Modeling Oxygen Depletion in Running Water
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CAUTION: These notes may still contain typos.

Dissolved oxygen (DO) is one of the most widely used indicators of overall ecological health of a body of water. Low DO causes immediate problems: Fish need at least 4 to 5 milligrams per liter (mg/L) to survive. Under low oxygen conditions, anaerobic (smelly) organisms can replace the aerobic microbes.

Dissolved Oxygen

The oxygen in a river or other water body is primarily dissolved from the atmosphere, though photosynthetic organisms produce oxygen. Oxygen is consumed by respiration and by chemical oxidation. Organic carbon in a body of water serves as food for microbes. Aerobic decomposers use oxygen as an electron acceptor in the biochemical processes that extract chemical energy from organic matter. Thus organic matter is called biochemical oxygen demand (BOD). If a river was healthy before we began discharging wastewater, a significant factor in its continued health or illness is the biochemical oxygen demand (BOD) added to it by wastewater. In water and sediment, as oxygen is depleted, other electron acceptors are used, including nitrate, sulfate, and carbon dioxide.

At equilibrium, dissolved oxygen is described by Henry's Law:

$$O_2(aq) \xrightleftharpoons{K'_{O_2}} O_2(g) \tag{1}$$

$$\frac{p_{O_2}}{[O_2]} = K'_{O_2} = 769.2 \text{ L atm mol}^{-1} @ 25°C \tag{2}$$

(This value of K'_{O2} is from the NIST Chemistry WebBook, 2005.) The partial pressure of oxygen in the atmosphere is 0.21 atm, so at equilibrium at 25°:

$$[O_2] = \frac{p_{O_2}}{K'_{O_2}} = \frac{0.21 \text{ atm}}{769.2 \text{ L atm mol}^{-1}} = 0.27 \text{ mmol L}^{-1} * 32 \text{ mg mmol}^{-1} = 8.7 \text{ mg L}^{-1} \tag{3}$$

When water is at equilibrium with air we say that the water is saturated with dissolved oxygen. So, $DO_{sat, 25°C} = 8.9$ mg/L. The solubility of oxygen in water decreases with increasing temperature, as expressed by an increase in K'. The value for other temperatures can be found using the van't Hoff equation:

$$K'_{T_2} = K'_{T_1} \exp\left(\frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right) \tag{4}$$

The value of $\Delta H^0/R$ is given in NIST (2005) from a number of sources as 1500 K. So, at 15°C the value of K' is:

$$K_{15}^{'} = 769.2 \exp\left(1500\left[\frac{1}{298} - \frac{1}{288}\right]\right) = 644.2 \text{ L atm mol}^{-1} \qquad (5)$$

So, $DO_{sat, 15°C} = 10.4$ mg/L.

The transfer of oxygen from the atmosphere to a river is driven by an oxygen deficit in the water, that is, a DO less than saturated. The process can be modeled as first order in that deficit. If we define $D = (DO_{sat} - DO)$, then the rate of reoxygenation is described by a constant, k_a:

$$\frac{dD}{dt} = -k_a D$$

$$\int_{D_0}^{D} \frac{dD}{D} = -k_a \int_0^t dt$$

$$\ln D\Big|_{D_0}^{D} = -k_a t\Big|_0^t$$

$$\ln\left(\frac{D}{D_0}\right) = -k_a t$$

$$D = D_0 e^{-k_a t} \qquad (6)$$

The oxygen deficit in water in contact with air will decay exponentially toward zero if there are no other processes affecting the dissolved oxygen content. Values of k_a are tabulated below:

Reaeration constants	
Water body	Ranges of k_a at 20°C
Small ponds and backwaters	0.1-0:23
Sluggish streams and large lakes	0.23-0.35
Large streams of low velocity	0.35-0.46
Large streams of normal velocity	0.46-0.69
Swift streams	0.69-1.15
Rapids and waterfalls	Greater than 1.15
Source: Peavy, Rowe and Tchobanoglous, 1985	

Many texts report the O'Connor-Dobbins formula for k_a, in which u is given in feet per second and H is the mean depth of the stream in feet:

$$k_a = \frac{12.9u^{0.5}}{H^{1.5}} \qquad (7)$$

Oxygen Demand

Organic matter or other oxygen demand will deoxygenate the water that contains it, provided that there are organisms to consume it (or proper conditions for chemical oxidation). This deoxygenation is first order in organic matter concentration, L.

$$-\frac{dD}{dt} = \frac{dL}{dt} = -k_d L$$
$$L = L_0 e^{-k_d t} \tag{8}$$

This model of course assumes that there is sufficient oxygen present to permit the decomposition from L_0 to L. In a volume of water that contains oxygen-demanding substrate and that is in contact with the air, both deoxygenation and reoxygenation will occur.

$$\frac{dD}{dt} = k_d L - k_a D \tag{9}$$

This equation applies to a well-mixed, fixed volume (or to a moving plug as described below). In a well-mixed reactor we assume that spatial derivatives would be equal to zero, so we can write an ordinary derivative for time.

Note that the standard laborabory test for oxygen demand is the BOD5 test, biochemical oxygen demand measured after a five day incubation at 20° C. Waste is mixed with an inorganic nutrient solution and oxygen content is measured before and after incubation. The loss of oxygen is assumed to be due to substrate consumption by decomposers. Often a bacterial seed is added to supplement the organisms present in waste. Nitrogenous oxygen demand can be inhibited so that only carbonaceous demand is measured. Equation 8 allows us to convert from BOD5 (L_0 - L_5) to ultimate BOD (L_0):

$$L_5 = L_0 e^{-5k_d}$$
$$L_0 = \frac{L_5}{1 - e^{-5k_d}} \tag{10}$$

Plug Flow Reactor

These reactions occur in natural waters including rivers. To model the dissolved oxygen level in a river, we need to assume a condition typically called "plug flow." Under this condition, a control volume is defined as a cross section of the river with a thickness of Δx along the flow axis of the river. This control volume is assumed to be well mixed. The river is flowing at a velocity u, and the entire well-mixed volume is pictured as moving downstream at that velocity. If the cross-section of flow is A, then the volume of the plug is $A\Delta x$. Note that if u is constant, then we can replace t with x/u in any equation involving time. In fact, we assume that the partial derivative with respect to time is zero.

If we were to watch a single point in the river (a fixed value of x), the concentration of the substance of interest would not change. A steady state exists at each point in the river, but the concentration changes as we move downstream.
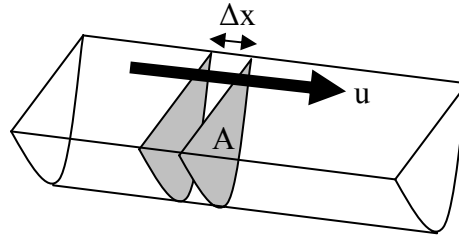
To check the suitability of the plug-flow assumption, the Peclet number and Reaction number of the system can be evaluated (see p. 62 in Schnoor, 1996).

If a quantity of BOD-containing waste is deposited into this plug, for example as it passes an outfall, we can model the change in oxygen concentration as it moves downstream. This is a classic environmental engineering model first published by Streeter and Phelps in 1925.

The Streeter-Phelps Equation

The Streeter-Phelps model assumes that deoxygenation is a first order process in substrate concentration and the reoxygenation is first order in oxygen deficit. It also assumes that there is no mixing across the upstream or downstream face of the plug and that cross-sectional area and velocity are constant, and of course that the plug is instantaneously mixed throughout its volume. Under these conditions, the only processes which affect oxygen content are deoxygenation and reoxygenation. If we denote dissolved oxygen concentration by C (with saturated content C_s), then equation 10 for a moving plug becomes:

$$\frac{dC}{dt} = -k_d L + k_a \left(C_s - C\right) \qquad (11)$$

In this case the moving plug is modeled as if it were a stationary well-mixed reactor. Time and space are interchangeable since:

$$t = \frac{x}{u}$$

$$dt = \frac{dx}{u} \qquad (12)$$

If we return to using D for the oxygen deficit, and we note that

$$D = C_s - C$$

$$\frac{dD}{dt} = -\frac{dC}{dt} \qquad (13)$$

Then we can rewrite equation 11 as a differential equation describing how the oxygen deficit changes with distance downstream:

$$u\frac{dD}{dx} = k_d L - k_a D \qquad (14)$$

We can use result 8 above, with t converted to x/u:

$$u\frac{dD}{dx} = k_d L_0 e^{-\frac{k_d}{u}x} - k_a D \qquad (15)$$

This can be rearranged to look like the standard form of a first order, linear ODE, which can be solved using an integrating factor (SOS Math, 2007). That standard form is:

$$\frac{dy}{dx} + p(x)y = q(x) \qquad (16)$$

The general solution is:

$$y = \frac{\int u(x)q(x)dx + C}{u(x)} \qquad (17)$$

Where the integrating factor, u(x), is:

$$u(x) = \exp\left(\int p(x)dx\right) \qquad (18)$$

We find the constant, C, using the boundary condition. Putting (14) into standard form:

$$\frac{dD}{dx} + \frac{k_a}{u}D = \frac{k_d L_0}{u}e^{\frac{-k_d x}{u}} \qquad (19)$$

Thus we have:

$$y = D$$

$$p(x) = \frac{k_a}{u} \qquad (20)$$

$$q(x) = \frac{k_d L_0}{u}e^{\frac{-k_d x}{u}}$$

Then:

$$u(x) = \exp\left(\int p(x)\,dx\right) = \exp\left(\int \frac{k_a}{u}\,dx\right)$$

$$u(x) = e^{\frac{k_a}{u}x} \tag{21}$$

So:

$$D = \frac{\int e^{\frac{k_a}{u}x}\,\frac{k_d L_0}{u}\,e^{\frac{-k_d}{u}x}\,dx + C}{e^{\frac{k_a}{u}x}}$$

$$D = \frac{\frac{k_d L_0}{(k_r - k_d)}\int e^{\frac{k_a - k_d}{u}x}\,\frac{(k_a - k_d)}{u}\,dx + C}{e^{\frac{k_a x}{u}}}$$

$$D = \frac{k_d L_0}{(k_a - k_d)}\,e^{-\frac{k_d}{u}x} + Ce^{-\frac{k_a}{u}x} \tag{22}$$

At x = 0, D = D₀, so:

$$D_0 = \frac{k_d L_0}{(k_a - k_d)} + C$$

$$C = D_0 - \frac{k_d L_0}{(k_a - k_d)} \tag{23}$$

Substituting back into (21):

$$D = \frac{k_d L_0}{(k_a - k_d)}\,e^{-\frac{k_d}{u}x} + \left(D_0 - \frac{k_d L_0}{(k_a - k_d)}\right)e^{-\frac{k_a}{u}x}$$

$$D = \frac{k_d L_0}{(k_a - k_d)}\left(e^{-\frac{k_d}{u}x} - e^{-\frac{k_a}{u}x}\right) + D_0 e^{-\frac{k_a}{u}x} \tag{24}$$

Equation 24 is known as the Streeter-Phelps equation. It describes the oxygen deficit downstream from a point where a river receives BOD-containing waste. The graph of such a deficit versus distance downstream is called a sag curve.

Sag Curve

Oxygen Deficit (mg/L) vs Distance Downstream (m)

$k_a = 2/d$ $L_0 = 10$ mg/L
$k_d = 0.6/d$ $D_0 = 0$ mg/L
$u = 25$ km/d
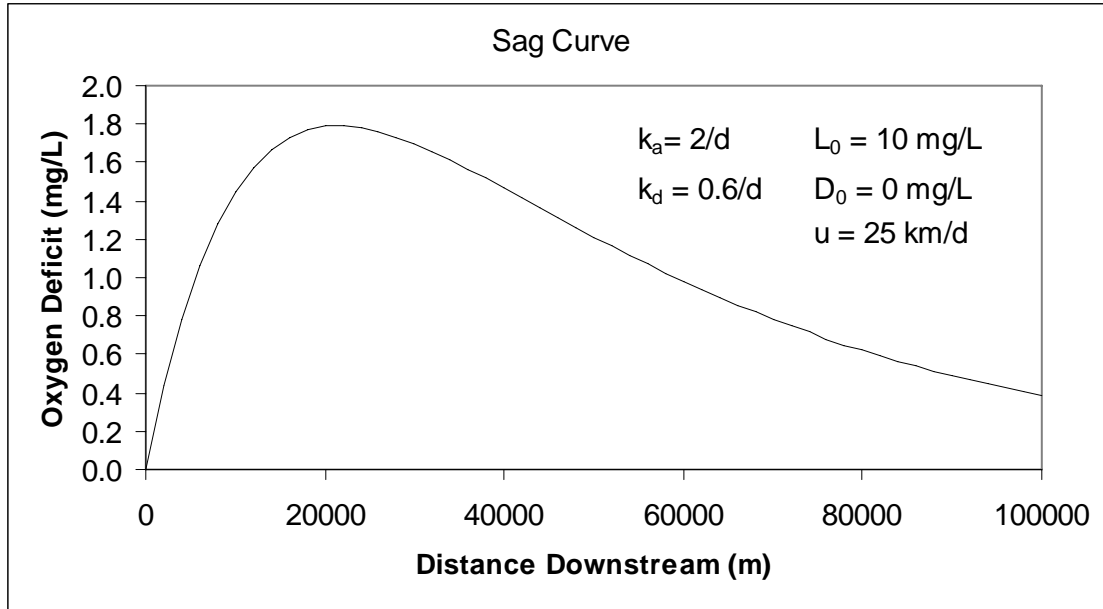
Critical Point

A valuable piece of information to be obtained from the Streeter-Phelps model is the maximum oxygen deficit for a given wasteload and the location downstream where this critical deficit occurs. To get the critical deficit, D_c, we look for a maximum in the function $D(t)$. This is most easily done using the original differential equation, (14) or (18) above. At the maximum, dD/dt will be zero, so:

$$\frac{k_a}{u} D_c = \frac{k_d L_0}{u} e^{\frac{-k_d x_c}{u}}$$

$$D_c = \frac{k_d L_0}{k_a} e^{\frac{-k_d x_c}{u}} \tag{25}$$

To get the critical distance, x_c, we can plug (25) into (24):

$$\frac{k_d L_0}{k_a} e^{\frac{-k_d}{u} x_c} = \frac{k_d L_0}{(k_a - k_d)} \left(e^{-\frac{k_d}{u} x_c} - e^{-\frac{k_a}{u} x_c} \right) + D_0 e^{-\frac{k_a}{u} x_c}$$

$$\left(\frac{k_d L_0 (k_a - k_d - k_a)}{k_a (k_a - k_d)} \right) e^{\frac{-k_d}{u} x_c} = \left(\frac{D_0 (k_a - k_d) - k_d L_0}{(k_a - k_d)} \right) e^{-\frac{k_a}{u} x_c}$$

$$e^{\frac{k_a - k_d}{u} x_c} = \frac{k_a}{k_d} \left(1 - \frac{D_0}{L_0} \frac{(k_a - k_d)}{k_d} \right)$$

$$\frac{k_a - k_d}{u} x_c = \ln\left[\frac{k_a}{k_d}\left(1 - \frac{D_0}{L_0}\frac{(k_a - k_d)}{k_d}\right)\right]$$

$$x_c = \frac{u}{k_a - k_d}\ln\left[\frac{k_a}{k_d}\left(1 - \frac{D_0}{L_0}\frac{(k_a - k_d)}{k_d}\right)\right] \tag{26}$$

A More Complete Streeter-Phelps Model

The Streeter-Phelps equations as derived above only take into account carbonaceous oxygen demand and reaeration through the water's surface. As discussed in Schnoor (1996), there are several other processes that affect dissolved oxygen in rivers. These include nitrogenous oxygen demand, sediment oxygen demand, photosynthesis and respiration and background oxygen demand. Nitrogenous oxygen demand (N) is exerted by reduced nitrogen compounds, primarily ammonia, which is used by nitrifying bacteria as an energy source.

Sediment oxygen demand (S) is exerted by particulate organics in river sediments. These have been deposited by historical waste discharges and can be significant, particularly downstream of an historically high-concentration outfall in a body of water to which discharge has more recently been limited. The sediment oxygen demand is expressed as a mass of oxygen per unit area of sediment per time. To convert this to per volume, S is divided by the depth, H, of the water column over the sediment. The time dimension is included in S, so no time constant is used in the rate expression.

Photosynthesis (P) by phytoplankton adds oxygen to the water during daylight periods. Respiration (R) occurs around the clock, but is typically a small fraction of photosynthesis. At night respiration consumes oxygen but the net effect averaged over the day is production rather than consumption. Both P and R are expressed in mass per volume per day.

Background oxygen demand (L_b) is constant demand exerted throughout the river. It can be viewed in two ways: oxygen demand carried into the river from non-point sources along the entire length or the sum of all discrepancies between the model predictions and observed oxygen content. The effect is the same, a constant deficit (D_b) in the water column.

Typical values for each of these is given in Table 6.3 (Schnoor, 1996, p. 246). Within the moving plug, the rate of oxygen consumption for each of these processes as follows:

Nitrogenous oxygen demand, $N(gO_2m^{-3})$:

$$\frac{dD}{dt} = u\frac{dD}{dx} = k_n N \tag{27}$$

Sediment oxygen demand, S $(gO_2m^{-2}d^{-1})$:

$$\frac{dD}{dt} = u\frac{dD}{dx} = \frac{S}{H} \tag{28}$$

Net respiration, R – P (mgO$_2$L^{-1}d^{-1}):

$$\frac{dD}{dt} = u\frac{dD}{dx} = R - P \tag{29}$$

One other process, which indirectly affects oxygen deficit, should be considered as well, sedimentation of particulate organic matter. Some of the carbonaceous BOD that is discharged in wastewater is in solid state rather than dissolved. This can be removed from the water column both by decomposition, which consumes oxygen, and by sedimentation, which does not. Sedimentation can be modeled as a first order reaction with a time constant, k_s. To take this process into account we need to introduce another constant as well. The consumption of BOD by decomposers is described by k_a. We define k_r to be the sum of k_a and k_s. So:

$$k_r = k_a + k_s$$
$$\frac{dL}{dt} = k_r L$$
$$L = L_0 e^{k_r t} \tag{30}$$

But sedimentation removes BOD without depleting oxygen. If we denote the oxygen deficit which is due only to the consumption of carbonaceous BOD as D_{CBOD}:

$$\frac{dD_{CBOD}}{dt} = k_a L = k_a L_0 e^{k_r t} \tag{31}$$

We now can write an enhanced equation giving the rate of oxygen depletion as affected by the range of processes described above. Note that we can write this rate either as dD/dt or as udD/dx:

$$\frac{dD}{dt} = u\frac{dD}{dx} = -k_a D + k_d L + k_n N + \frac{S}{H} + (R - P) + k_b L_b \tag{32}$$

Even with the additional terms this remains a first order, linear ordinary differential equation. It will turn out to be easier to solve than it might seem at first glance. The first thing to note is that the last term, kbLb is the rate of consumption of background oxygen demand. We assume that this rate is att steady state. In other words, dD$_b$/dt (or udD$_b$/dx) is zero. So:

$$\frac{dD_b}{dt} = u\frac{dD_b}{dx} = 0 = -k_a D_b + k_b L_b$$
$$k_a D_b = k_b L_b$$

$$D_b = \frac{k_b L_b}{k_a} \tag{33}$$

Thus the final equation describing D(x) will have a constant D_b added to the right hand side. And we will drop $k_b L_b$ from the differential equation we are about to solve.

Superposition

Equation 32 can be easily solved using the principle of superposition. All we need to do is extend the general solution to a first order, linear ODE given in equation 17 above. First, let's write equation 32 in standard form (see equation 16 above if you don't remember that). While we're at it, let's plug in solutions for L and N and remove the background demand term:

$$\frac{dD}{dx} + \frac{k_a}{u} D = \frac{k_d}{u} L_0 e^{-\frac{k_r}{u}x} + \frac{k_n}{u} N_0 e^{\frac{k_n}{u}x} + \frac{S}{uH} + \frac{(R-P)}{u} \tag{34}$$

Now we have a more complicated q(x):

$$q(x) = \frac{k_d}{u} L_0 e^{-\frac{k_r}{u}x} + \frac{k_n}{u} N_0 e^{\frac{k_n}{u}x} + \frac{S}{uH} + \frac{(R-P)}{u} \tag{35}$$

This is not a problem. First, let's rework the standard solution (equation 17) so that the boundary condition is used to give a general solution for the constant. Recall that at x = 0, y = y_0. So:

$$y_0 = \left[\frac{\int u(x) q(x) dx + C}{u(x)} \right]_{x=0}$$

$$C = u(0) y_0 - \left[\int u(x) q(x) dx \right]_{x=0} \tag{36}$$

If we plug (36) into (17):

$$y = y_0 \frac{u(0)}{u(x)} + \left[\frac{\int u(x) q(x) dx}{u(x)} \right]_{x=x} - \left[\frac{\int u(x) q(x) dx}{u(x)} \right]_{x=0}$$

$$y = y_0 \frac{u(0)}{u(x)} + \frac{1}{u(x)} \int_0^x u(x) q(x) dx \tag{37}$$

This will be very easy to apply. In equation 32, we have q = q_1 + … +q_N, so we observe that:

$$y = y_0 \frac{u(0)}{u(x)} + \frac{1}{u(x)} \int_0^x u(x) q_1(x) dx + \ldots + \frac{1}{u(x)} \int_0^x u(x) q_N(x) dx \tag{38}$$

In the case of equation 34,

$$p(x) = \frac{k_a}{u} \tag{39}$$

So,

$$u(x) = \exp\left(\int p(x)dx\right) = \exp\left(\int \frac{k_a}{u}dx\right)$$

$$u(x) = e^{\frac{k_a}{u}x}$$

$$\frac{1}{u(x)} = e^{-\frac{k_a}{u}x}$$

$$u(0) = 1 \tag{40}$$

Equation 38 tells us that we can carry out definite integration on each component of q(x) individually and put them together at the end. For example, for carbonaceous oxygen demand:

$$e^{-\frac{k_a}{u}x}\int_0^x e^{\frac{k_a}{u}x}\frac{k_d L_0}{u}e^{-\frac{k_r}{u}x}dx = \frac{k_d L_0}{k_a - k_r}e^{-\frac{k_a}{u}x}\left[e^{\left(\frac{k_a-k_r}{u}\right)x}\right]_0^x$$

$$= \frac{k_d L_0}{k_a - k_r}e^{-\frac{k_a}{u}x}\left[e^{\left(\frac{k_a-k_r}{u}\right)x} - 1\right] = \frac{k_d L_0}{k_a - k_r}\left[e^{-\frac{k_r}{u}x} - e^{-\frac{k_a}{u}x}\right] \tag{41}$$

This looks familiar, only slightly different from the original Streeter-Phelps. Nitrogenous oxygen demand is very similar. Let's just do the integral for sediment oxygen demand, which is a little different:

$$e^{-\frac{k_a}{u}x}\int_0^x e^{\frac{k_a}{u}x}\frac{S}{uH}dx = \frac{S}{k_a H}e^{-\frac{k_a}{u}x}\left[e^{\frac{k_a}{u}x}\right]_0^x = \frac{S}{k_a H}\left(1 - e^{-\frac{k_a}{u}x}\right) \tag{42}$$

The integral for net respiration is very similar. We need to retrieve the steady-state background oxygen demand from equation 33 above. When we put it all together we get our expanded and improved Streeter-Phelps:

$$D = D_0 e^{-\frac{k_a}{u}x} + \frac{k_d L_0}{(k_a - k_r)}\left(e^{-\frac{k_r}{u}x} - e^{-\frac{k_a}{u}x}\right) + \frac{k_n N_0}{k_a - k_n}\left(e^{-\frac{k_n}{u}x} - e^{-\frac{k_a}{u}x}\right)$$

$$+ \frac{S}{k_a H}\left(1 - e^{-\frac{k_a}{u}x}\right) + \frac{R - P}{k_a}\left(1 - e^{-\frac{k_a}{u}x}\right) + \frac{k_d L_b}{k_a} \tag{43}$$

If we have time, I will talk a little about how this is implemented in computer models of river water quality. A widely used package, QUAL2K, is available from the USEPA at http://www.epa.gov/athens/wwqtsc/html/qual2k.html. This software is a newer generation (Windows-based) of the QUAL-2E discussed in Schnoor (1996).

References

NIST Chemistry WebBook. June 2005. NIST Standard Reference Database Number 69. Retrived 20 March 2007 from http://webbook.nist.gov/chemistry/.

Peavy, H.S., D.R. Rowe, & G. Tchobanoglous. 1985. *Environmental Engineering*. Columbus, OH: McGraw-Hill.

Schnoor, J. L. 1996. *Environmental Modeling*. New York: Wiley & Sons.

SOS Mathematics Differential Equations. 2007. Retrieved 20 March 2007 from http://www.sosmath.com/diffeq/diffeq.html.

Stumm, W. & J.J. Morgan. 1981. *Aquatic Chemistry*. New York: Wiley & Sons.