

A Review of Dissolved Oxygen and Biochemical Oxygen Demand Models for Large Rivers

Husnain Haider¹, Waris Ali² & Sajjad Haydar³

1. Assistant Professor, Institute of Environmental Engineering & Research (IEER), Univ. of Engg. & Tech. Lahore, Pakistan, T:092-042-99029248, F: 092-042-99029415, E: hhaider@uet.edu.pk, haider42@yahoo.com
2. Professor, Institute of Environmental Engineering & Research, Univ. of Engg. & Tech. Lahore, Pakistan, E: warisali@uet.edu.pk
3. Professor, Institute of Environmental Engineering & Research, Univ. of Engg. & Tech. Lahore, Pakistan, E: sajjad@uet.edu.pk

Abstract

Development and modifications of mathematical models for Dissolved Oxygen (DO) are reviewed in this paper. The field and laboratory methods to estimate the kinetics of Carbonaceous Biochemical Oxygen Demand (CBOD) and Nitrogenous Biochemical Oxygen Demand (NBOD) are also presented. This review also includes recent approaches of BOD and DO modeling beside the conventional ones alongwith their applicability to the natural rivers. The most frequently available public domain computer models and their applications in real life projects are also briefly covered. The literature survey reveals that currently there is more emphasis on solution techniques rather than understanding the mechanisms and processes that control DO in large rivers. The DO modeling software contains inbuilt coefficients and parameters that may not reflect the specific conditions under study. It is therefore important that the selected mathematical and computer models must incorporate the relevant processes specific to the river under study and be within the available resources in term of data collection.

Key Words: Dissolved Oxygen Modeling, Biochemical Oxygen Demand, Sediment Oxygen Demand, Reaeration, Photosynthesis, Rivers

1. Introduction

Dissolved Oxygen (DO) is one of the most important parameter reflecting the ecological health of a river and is controlled by a number of physical, chemical and biological processes such as, settling and oxidation of Carbonaceous Biochemical Oxygen Demand (CBOD) and Nitrogenous Biochemical Oxygen Demand (NBOD), sediment oxygen demand, photosynthesis and respiration and atmospheric reaeration [1]. When the processes related to the consumption of DO exceed the processes contributing to the DO in the river, the DO levels can reach to very low values. Low DO levels or anaerobic conditions can kill fish and unbalance the aquatic ecosystems [2].

Mathematical models are extensively used to develop appropriate wastewater control strategies to maintain adequate DO levels in the rivers. The selection of an appropriate model depends on river specific water quality processes, data requirements

for calibration and verification and availability of technical and financial resources. The review of the literature on DO and Biochemical Oxygen Demand (BOD) modeling of rivers reveals that new approaches and techniques developed for hypothetical streams or under specific field conditions are difficult to apply to a particular situation due to excessive data requirements and thus are not universally applicable. The main purpose of such approaches is sometimes to introduce the use of advanced mathematical techniques and computer applications without providing understanding of stream specific water quality processes.

This paper presents a review of the BOD and DO models being used in the development of water quality management programs for large rivers receiving high pollution loads from mega cities with a view to provide a better understanding of the associated processes so that the strategies to control dissolved oxygen are formulated on rational basis.

DO Modeling in Rivers

Water quality in a river changes due to the physical transport, diffusion, and physical, chemical and biological processes. All of these processes can be described by the following non-steady state three dimensional (extended) mass transport equation [3];

$$\underbrace{\frac{\partial c}{\partial t}}_{\text{Change in Conc. with time}} + \underbrace{u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + w \frac{\partial c}{\partial z}}_{\text{Advection}} = \underbrace{\frac{\partial}{\partial x} \left(\epsilon_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(\epsilon_y \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left(\epsilon_z \frac{\partial c}{\partial z} \right)}_{\text{Dispersion}} + \underbrace{r(c, p)}_{\text{Reaction}} \quad (1)$$

where c is the mass concentration of the substance; t is the time; x , y and z are the coordinates in spatial frame; u , v and w are the corresponding velocity components in x , y and z directions; r is the rate of change in the substance concentration due to the physical, chemical and biological processes as a function of concentration “ c ” and model parameters “ p ”; and ϵ_x , ϵ_y and ϵ_z are the turbulent diffusion coefficients in x , y and z dimensions

For the large rivers, where length is very large as compared to width and depth, Eq (1) is commonly used as a one-dimensional advection–dispersion equation and can be written as [4-5];

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left(D_L \frac{\partial C}{\partial x} \right) + r(C, P) \quad (2)$$

where U is the cross-sectional average flow, D_L is the longitudinal dispersion coefficient, C is the vector of averaged concentrations of the constituents based on average cross-section, $r(C, P)$ is the change of concentrations due to physical, chemical and biological processes

If dispersion is neglected for a river segment, Eq (2) can be written as [5];

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = r(C, P) \quad (3)$$

The DO concentration is a function of numerous physical and biochemical processes shown in Fig 1. The principal inputs affecting the DO are municipal and industrial waste discharges, partially combined sewer overflows and separate sewer discharges. The important DO related reactions include: i) Reaeration from the atmosphere, ii) Photosynthesis oxygen production, whereas the sinks of DO include; i) Oxidation of CBOD, ii) Oxidation of NBOD, iii) Oxidation demand of sediments of water body, SOD and iv) Use of oxygen for respiration by aquatic plants. Thus the reaction term $r(C, P)$ in the above equations (1 – 3) is;

$$R(C, P) = \text{Atmospheric Reaeration} - \text{CBOD Oxidation} - \text{NBOD Oxidation} - \text{Sediment Oxygen Demand} + \text{Photosynthesis by the aquatic plants} - \text{Respiration by the aquatic plants} \quad (4)$$

The changes in concentration of DO (C) due to all the sources and sinks can thus be mathematically presented as [1, 6];

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = K_a (C_s - C) - K_d L - K_n L_n - S + P - R \quad (5)$$

where C_s is the concentration of dissolved oxygen at saturation, the actual concentration of DO can be presented as C in the river, K_d is the deoxygenation rate coefficient of carbonaceous organic matter, concentration of CBOD in the river is L , K_n is the NBOD deoxygenation rate coefficient, the concentration of NBOD is L_n , P and R are the photosynthesis and respiration in the river respectively, S is the oxygen consumption by the sediment and the distance in the river along the direction of flow is x .

The change in DO at any location with respect to time is zero under steady-state conditions, i.e; $\partial C / \partial t = 0$, and thus Eq (5) becomes [1];

$$U \frac{dC}{dx} = K_a (C_s - C) - K_d L - K_n L_n - S + P - R \quad (6)$$

The only sink of DO considered in the classical Streeter-Phelps model [8] is CBOD and reaeration from the atmosphere as the only source of oxygen. Therefore, Eq (6) becomes;

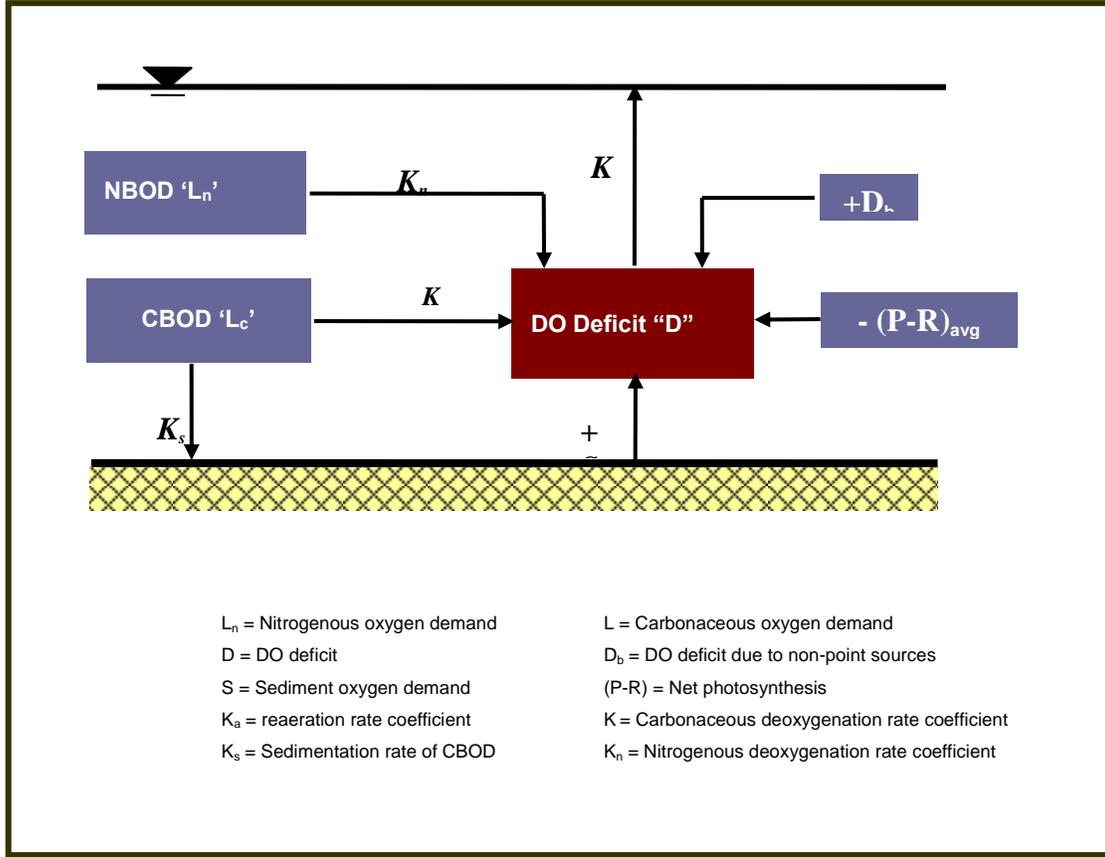


Fig 1: DO sources and sinks in a surface water body [7]

$$U \frac{dC}{dx} = K_a (C_s - C) - K_d L \quad (7)$$

Eq (7) can be conveniently solved by expressing it in DO deficit terms "D" as;

$$D = C_s - C \quad (8)$$

Now atmospheric re-aeration has become a sink, whereas CBOD will work as a source for DO deficit in the river thus Eq (8) becomes;

$$U \frac{dD}{dx} = K_d L - K_a D \quad (9)$$

Eq (9) can be solved in terms of dissolved oxygen deficit "D" as [1];

$$D = D_0 e^{-K_a \frac{x}{U}} + \frac{K_d L_0}{K_a - K_d} (e^{-K_d \frac{x}{U}} - e^{-K_a \frac{x}{U}}) \quad (10)$$

where the initial DO deficit due to mixing of wastewater with the DO saturated river water is D_0 and L_0 is the corresponding CBODU. The term " x/U " is essentially the time of travel " t " of the river flow and thus Eq (10) becomes;

$$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_d} (e^{-K_d t} - e^{-K_a t}) \quad (11)$$

Quinn & Jacobs (2005) used Streeter-Phelps Eq (11) to determine critical DO levels to determine water quality management strategies in the San Joaquin River [9]. Jha & Ojha (2005) also used Eq (11) to simulate DO in River Kali, India [10].

The particulate form of CBOD is removed by sedimentation. Therefore, including the effect of settling of CBOD in equation (11) the resultant equation is;

$$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_r} (e^{-K_r t} - e^{-K_a t}) \quad (12)$$

where K_r is the CBOD removal rate coefficient as sum of deoxygenation rate coefficient (K_d) and rate of settling (K_s).

In the overall balance of dissolved oxygen in any river receiving wastewater, the process of nitrification should always be considered in the modelling and management of DO of the large rivers. If NBOD is also included in Eq (12) the modified form of Streeter-Phelps equation can be written as [1];

$$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_r} (e^{-K_r t} - e^{-K_a t}) + \frac{K_n L_{n0}}{K_a - K_n} (e^{-K_n t} - e^{-K_a t}) \quad (13)$$

where L_o is the CBODU as already described and L_{no} is the ultimate NBODU in the river after mixing of the wastewater. The dissolved oxygen deficit determined by using Eq (11) and (13) can be brought into the terms of DO concentration with the help of Eq (8). Haider & Ali (2010) successfully used Eq (12) and (13) to model DO in a River Ravi in Pakistan with highly variable flows [11]. The study results revealed a very small value of Sum of Square of Residuals (SSR) of 1.5 with Eq (13) as compared to Eq (12) (i.e., for overall BOD with SSR value of 10) when the simulation results were compared with the field measurements.

The other sources and sinks of dissolved oxygen (i.e., P&R and SOD) at any time “t” given in Eq (6) can be solved individually. The solutions of all of these sources and sinks can be summed to yield the overall solutions in terms of DO deficit as [1, 6-7];

$$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_r} (e^{-K_r t} - e^{-K_a t}) + \frac{K_n L_{n0}}{K_a - K_n} (e^{-K_n t} - e^{-K_a t}) + \frac{S}{K_a H} (1 - e^{-K_a t}) + \frac{(R - P)}{K_a} (1 - e^{-K_a t}) \quad (14)$$

Song and Brown (1990) used modified form of Streeter-Phelps Eq (14) to assess the uncertainty with correlated inputs using sensitivity analysis, First Order Error Analysis (FOEA) and Monte Carlo Simulation (MCS) on a hypothetical stream [12]. Canale et al. (1995) used equation (14) to model DO in river Seneca, New York and found reasonable results [13].

Some of the commonly used BOD and DO models are presented in Table 1 [14]. Jha et al. (2007) developed a refined model to simulate BOD and DO from both point and non-point sources for Kali River, India (Eq 6, Table 1) [14]. Their model excluding non-point sources is similar to the model proposed by Camp (1963) (Eq 1, Table 1) [15] and excluding SOD and K_s is similar to classical Streeter – Phelps Eq (11). NBOD in their study was not considered separately as included in Eq (13 & 14). They observed very strong coefficient of correlation of 0.996 for calculated DO and observed DO in the field. One of the reasons for this strong correlation could be the prevailed anaerobic conditions in about 50 % of the reach, therefore, for zero DO no comparison can be made between observed and model values.

NBOD has not been considered in any of the models listed in Table 1, whereas, it could be one of the most important sink of DO particularly in polluted rivers. NBOD is almost equal to CBOD in raw wastewaters [1,16]. Non-point source discharges can also have sufficient NBOD loads, particularly, if they have passed through agricultural lands [2].

Surface water ecosystems are sometimes invaded by rare species such as zebra mussels (*Dreissena polymorpha*, Pallus). These attached filamentous organisms are commonly known as “sewage fungus” and grow mostly in channels receiving raw sewage. Zebra mussels is one of the most famous freshwater organisms and oxygen depletion due to them is known as Zebra mussels Oxygen Demand (ZOD). Their population is found in abundance when sufficient phytoplankton (i.e., food source) and rocks to provide attachment are present [17]. The highest ZOD due to violating minimum DO standards of 4mg/L was observed in Seneca River due to the presence of favorable environment for growth of Zebra mussel [18].

Table 1: BOD and DO models for rivers

Eq #	Name	BOD Model	DO Model
1.	Camp (1963) [15]	$L = L_0 e^{-K_d t}$	$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_d} (e^{-K_d t} - e^{-K_a t})$
2.	Gundelach & Castillo (1976) [22]	$L = L_0 e^{-(K_d + K_s)t} + \frac{B}{(K_d + K_s)} (1 - e^{-(K_d + K_s)t})$	$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - (K_d + K_s)} (e^{-(K_d + K_s)t} - e^{-K_a t}) + \frac{K_d B}{K_a (K_d + K_s)} (1 - e^{-K_a t}) - \frac{K_d B}{(K_a - (K_d + K_s))(K_d + K_s)} (e^{-(K_d + K_s)t} - e^{-K_a t}) - \frac{(P - R)}{K_a} (1 - e^{-K_a t})$
3.	Bhagrava (1983) [23]	$L = L_0 e^{-K_d t} + (1-p)[L_1 e^{-K_d t} + L_2 e^{-K_d t_1} + L_3 e^{-K_d t_2} + \dots + L_n e^{-K_d t_{(n-1)-t}}] + \left[L_1 \left(1 - \left(\frac{1}{T} \right) t_{0-T} \right) + L_2 \left(1 - \left(\frac{1}{T} \right) t_{1-(1+T)} \right) \right] p + L_3 \left(1 - \left(\frac{1}{T} \right) t_{2-(2+T)} \right) + \dots + L_n \left(1 - \left(\frac{1}{T} \right) t_{n-1-(n-1+T)} \right)$	$\frac{dD}{dt} = -K_d \left[L_0 e^{-K_d t} + (1-p)[L_1 e^{-K_d t} + L_2 e^{-K_d t_1} + L_3 e^{-K_d t_2} + \dots + L_n e^{-K_d t_{(n-1)-t}}] + p \left[L_1 \left(1 - \left(\frac{1}{T} \right) t_{0-T} \right) + L_2 \left(1 - \left(\frac{1}{T} \right) t_{1-(1+T)} \right) \right] + L_3 \left(1 - \left(\frac{1}{T} \right) t_{2-(2+T)} \right) + \dots + L_n \left(1 - \left(\frac{1}{T} \right) t_{n-1-(n-1+T)} \right) \right] + K_a D$
4.	Jolanki (1997) [24]	$L(l) = L_0 F^{\beta_1} + \frac{(L_d + B\phi(l))}{\beta_1} [1 - F^{\beta_1}]$, where; $F = \frac{Q_u}{Q_u + q_1 l}$; $\beta_1 = 1 + K_d \phi(l) = \frac{q_1}{v}$	$C_{ox}(l) = \left[\frac{(L_d + B\phi(l))}{\beta_1} - L_0 \right] \frac{K_d}{K_a - K_d} (F^{\beta_1} - F^{\beta_2}) + C_{ox_0} F^{\beta_2} + \left[C_{ox_{sat}} (\beta_2 - 1) - \frac{L_d + B\phi(l)}{\beta_1} (\beta_1 - 1) + \phi(l)(P - R) + C_{ox_d} \right]$ where; $\beta_2 = 1 + K_d \phi(l)$
5.	Maldeniv et al. (2005) [25]	$L = L_0 e^{-(K_d + K_s)t} + S_d \frac{(1 - e^{-(K_d + K_s)t})}{(K_d + K_s)}$	$D = D_0 e^{-K_a t} + \frac{K_d L_0}{K_a - K_r} (e^{-K_r t} - e^{-K_a t}) + \frac{K_n L_{n0}}{K_a - K_n} (e^{-K_n t} - e^{-K_a t}) + \frac{S}{K_a H} (1 - e^{-K_a t}) + \frac{(R - P)}{K_a} (1 - e^{-K_a t}) + \frac{K_d S_d}{K_r K_a} (1 - e^{-K_a t}) - \frac{K_d S_d}{K_r (K_a - K_r)} (e^{-K_r t} - e^{-K_a t})$
6.	Jha and Ojha (2007) [14]	$L = L_0 e^{-(K_d + K_s)t} + \frac{L_d q l (1 - e^{-(K_d + K_s)t})}{(K_d + K_s)(Q_u + q l)} + \frac{B Q_u (1 - e^{-(K_d + K_s)t})}{(K_d + K_s)(Q_u + q l)}$	$D = D_0 e^{-K_a t} + \frac{K_d Q_u L_0 (e^{-(K_d + K_s)t} - e^{-K_a t})}{(K_a - (K_d + K_s))(Q_u + q l)} + \frac{K_d Q_u L_d q l (1 - e^{-K_a t})}{K_a (K_d + K_s)(Q_u + q l)^2} + \frac{K_d Q_u L_0 (e^{-(K_d + K_s)t} - e^{-K_a t}) L_d q l}{(K_a - (K_d + K_s))(K_d + K_s)(Q_u + q l)^2} + \frac{K_d Q_u^2 B (1 - e^{-K_a t})}{K_a (K_d + K_s)(Q_u + q l)^2} + \frac{K_d Q_u^2 B (e^{-(K_d + K_s)t} - e^{-K_a t})}{(K_a - (K_d + K_s))(K_d + K_s)(Q_u + q l)^2} + \frac{D_d q l (1 - e^{-K_a t})}{K_a (Q_u + q l)} - \frac{(P - R) Q_u (1 - e^{-K_a t})}{K_a (Q_u + q l)}$

where L is the BOD in the water at any point downstream of a river, mg/L; L_0 is the initial BOD in the river below the wastewater discharge, mg/L; K_d is the biochemical decomposition rate coefficient of organic matter, day⁻¹; K_a is the reaeration rate coefficient, day⁻¹; t is the travel time in the river, days; t_{1-p} , t_{2-t} , ... + $t_{(n-1)-t}$ is the travel time of different reaches of the river; D is the DO deficit of the river, mg/L; p is the fraction of settleable BOD; L_d is the distributed source, mg/L; Q_u is the flow rate at the start of the river study reach, m³/s; q is the lateral rate of inflow, m³/s; A is the area of the wetted river cross-section, m², l is the downstream distance along the river length, m; v is the average velocity of the flow, m/s; C_{ox} is the dissolved oxygen concentration in the river, mg/L; $C_{ox,0}$ is the initial DO concentration after mixing of the wastewater, mg/L; $C_{ox,d}$ is the concentration of DO in the lateral inflow to the river, mg/L and $C_{ox,sat}$ is the DO at saturation concentration, mg/L.

Source: Jha et al. (2007) [14]

Gelda et al. (2001) developed and calibrated a dynamic 2-D DO model based on Zebra Mussels Oxygen Demand (ZOD) for a 2.3Km stretch of Seneca River, N.Y, USA [19]. They also described the impact of zebra mussel on DO and modified the CE-QUAL-W2 for their study [20]. For DO modeling including ZOD the following equation was used [21];

$$\frac{dD}{dt} = \frac{K_L(C_s - C_{\text{surface}})}{H_s} + (P - R) - (K_c \text{CBOD}_u) - (K_n \text{NBOD}) - (S + Z) \left(\frac{W_t - W_b}{A} \right) \quad (15)$$

where H_s is surface layer thickness, Z is ZOD, W_t is the width of the channel at the top of the segment, W_b is the width of the channel at the bottom of the segment, and A is the cross-sectional area of the segment. The modeling results revealed that ZOD is the most dominant source of DO depletion in the river as compared to the other sinks [19].

3. Carbonaceous Biochemical Oxygen Demand “CBOD”

The carbonaceous Organic Matter (OM) present in the wastewater and in the rivers acts as an energy source of heterotrophic micro-organisms. During this process the organisms utilize oxygen to decompose the organic matter present in the wastewater; this amount of oxygen utilized is known as Carbonaceous Biochemical Oxygen Demand (CBOD). Particulate CBOD can settle in low velocity regions in the rivers and streams and can re-suspend during the high flow seasons when river velocities are more than the scouring velocities. It is always important to distinguish between CBOD5 and BOD5 for river water quality modeling by using a nitrification suppressant. The process can be modeled as the following first order reaction in the rivers [1];

$$\frac{dL}{dt} = -KL \quad (16)$$

where L is the oxidizable carbonaceous OM remaining in the BOD bottle, K is the rate of oxidation of CBOD in the bottle and t is the incubation time (Fig 2). The integral form of Eq (16) is;

$$L = L_0 e^{-Kt} \quad (17)$$

where L_0 is the amount of carbonaceous organic matter present at the start of the BOD test and is designated as ultimate CBOD (CBODU).

It is difficult to determine CBODU every time for estimating the total pollutional load entering in the river, therefore, its common to develop a relationship between y_5 (CBOD5) and L_0 in terms of a ratio “ f ” [1];

$$f = \frac{L_0}{y_5} = \frac{1}{(1 - e^{-K5})} \quad (18)$$

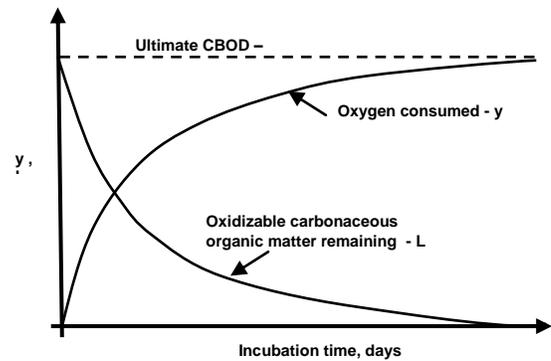


Fig 2: First order CBOD progression [1]

To determine L_0 and K , long-term BOD data are analysed. Method of least square and Thomas Method are the most common ones used for the purpose [13, 26-27]. Former involves fitting of a curve in data points, whereas, the latter one is based on similarity of two series function [28].

The CBOD in particulate form first converts into dissolved form and then decomposes through bacterial oxidation so its rate of removal is slower than the dissolved CBOD. Moreover, CBOD of treated effluents also decomposes at a slower rate, as the secondary treated effluents become more resistant to biodegradation due to the utilization of readily biodegradable organic matter first. Therefore, if total CBOD is subdivided into slowly biodegradable BOD and readily biodegradable BOD Eq (18) can be further written as [29];

$$\frac{L_0}{y_5} = \frac{1}{1 - [(1 - \alpha)e^{-5K_{fbod}} + \alpha e^{-5K_{sbod}}]} \quad (19)$$

where, α is the ratio between slowly bridgeable and readily biodegradable BOD and K_{sbod} and K_{fbod} are the respective rates.

Some researchers have tried to study the order of BOD reaction other than 1st order decay. Young and Clark (1965) expressed the second order BOD equation in the following form;

$$L = \frac{L_o}{1 + K_2 L_o t} \quad (20)$$

where K_2 is the 2nd order BOD rate constant. In terms of BOD exerted “y” from the experimental data Eq (20) becomes;

$$y = \frac{K_2 L_o^2 t}{1 + K_2 L_o t} \quad (21)$$

K_2 and L_o in the above equations can be determined by using method of least square with Eq (21) and the laboratory values of y Vs. t [30].

Adrian et al (1999) and Hewitt et al. (1979) expressed a 3/2 order equation for BOD exerted as [31-32];

$$y = L_o = \frac{4}{K_{3/2}^2 (T - t)^2} \quad (22)$$

where $K_{3/2}$ is the three-half order BOD rate constant. However, none of the above mentioned equation expressing CBOD with orders other than first order has been used in real time water quality modeling studies. To the present time, for most of the domestic wastewaters the first order Eq (17) gives reliable estimates for both the wastewaters and river [10,13,14,25,33].

A factor to incorporate the effect of settling was first added in first order BOD rate by Velz and Gannon (1962) [34]. This factor was not rational, as Type 1 and Type –II settling occur only for a short distance from the outfall in the rivers [35]. Bhargava (1986 a&b) divided the BOD of untreated wastewaters into settleable and non-settleable portion from a single point source outfall and estimated the dissolved and particulate portion by using Imhoff cones [36-37]. Tyagi et al. (1999) further included the effect of variability of the source strength with respect to time [35]. Later Bhargava (2008) developed a composite model considering the effect

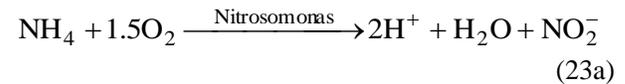
of settleable BOD for a hypothetical river receiving wastewater from multiple outfalls located at different assumed distances as a function of the time required to achieve removal of settleable BOD [38]. However, its application for DO management of a polluted river with variable levels of treatment can not be greatly justified as settleable BOD gets removed during primary treatment.

Most of these models however have not been applied on actual natural systems in the field. The calibration and verification of such models also seems difficult, particularly under limited resources.

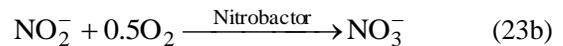
4. Nitrogenous Biochemical Oxygen Demand “NBOD”

The first stage CBOD is followed by a second stage that constitutes the oxidation of the nitrogenous compounds that may be present in the wastewater or river water. This is known as Nitrogenous BOD (NBOD) [1]. NBOD usually starts after 7 to 10 days in the BOD bottle due to insufficient population of nitrifiers. Typically, carbonaceous micro-organisms double their population in 20 to 45 min, whereas, nitrifiers (i.e., nitrosomonas and nitrobactor) take 18 to 36 hours to reach to double of their initial population [39].

The NBOD results from the oxidation of the ammonia to nitrites and then from nitrites to nitrates. A generalized nitrogen process in natural water bodies can be written as [1];



About 3.43g of oxygen is utilized for 1g of nitrogen oxidized to nitrite in the first step, whereas, the Nitrites are further oxidized by Nitrobactors as;



Oxygen utilization in this step is 1.14 g for 1 g of nitrite-N oxidized to nitrate-N. Therefore, the overall oxygen utilized is 4.57g per gram of ammonia-N oxidized to nitrate-N under alkaline conditions with pH greater than 6 (minimum). Therefore, the total concentration of nitrogenous oxygen demanding waste can be estimated by using the equation;

$$L_{n0} = 4.57 (N_o + N_a) \tag{24}$$

where L_{n0} is the ultimate NBOD (NBODU) and N_o and N_a are the organic and ammonia-N concentrations in mg/L respectively.

The NBOD can be modeled as first order kinetics under minimum DO concentration up to about 1mg/L in the river water as [1]

$$\frac{dL_n}{dt} = -K_n L_n \tag{25}$$

where L_n is NBOD and K_n is the overall oxidation rate of NBOD. The integral form of the above first order equation is;

$$L_n = L_{n0} e^{-K_n t} \tag{26}$$

Chapra (1997) suggested a range of 0.1 – 0.5 day⁻¹ for K_n for deep rivers and reported values greater than 1.0 day⁻¹ for shallow rivers in certain cases [16]. Thomann & Mueller (1987) mentioned that K_n is approx equal to CBOD rate coefficient [1]. Schnoor (1996) stated that both the CBOD and NBOD rates lie between 0.05 – 0.5 day⁻¹ [7].

5. BOD Rates

The oxidation of BOD in natural streams involves different processes which do not occur in a BOD bottle. Therefore, the river deoxygenation rate K_d is different from the BOD bottle rate. These processes may include bio-sorption by biological slimes at the bed of a river, natural turbulence and roughness, and the density, population and types of attached organisms [1]. Furthermore, the overall removal rate coefficient (K_r) in the river includes both deoxygenation and settling of carbonaceous OM as given in Eq (27). The rate coefficients K_r and K_d in Eq (12 & 13) effect dissolved oxygen levels in the river. These rates are dependant on type and source of wastewater and associated chemical and bio-physical factors in a specific river (Fig 3). K_r in (Eq 12) can be estimated from CBOD profile in the river generated through river survey data [10,16].

$$K_r = K_d + K_s \tag{27}$$

where K_s is the removal rate coefficient due to settleable organic matter. Now K_d can relate to BOD bottle rate as;

$$K_d = K + \phi \tag{28}$$

where the component of the above equation K is the characteristic of type of wastewater and can be determined from the long-term BOD analysis. It is also known as CBOD bottle rate coefficient. The other component “ ϕ ” in Eq (28) reflects the river conditions which are not present in the BOD bottle environment [40].

Some empirical formulas have also been developed by Hydrosience (1971) and Wright & McDonnell (1979) to estimate K_d are presented in Table 2 [1,41-42]. But their use in actual water quality modeling studies has not been frequently observed in literature. Canale et al. (1995) estimated CBOD rate constant “ K ” in the river Seneca, NY, USA by inhibiting the nitrification in BOD bottles under low flow conditions. A value of 0.11 day⁻¹ was found using Thomas Method [13].

The K_s in (Eq 27) can be estimated by knowing the settling velocity of the particulate CBOD “ v_s ” and average depth “ H ” of the river [16];

$$K_s = \frac{v_s}{H} \tag{29}$$

The effect of settling is more important for shallow water bodies with less than 1m depth [16]. Secondary level of wastewater treatment removes major portion of particulate BOD (i.e; suspended solids < 30mg/L). Therefore K_s in Eq (27) may be neglected for secondary treated effluents [1]. Jha and Ojha (2007) used values of K_s (BOD settling rate) ranging between 0.4 to 0.6 day⁻¹ [14]. These values seem to be quite high as if added into the river deoxygenation rate K_d in Eq (23), the total value of removal rate “ K_r ” may reach to much higher than 0.5 day⁻¹ (i.e., the maximum value given in literature).

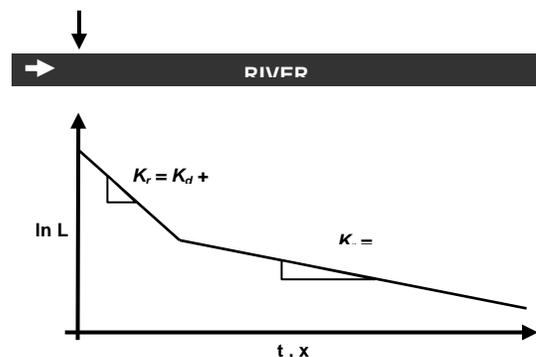


Fig 3: CBOD rates downstream from a point source outfall (Source: Chapra 1997)

Wright and McDonnell (1979) observed that for higher flows greater than 22.7 m³/s, K_d values were comparable with bottle rates (K) and concluded that BOD bottle rates determined from conventional laboratory examinations could be used for the larger rivers and streams [42,1].

The BOD bottle rate “ K ” depends on the degree of treatment for municipal waste discharges. Actually, the residual material becomes more resistant to treatment with the increase in degree of treatment, which means, as the degree of treatment increases the rate of biodegradation decreases. Typical ranges of CBOD bottle rates (K) for municipal wastewaters at different levels of wastewater treatment are given in Table 3 [16]. In fact, the biokinetic rate coefficients in the rivers (i.e., K_r and K_d) also change with the level of treatment. The difference between K_r , K_d and K reduces with increase in level of treatment (i.e., primary, secondary, secondary with nitrification). Water quality studies of Upper Mississippi River revealed that for the effluents treated at or higher than secondary level, the river removal rate K_r becomes almost equal to the bottle rate K [33,43].

Haider and Ali (2010a) estimated the effect of treatment of the Lahore wastewaters on the carbonaceous and nitrogenous biokinetic rate coefficients in the River Ravi [40]. The results of their study suggested that the river rate coefficients need to be reduced by a factor ranging between 1.5 to 5 depending on the level of treatment (i.e., primary, secondary and secondary with nitrification) to achieve desired DO standards.

Table 2: River deoxygenation formulas [1]

Sr No	Name of Investigator	Formula	Parameters Range
1	Hydroscience (1971) [41]	$K_d = 0.3 (H/8)^{0.434}$ $K_d = 0.3$	$0 \leq H \leq 8$ $H > 8$
2	Wright and McDonnell (1979) [42]	$K_d = 10.3Q^{-0.49}$ $(0.08 \text{ to } 4.24/\text{day})$	$H = 0.9 - 32$ $P = 11.8 - 686$ $Q = 4.6 - 8760$

where: K_d = deoxygenation rate constant (base e), day⁻¹
 U = mean stream velocity, ft/sec
 H = mean stream depth, ft
 Q = flow rate, cfs
 P = wetted perimeter, ft

In some of the past and recent studies different DO models and software were used to manage DO without considering the effect of wastewater treatment on biokinetics of the river system. Ha and Bae (2001) assessed the impact of variable treatment levels on Bokha Stream, Korea by using the built-in BOD decay coefficients in the software [44]. Radwan et al. (2003) also modeled BOD and DO in river Dender, Belgium with the help of default values for different rate coefficients [45]. The values of 0.25day⁻¹ and 0.5day⁻¹ of K_d and K_r respectively were used by Murty & Shallamudi (2006) for BOD and DO modeling of rivers, they further reduced K_d to 0.2day⁻¹ for the entire change in wastewater treatment (i.e., 35% to 98%) [46]. Singh et al. (2007) determined optimum removal efficiencies of BOD for five wastewater drains discharging in river Yamuna, India by using a consistent value of 1.3 day⁻¹ (i.e., does not coincide with the reported literature values for domestic wastewaters) of BOD deoxygenation rate coefficient to [47]. Campolo et al. (2002) carried out different simulations based on degree of treatment and flow augmentation alternatives to achieve desired DO standards of 4mg/L in the River Arno, Italy [48]. In their study, water quality parameters and rate coefficients were neither calibrated through field measurements nor changed with respect to the change in degree of treatment.

Table 3: CBOD bottle rate coefficients “ K ” and CBODU/CBOD5 of municipal wastewaters

Degree of Treatment	K (day ⁻¹) @ 20°C		CBODU/CBOD5
	Approximate range	Average	
Untreated/ raw wastewater	0.2 – 0.5	0.35	1.2
Primary	0.1 – 0.3	0.2	1.6
Activated Sludge	0.05 – 0.1	0.075	3.2

Source: Chapra (1997) [16]

K_d is determined at a reference temperature of 20°C. Therefore following temperature correction must be applied in case of temperature variation [1];

$$(K_d)_T = (K_d)_{20} (\theta)^{T-20} \tag{30}$$

where $(K_d)_T$ and $(K_d)_{20}$ are deoxygenation rate coefficients at any temperature “ T ” and 20°C respectively. “ θ ” value ranges between 1.02 and 1.09. The most commonly used value is 1.047 [49].

6. Computer Models

Computer models and simulations provide rapid evaluation of inputs and outputs for long-term decisions. Most of the software are Public Domain Models (PDM) and are available free at the internet. These models have been used by different water quality regulating agencies all around the globe to resolve the water pollution problems in natural systems. Details of the commonly available water quality computer models are very well covered by Kannel et al. (2010) and Cox (2003a) [50-51].

Kannel et al. (2010) conducted a comprehensive review of these models based on conceptualization, processes (biological, physical and chemical), requirements of the input data, model limitations and strengths and their applications [50]. A brief review of these state-of-the-art public domain water quality models is presented in Table 5, especially in the context of DO modeling in rivers and streams. If selected properly any of these PDM can give useful results. Among the PDM mentioned in Table 5, SIMCAT and TOMCAT are over-simplistic and do not include some of the most important DO related parameters. However, TOMCAT includes nitrification and can give reasonable results for the rivers where P&R and SOD are not occurring.

QUAL2E was from the result of the historic development of oxygen, nitrogen and phosphorous models based on modification to classical Streeter-Phelps DO Sag model (Eq 13, 14). Later, QUAL2E was further enhanced and called QUAL2EU with uncertainty analysis option. QUAL2E/ QUAL2EU is one of the most widely used PDM and can provide a rational approach of modeling for one-dimensional modeling of the well mixed rivers and also can simulate water quality parameters on a diurnal time scale [52]. Different researchers have successfully used QUAL2E for water quality management of rivers all around the globe [48,52,53-62]. Ghosh & McBean (1998) found that main problem in using enhanced water quality models in developing countries is lack of the data required for their calibration and verification [56]. Yang et al (2011)

used QUAL2E model for dissolved oxygen management of the Putzu River, southern Taiwan. They used QUAL2E for DO modeling to assess the natural assimilative capacity of the river and LINDO for allocating optimum waste loads to achieve required standards. They however considered overall BOD and SOD only for the DO analysis without addressing ammonia and photosynthesis [63].

QUAL2K or (Q2K) is a new version of QUAL2E and includes more processes [64]. It possesses MS Excel based graphical user interface and can deal with unequally-spaced river segments. It can simulate slow CBOD and fast CBOD separately. Moreover, non-living particulate organic matter (i.e., detritus) can also be simulated (Chapra and Pelletier 2003). Later, Pelletier and Chapra (2005) further improved QUAL2K and the improved model is called as QUAL2Kw, which can deal with the dynamically calculated water quality inputs [65]. Park and Lee (2002) used both QUAL2E and QUAL2K for modeling of DO, BOD and nitrogen in Nakdong River, Korea [66]. The study results revealed that QUAL2K (i.e., modified form of QUAL2E) presented stronger agreement with the field data. According to the authors the reason for this better performance of QUAL2K is its ability to simulate dead algae (as an addition to BOD), fixed plant DO and the process of denitrification.

WASP6 is another public domain program (Table 5) used to assess the impact of several biochemical processes including nutrients, phytoplankton, CBOD, NBOD and SOD on DO. It has 4 complexity levels varying from Streeter-Phelps to non-linear DO balance. It also simulates the effect of dead algae on DO balance. WASP6 considers upward re-suspension velocity of settling particulates during high flows in addition to settling velocity [67]. WASP7 is enhancement of the previous WASP versions and is a dynamic compartmental-modeling program including both the overlaying water column and underlying benthos. It can be used for one, two and three dimensional modeling and a variety of pollutant types [50]. However, the data requirements are so large that its use cannot be justified particularly for large rivers in developing countries.

The QUSAR model is available free at public domain as PC-QUSAR. This model can be run in both the dynamic and planning mode. Time series

data as the input is required to estimate flow and water quality parameters over a period of time in dynamic mode, whereas, the planning mode uses conventional method of Monte Carlo simulation to generate a cumulative frequency distribution of the water quality parameters from a given set of inputs and operating conditions. Both of these models (i.e., WASP and PC-QUSAR) give different output format, the WASP generates two sets of output data, one is based on observed values and the other on user-edited values. The output data generated in the QUSAR planning mode helps in setting required

standards to meet river quality objectives. However, this model again (like WASP7) possesses extensive data requirements [50]

MIKE 11 is another 1-D water quality model for rivers and streams, however this is not a freeware. It is a dynamic model like QUSAR and thus data requirements are much larger than QUAL2E. It

simulates almost all of the processes, which QUAL2K simulates, however, it does not consider Nitrite as an intermediate product in the nitrification process [5]. Radwan et al. (2003) used MIKE11 for

Table 5: Description and information of commonly used river DO modeling software

Model	Type	Modeling approach	DO related processes	Modeling Capability	Strength	Limitation	Source Information
SIMCAT	1D, steady state, stochastic	CSTRS	CBOD, Reaeration	DO, CBOD, ammonia, conservative parameters	Runs quickly with limited data, auto-calibration	Over simplistic approach	Warn (1987) [68]
TOMCAT	1D, steady state	CSTRS	CBOD, reaeration, nitrification	DO, CBOD, ammonia, chloride, conservative parameters	Runs quickly with limited data, better accuracy than SIMCAT	Over simplistic approach	Bowden & Brown (1984) [69]
QUAL2EU	1D, steady state/dynamic	Advection dispersion equation, equal river reaches	CBOD, reaeration, nitrification, SOD, reaeration, P&R	DO, CBOD, temperature, algae, N (ON, NH ₃ , NO ₂ , NO ₃), P(OP, PO ₄), coliforms, SOD	Widely used, automatic uncertainty analysis	Does not include CBOD addition from dead algae, not suited for rivers with temporal variations	Brown & Branwell 1987 [52] QUAL2E (www.epa.gov/ceampubl/swate)
QUAL2Kw	1D, steady flow	Advection dispersion equation, unequal river reaches	CBOD, reaeration, nitrification, SOD, reaeration, P&R	DO, CBOD, Temperature, pH, N(ON, NH ₃ , NO ₂ , NO ₃), P(OP, PO ₄), total inorganic carbon, phytoplankton, bottom-algae, SOD, detritus, pathogen	Includes addition of CBOD from dead algae	Does not simulate branches	Chapra & Pelletier 2003 [64] QUAL2K (www.epa.gov/ATHENS/wwqtsc)
WASP7	1D, 2D, 3D, dynamic	Advection dispersion equation, dynamic compartmental	CBOD, SOD, reaeration, P&R, nitrification	DO, CBOD, Temperature, pH, N(ON, NH ₃ , NO ₂ , NO ₃), P(OP, PO ₄), coliform, salinity, SOD, bottom-algae, silica, pesticides, organic chemicals	Includes addition of CBOD from dead algae	Extensive data requirements, unlinked sub-models, dam-break situations; and small mountain streams can't be modeled	Wool et al. 2001 [67] WASP5 (www.epa.gov/ceampubl/swater) WASP7 (www.epa.gov/ATHENS/wwqtsc)
QUSAR, PC-Qusar	1D, dynamic stochastic	CSTRS	CBOD, SOD, reaeration, P&R, nitrification	DO, CBOD, nitrate, SOD, ammonia, un-ionized ammonia, temperature, Ecoli, pH	Includes addition of CBOD from dead algae	Required extensive data	Whitehead et al., 1997 [70] http://www.ceh.ac.uk/products/software/CEHSoftware-PC-QUSAR_000.htm

Source: Kannel et al. (2010) [50]

water quality modeling of Molenbeek Brook creek, Belgium. MIKE11 can be used for different levels (1–6) based on the data availability and process complexity [45].

7. Conclusions

Mathematical models for dissolved oxygen are extensively used to develop management strategies for maintaining the river water quality for its beneficial uses. There are number of models and solution techniques available in literature for this purpose. However, it is important that the mathematical model selected for this use purpose reflects the conditions pertaining to the specific river. To aid in this decision, this paper presents a review of various DO models and the condition under which they are best suited.

The dissolved oxygen in the river is controlled by a number of processes for which data needs to be collected to completely describe the model, therefore the review of these DO related processes is also provided so that the data requirements can be identified. Where the available data and resources are limited, simplified DO models can be used in many situations. The applicability of the modified form of the classical Steeter- Phelps model to include all the important DO related phenomena in a specific river or a stream is therefore also discussed. This basic model and its modifications are still being used (providing the basic guidelines) for modeling of DO in rivers and streams where data availability is limited.

Most of the recent work seems to be emphasizing on use of mathematical and computer advancements to simulate different processes in a smaller period of time sometimes based on literature and built-in values without proper estimates of process rate coefficients. Some of the computer software have automatic calibration processes and the calibrated model is completely based on the built-in rate coefficients which may not give insight to the important DO sources and sinks. In this way the allocated waste loads could be either under or over estimated. For examples, CBOD based load allocation studies may not meet un-ionized ammonia standards even when the river water quality is complying with the required DO standards. Thus the

models should be selected keeping in view the time, cost and a specific application depending on the conditions of the large river system.

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