment has lowered the deoxygenation rate, k_d, in the receiving water. This data also indicates that the majority of k_d rates are below 0.1 day^{-1}, with the exception of extremely shallow waters such as the Shirtee Creek.

Nitrification in Wastewater and Receiving Water

Several issues related to in BOD/DO modeling are:

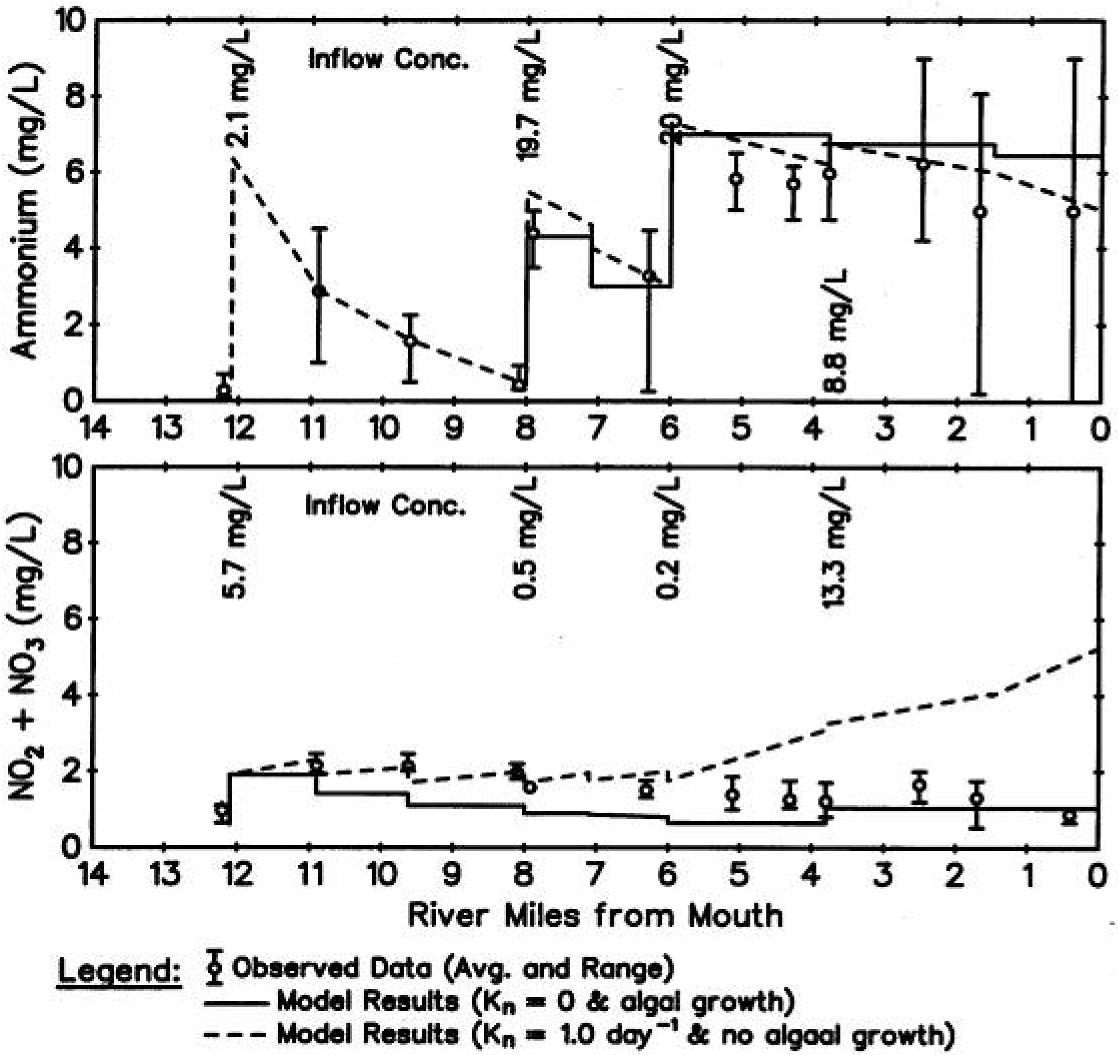
1. The variability of k_n as a function of the water body physical characteristics,
2. Algal effects on k_n, and
3. Seasonal variations of k_n and ammonia removal requirements.

To derive the in-stream nitrification rate when modeling NBOD, the standard procedure involves plotting the NBOD loading rate (calculated from field data) with the travel time (as in the process of deriving the in-stream k_d rate for CBOD). The slope of the best-fit straight-line from this regression analysis yields the nitrification rate, k_n, in the receiving water. The following figure shows such a derivation for the Upper Patuxent River in Maryland. Note that the k_n rate also changes from the pre-operational value to a lower value following the treatment upgrade at the Parkway treatment plant.



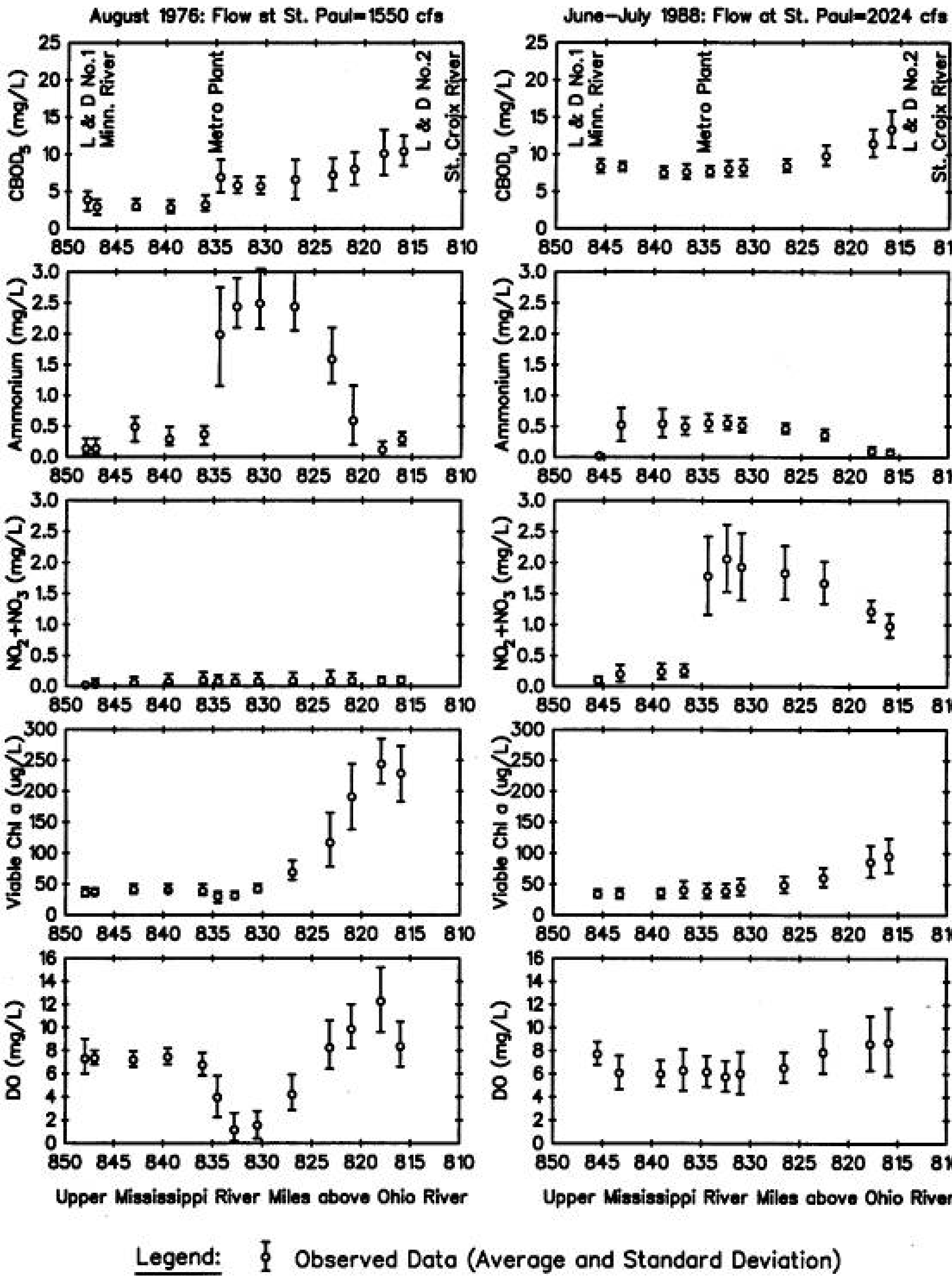
Algal Effect and In-stream Nitrification

Much like the derivation of the in-stream k_d rate for CBOD, high concentrations of algae, either suspended or attached, significantly affect the k_n rate derivation. Plotting the ammonia loading rate in the receiving water vs. time of travel reflects only the ammonia loss. Such an approach could result in the overestimation of k_n where algal effects are significant because algae consume ammonia as a key nutrient (Lung, 1993). A k_n rate derivation based on the total loss of ammonia would include ammonia uptake by algae as well as ammonia oxidation. In many cases, observing a concurrent increase of nitrate proves a better approach for estimating k_n because a nitrate increase results directly from ammonia oxidation in the stream. As a cautionary note, under some conditions, algae can uptake nitrate as well as ammonia. Therefore, the k_n rate derived from nitrate increase would represent the minimum. The following figure shows relatively constant nitrate concentrations throughout a stream reach. As a result, the 1.0 day^{-1} k_n rate based on the reduction of ammonia concentrations alone five times exceeds the rate derived from the nitrate data. As such, algal uptake of ammonia instead of nitrification may have caused the reduction in ammonia concentrations. Results from that analysis serve as the basis to reject nitrification at the point sources along the river.



Receiving Water Response to Nitrification at Wastewater Treatment Plant

The figure below shows the impact of nitrification process at the Metro Plant on the ammonium and nitrate concentrations in the Upper Mississippi River. Data from a water quality survey in 1976 prior to the installation of the nitrification process at the Metro Plant show much higher ammonium concentrations in the Upper Mississippi River below the Metro Plant. In fact, the receiving water ammonium concentrations were so high in 1976 that ammonia standards were violated while the concurrent nitrate concentrations were low. By 1988 when the nitrification process at the Metro Plant was in full operation, the low effluent ammonium concentrations resulted in much lower receiving water ammonium levels, thereby meeting the ammonia standard. Yet the nitrate concentration in the Upper Mississippi River sharply increased. This data indicates that while the total inorganic nitrogen concentrations between 1976 and 1988 are about the same, its composition is much different. Also it is not surprising that dissolved oxygen concentrations in 1988 are much improved over those in 1976, further confirming the water quality benefit of nitrification.



Methods of Deriving Stream Reaeration Coefficient

1. Use empirical formulas to assign stream reaeration coefficients
2. Conduct field studies to directly measure reaeration coefficients

3. Use a DO model to back calculate the reaeration coefficients

The following table presented by Rathbun (1998) may be used to provide an initial estimate of stream reaeration coefficients.

Summary of Stream Reaeration Equations

Equation	Range of Velocity V (m/s)	Range of Depth D (m)
Shallow-flow (Owens et al., 1964):		
(day^{-1} at 20 ^oC) = $6.92V^{0.73}D^{-1.75}$	0.040 - 0.558	0.12 - 0.75
Intermediate-depth (Churchill et al., 1962):		
(day^{-1} at 20 ^oC) = $5.01\ V^{0.969}D^{-1.673}$	0.564 - 1.52	0.646 - 3.48
Deep-flow (O'Connor and Dobbins, 1958):		
(day^{-1} at 20 ^oC)= $3.93\ V^{0.50}D^{-1.50}$	0.058 - 1.28	0.274 - 11.3

The attached figure from Rathbun (1998) shows empirical equations for stream reaeration coefficient as a function of river velocity and flow depth.

Dam Reaeration

A commonly used equation to quantify the oxygen input from dam reaeration is given by Butts and Evans (1983):

$$D_a - D_b = [1 - \frac{1}{1 + 0.116abH(1 - 0.034H)(1 + 0.046T)}]D_a$$

where

D_a = dissolved oxygen deficit above the dam (mg/L)

D_b = dissolved oxygen deficit below the dam (mg/L)

T = water temperature (^oC)

H = height through which water falls (ft)

a = 1.80 in clean water

= 1.60 in slightly polluted water

= 1.00 in moderately polluted water

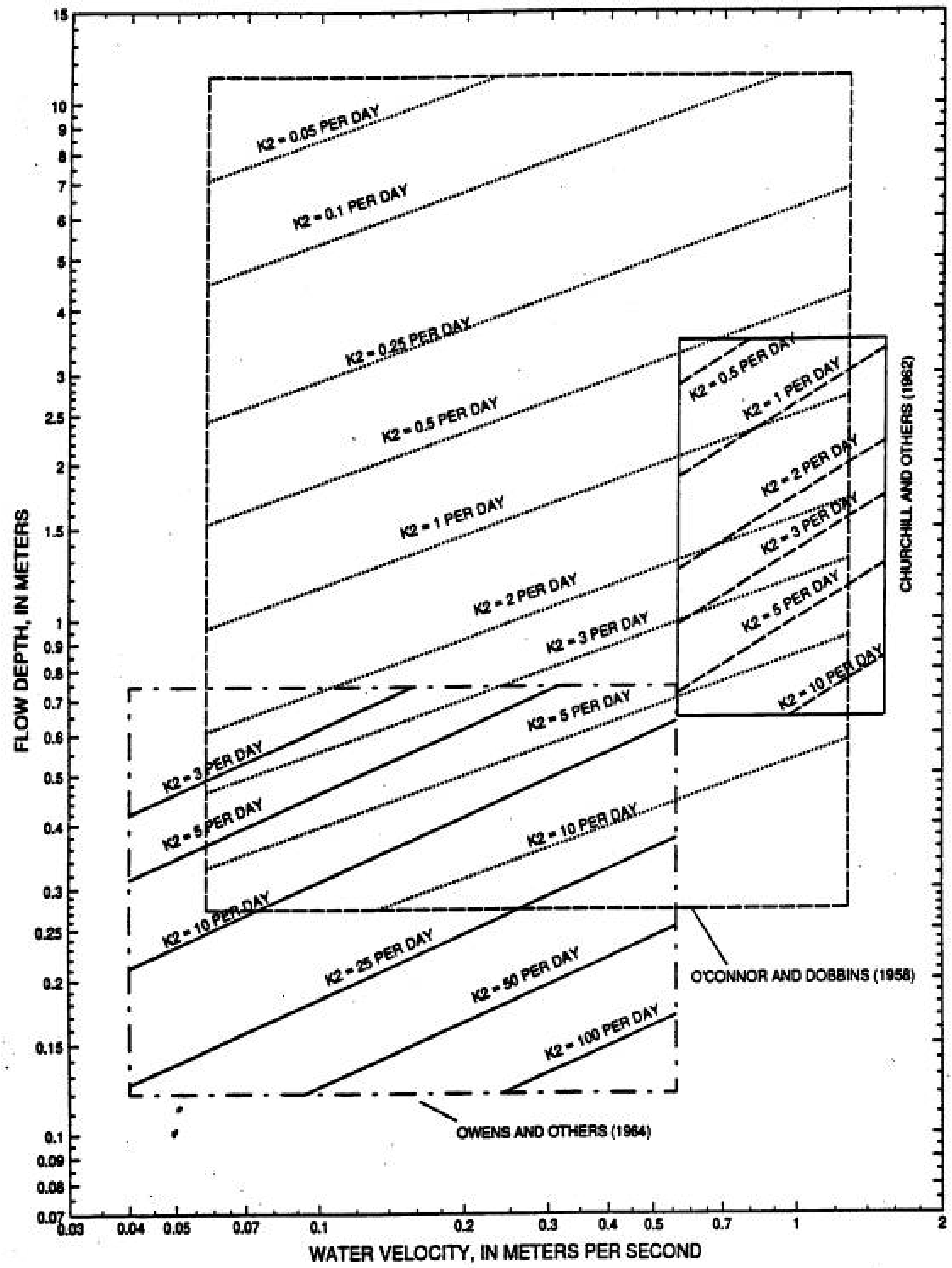
= 0.65 in grossly polluted water

b = 0.70 to 0.90 for flat, broad crested weir

= 1.05 for sharp crested weir with straight slope face

= 0.80 for sharp crested weir with vertical face

= 0.05 for sluice gates with submerged discharge



Reaeration on Lakes and Estuaries

One of the most used empirical equations for reaeration over a lake surface is by Banks and Herrera (1977):

$$K_L = 0.728W^{0.5} - 0.317W + 0.0372W^2$$

where K_L is mass transfer coefficient (m/day) and W is wind speed measured 10 m above the water surface (m/s).

In the eutrophication model for the Potomac Estuary, Thomann and Fitzpatrick (1982) used the following equation for the reaeration coefficient:

$$K_a = 3.93\frac{V^{0.5}}{D^{1.5}} + \frac{0.728W^{0.5} - 0.317W + 0.0372W^2}{D}$$

in which V is tidally averaged, longitudinal velocity (m/s), D is depth (m), and W is wind speed (m/s). Note that the first part of the above equation is the O'Connor-Dobbins Eq. (see Table 1) and the second part is the equation from Banks and Herrera. Other empirical equations for lakes and estuaries include Harleman et al. (1977), Hartman and Hammond (1985), Broecher et al. (1978), and Wanninkhof et al. (1991).

Reaeration in Small Streams

The reaeration process is particularly important in the DO budget. There are numerous documents, which state that the Tsivoglou equation is particularly suitable for small and shallow streams (McCutcheon, 1989; St. John et al., 1984; Thomann and Mueller, 1987). In several WLA guidance manuals, the EPA (1986, 1990, 1991, and 1995) also recommends the use of the Tsivoglou equation for small and shallow streams. The equation is most appropriate for streams with depths up to 2 - 3 ft and velocities between 0.3 ft/sec and 0.6 ft/sec (EPA, 1984). The following table presents a comparison of predicted (using the Tsivoglou equation) and observed reaeration coefficients on small streams in Wisconsin (Grant, 1976). Again, the Tsivoglou equation is accurate when compared with the data.

Quantifying correct reaeration coefficients for the receiving water is a crucial step in BOD/DO modeling for wasteload allocations (WLA) and is illustrated in the following case study. In a WLA modeling study of Shirtee Creek in Alabama in 1991, the Alabama Department of Environmental Management (ADEM) selected the Langbien and Durum (1967) Equation for stream reaeration in the QUAL2E model. The QUAL2E model of Shirtee Creek was calibrated with two sets of data collected in August 1989 and October 1990. The calibrated model was then run under the 7-day 10-year low flow conditions to develop effluent $CBOD_5$ limits for two point source dischargers: the City of Sylacauga wastewater treatment plant and Avondale Mills (a textile mill).

To meet the 5-mg/L daily average dissolved oxygen standard for Shirtee Creek, ADEM developed stringent $CBOD_5$ limits for the point sources. To challenge these limits, the consultant for Avondale Mills used the STREAM (see notes on this code) model and conducted two stream surveys in the winter of 1991 and August 1991 to support their modeling analysis. The consultant's STREAM model was able to reproduce the 4 sets of field data (two by ADEM and two by the consultant). However, the consultant used the Tsivoglou Equation to calculate the stream reaeration coefficient while ADEM used the Langbien and Durum Equation. In using the calibrated STREAM model, the consultant predicted much less stringent effluent $CBOD_5$ limits for the point source discharges.

Reaeration Coefficients (day^{-1}) at 25 ^{o}C for Small Streams[1]

	Measured	Tsivoglou's Eq.
Black Earth Creek	8.46	7.8
Mud Creek Tributary	10.7	4.2
Dodge Branch	33.1	34.6
Isabelle Creek	14	-
Madison Effluent Channel	2.06	4.1
Mill Creek	3.31	2.2
Honey Creek	18.4	27.4
West Branch Sugar River	42.5	36.4
Koshkonong Creek	6.09	4.8
Badger Mill Creek	7.98	9.1

1. from Grant (1976) on Ten Small Streams in Wisconsin.

The reaeration coefficients used in these two modeling analyses are summarized in Table 3. The reaeration coefficients differ significantly between the two equations, thereby leading to contrasting assessments of the effluent CBOD limits. The foremost question then is which equation is more appropriate for Shirtee Creek? First, a literature review on surface mass transfer and reaeration coefficients in streams indicated that the Tsivoglou equation is more suitable for small and shallow streams like Shirtee Creek. The EPA (1971) summarized reaeration coefficient as a function of depth (see figure above). In the August 1989 survey, the water depth is less than 2 ft, often even below 1 ft in the upstream reaches, making the average stream velocity close to 0.5 ft/sec. The reaeration coefficients, ranging between 4 day^{-1} to 10 day^{-1}, are reasonable based on the average stream velocity (see figure from Rathbun). The reaeration coefficient values calculated by the Tsivoglou equation are either within or very close to this range, with the exception of one value in the reach between mile 0.75 and 2.02 where the steep channel slope contributes to a high value. [Note that this reach is not a critical reach as far as the dissolved oxygen levels are concerned.] On the contrary, the values calculated by Langbien and Durum equation are considerably lower than the literature values; they are off by an order of magnitude.

A review of the Langbien & Durum equation by Covar (1976) questioned the merit of using considerably dissimilar data to derive a single equation. Langbien and Durum (1967) used field data of O'Connor and Dobbins (1958) and of Churchill et al. (1962) with the laboratory data of Krenkel and Orlob (1963) and of Streeter et al. (1936). These data cover a wide range of conditions and should have been used separately to develop equations for streams with conditions similar to those used in Langbien and Durum's derivation.

Table 3. Comparison of Reaeration Coefficients (day^{-1}) at 20 °C

Mile Point	Aug. 1991[1]	March 1991[1]	Aug. 1989[1]	Aug. 1989[2]	Oct. 1990[2]
0.0-0.53	5.074	6.266	5.392	9.77	1.82
0.53-0.75	9.886	11.79	14.62	0.76	0.1
0.75-2.02	14.94	17.05	17.45	0.76	2.25
2.02-3.95	8.427	9.222	9.181	0.76	1.44
3.95-6.07	4.897	3.598	3.072	0.76	1.44

1. Tsivoglou Eq.
2. Langbien and Durum Eq.

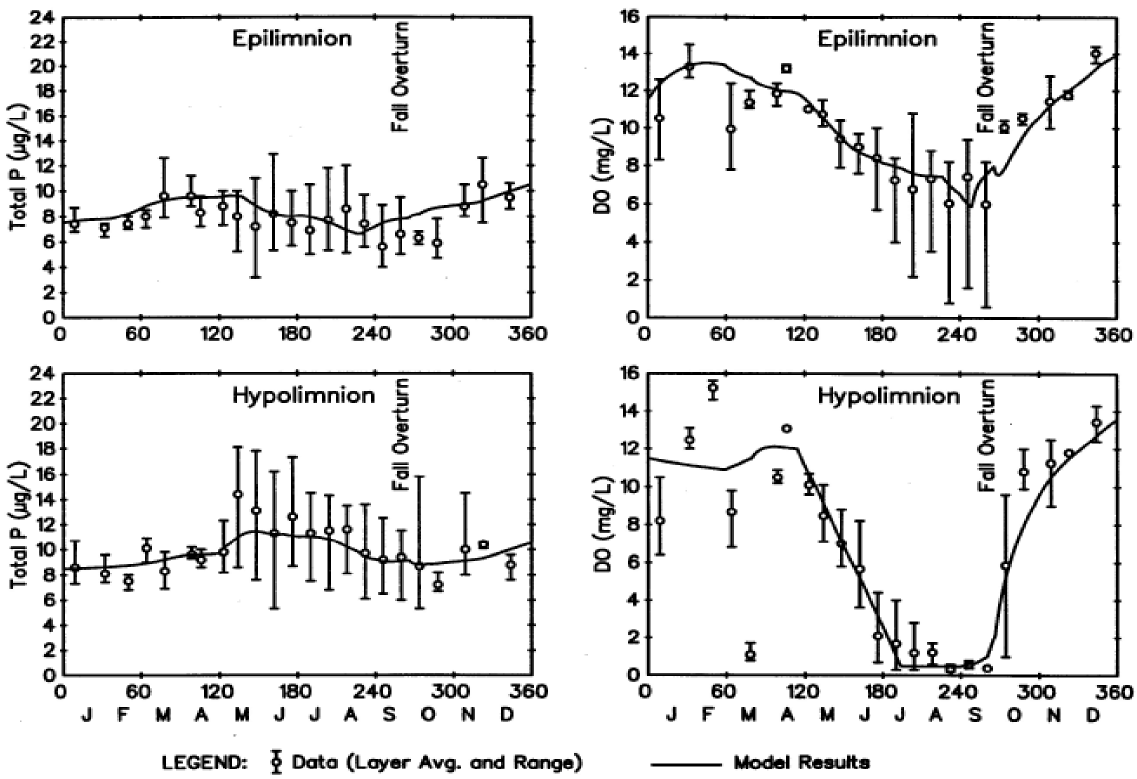
Back Calculate Reaeration Coefficient Using a DO Model

A good example is shown in Platte Lake, Michigan. The lake water column is divided into two layers (epilimnion and hypolimnion) due to strong vertical stratification of temperature and dissolved oxygen during the summer months. The processes in the epilimnion are inflow from the watershed, outflow at the outlet, vertical exchange with the hypolimnion, and surface reaeration. The processes in the hypolimnion include exchange with the epilimnion and oxygen consumption in the hypolimnion due to sediment oxygen demand and algal respiration. Note the hypolimnetic oxygen consumption is determined using the methodology by Chapra and Canale (1991). The dissolved oxygen mass loading rates via inflow and outflow are independently quantified using measured flows and DO concentrations. The vertical diffusion coefficient, which characterizes the exchange process between the two layers, is quantified using the gradient method (described in Mass Transport notes) with temperature data. The only coefficient left to be determined is reaeration because all other processes have already been independently calculated.

This DO model is then used to calibrate the reaeration coefficient by reproducing the DO concentrations in the epilimnion and hypolimnion.

The attached figure shows the model results vs. data in both layers for 1991. This approach is similar to that used by Gelda et al. (1996) for Onondaga Lake in Syracuse, NY, with the exception that a two-layer model is used for Platte Lake to account for the significant vertical stratification of temperature and dissolved oxygen. While the calculation for Onondaga Lake is only for a period of 35 days following the fall overturn, the Platte Lake simulation is performed for an entire year. The calibrated reaeration coefficient for Platte Lake is 0.03 day^{-1} for the year until the fall overturn. A higher value of 0.15 day^{-1} is needed following the fall overturn to account for the sharp rise of dissolved oxygen concentrations in the lake. [Note that Gelda et al. (1996) calibrate a reaeration coefficient of 0.055 day^{-1} for Onondaga Lake following the fall overturn.] Additional tuning with wind speed dependent reaeration rates on a time-variable basis would improve the match with the data.

The above calculation, called the whole lake technique, is based on measured dissolved oxygen concentrations in the water column over time. This analysis is particularly appealing and useful because it is nonobtrusive (Chapra, 1997); that is, it does not require using tracers and dyes, characteristic of a comprehensive field study. Most often the reaeration process is the dominating process in the dissolved oxygen budget of the water column (in Platte Lake, the epilimnion). Because the model results are sensitive to varying the reaeration coefficient, this estimating technique becomes even more attractive.



Saturated DO Levels

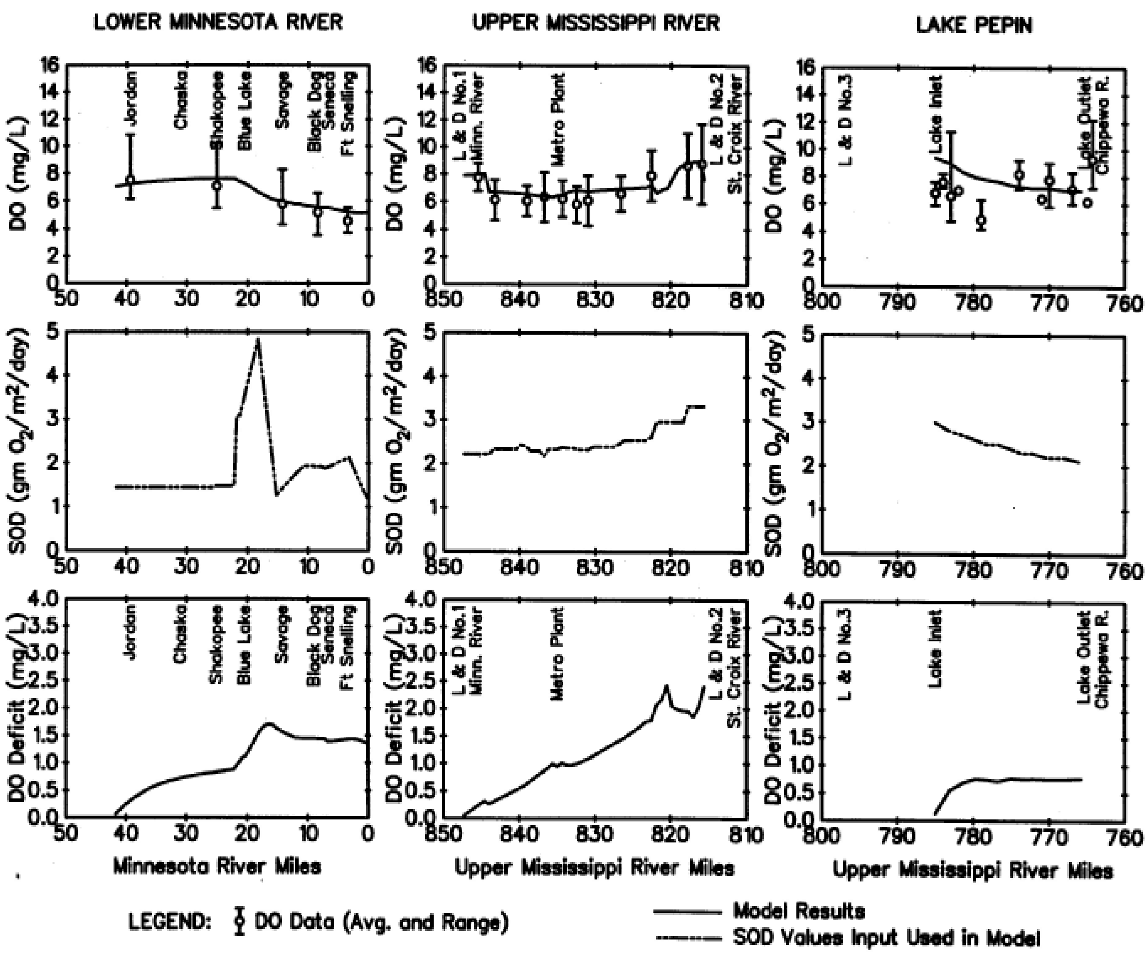
A highly accurate equation is recommended by EPA (1995):

$$C_{sf} = \frac{468}{31.5 + T}$$

where C_{sf} is the freshwater DO saturation concentration in mg/L and T is water temperature in $^{\circ}$C. This equation is accurate to within 0.03 mg/L as compared with the Benson-Krause equation on which the Standard Methods tables are based (McCutcheon, 1985). Other factors affecting the DO saturation level are salinity and altitude. See Lung (2001) for quantifying their effects.

Sediment Oxygen Demand (SOD)

Model Calibration to Determine SOD: Calibrating the SOD values requires that other processes in the dissolved oxygen budget be accurately quantified via an independent data analysis. The attached figure shows the sediment oxygen demand and its impact on the receiving water dissolved oxygen profiles in the Lower Minnesota River, the Upper Mississippi River, and Lake Pepin (all in the state of Minnesota). The first row in that figure for each of the three study sites is the model calculated DO profile vs. field data collected in 1988. The calibrated SOD values in each case are displayed in the second row of panels. In general, SOD values between 2 and 3 gm $O_2/m^2/day$ are commonly observed following the discharge of municipal wastewaters. Note the excessively high value of 5 gm O_2/m^2 /day immediately below the Shakopee Plant discharge on the Minnesota River. Also note that the SOD progressively increases in the Upper Mississippi River toward Lock & Dam No. 2 as a result of yearly deposits accumulating behind the dam. On the other hand, the SOD values in Lake Pepin decrease slightly in the downstream direction. Because Lake Pepin is a natural impoundment on the Upper Mississippi River, there is no dam at the lake outlet to trap oxygen consumption material. The third row of panels in that figure presents the dissolved oxygen deficit in mg/L resulting from the SOD along each of the three systems.



Field Measurement of SOD:

1. Using in situ chambers
2. Sediment core extraction and lab measurement

See Hatcher, 1986; Murphy and Hicks, 1986; and Whittemore, 1986 for field techniques.

The procedure for incorporating the SOD in dissolved oxygen modeling is either to measure or calibrate the SOD as an areal flux of oxygen to the sediment and use that consumption rate as a sink in the mass balance models. Where the contemplated control measures would not affect the SOD, this procedure is perfectly justifiable (Di Toro et al., 1990). However, most control alternatives affect the supply of organic particles to the sediment. Hence an important issue to be addressed in many water quality modeling studies is the effect this reduction has on the resulting SOD. Today, modeling techniques are available to predict the reduction of the SOD over time following pollution abatement. An engineering approach is to use a modeling framework that explicitly couples particulate organic carbon deposition and sediment oxygen demand, which is based on the landmark paper by Di Toro et al. (1990). More information is available in the notes for the eutrophication topic later.