

## Biochemical Oxygen Demand

The direct emission of sewage into streams can have devastating effects on stream water quality by spreading disease and creating a high oxygen demand on the receiving water. Microorganisms present in the stream and wastewater will slowly oxidize the introduced waste, and in doing so, will consume the available oxygen normally present in the stream. Under these conditions, the oxygen levels cannot be replaced by re-aeration at a quick enough rate for larger organisms (such as fish, macro-invertebrates) to survive. This component of EnviroLab shows the analysis of a biochemical oxygen demand (BOD) data set for three different water samples.

A BOD determination is performed by taking a water sample and incubating it over a 5- or 20-day period while monitoring the dissolved oxygen concentration every 12 hours. In a sample containing high concentrations of BOD, the sample should be diluted to ensure that the original oxygen level present in the water sample is not fully consumed. There are several requirements for the water used in the dilution of the sample. Distilled water should not be used, as microorganisms require certain salts to carry out metabolism. Thus, potassium, sodium, calcium, magnesium, iron, and ammonium salts are added to the dilution water. Also, the water should be buffered between a pH range of 6.5 to 8.5 with phosphate buffer. In some cases, certain water samples may require a “seed” of viable microorganisms to complete the degradation process. A general rule-of-thumb has been developed to provide sufficient accuracy in determining BOD values. This states that at least 2 mg/L of oxygen must be used over the course of the experiment, but at least 0.5 mg/L must remain in the final sample. The oxygen concentration can be measured by the Winkler Titration Method (for dissolved oxygen concentration), which is shown elsewhere in EnviroLab, or by utilizing a dissolved oxygen probe. A complete description of the procedure for the handling of samples, making dilution water, incubating samples, and determining oxygen concentration may be found in Standard Methods for the Examination of Water and Wastewater (1998).

In general, the utilization of oxygen by microorganisms is considered to be a pseudo-first order process. In a closed system (no re-aeration does not take place), the rate of oxygen consumption is commonly described by

$$L = L_o e^{-kt} \quad \text{Eq 1}$$

Wherein  $t$  is time,  $L$  is the concentration of oxygen at time  $t$ .  $L_o$  is the original concentration of oxygen in a sample, and  $k$  is the rate constant, which is generally around 0.17/day for sewage waste. Equation 1 is used to draw the line representing the removal of oxygen in EnviroLand.

A similar expression can be used to describe the oxidation of BOD in the sample as it is the inverse of the oxygen consumption,

$$L = L_o - L_o e^{-kt} \quad \text{Eq 2}$$

where  $L$  is the concentration of biodegradable organic matter at time  $t$ ,  $L_o$  is the original concentration of biodegradable organic matter, and  $k$  and  $t$  are the same variables as in equation 1.

Traditionally, we are concerned with the amount of oxygen required to oxidize a BOD sample over a 5-day period. This time period was established years ago in England and resulted from the fact that it required 5 days for water in most streams to reach the ocean. The microorganisms continue to exert an oxygen demand on the stream after this time and the ultimate BOD can be determined by conducting the experiment over a 20-day period. The ultimate BOD allows for an accurate calculation of the  $L_o$ .

An alternate method in determining  $L_o$  is to measure the BOD over a 5-day period, fit the data to Equation 2 using a  $k$  value of 0.17, and solving for  $L_o$ . However, experience has shown that this method does not work due to the non-first-order nature of the microbial degradation process. The ultimate BOD,  $L_o$ , can be determined using the Thomas slope method (Snoeyink and Jenkins, 1980) illustrated in EnviroLand, which linearizes the data in the form

$$\left(\frac{t}{y}\right)^{1/3} = (L_o k)^{-1/3} + \left(\frac{k^{2/3}}{6L_o^{1/3}}\right)t \quad \text{Eq 3}$$

where  $t$  is time,  $y$  is the BOD in mg/L at time  $t$  ( $L$  in Equation 2),  $L_o$  is the original concentration of biodegradable organic matter, and  $k$  is the rate constant.

Note that equation 3 is the equation of a line, where

$$(L_o k)^{-1/3} = \text{the } y\text{-intercept, } b$$

$$\frac{k^{2/3}}{6L_o^{1/3}} = \text{the slope of the line, } a$$

By substitution,  $k = 6b/a$  and  $L_o = 1/(ka^3)$ . By plotting an experimental data set of lab measurements (BOD as function of time) according to Equation 3, the rate constant and ultimate BOD can be estimated.

References:

Sawyer, C.N. and P.L. McCarty. 1978. Chemistry for Environmental Engineering. McGraw-Hill Book Company, New York.

Snoeyink, V.L. and D. Jenkins. Water Chemistry, John Wiley & Sons, New York, 1980.

Standard Methods for the Examination of Water and Wastewater (19<sup>th</sup> Ed.), American Water Works Association, 1998.