APPENDIX B - DEPARTMENT OF ENVIRONMENTAL QUALITY

pH modeling report
Little River
pH Model
DEQ Headquarters
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The following sections discuss the theory and application of the pH model used to determine the periphyton loading capacities.

**Photosynthesis and the Carbonate Buffering System**

Periphyton is important because of its ability to photosynthesize. The essence of the photosynthetic process centers about chlorophyll containing plants that can utilize radiant energy from the sun, convert water and carbon dioxide into glucose, and release oxygen. The photosynthesis reaction can be written as (Thomann and Mueller, 1987):

$$6 \text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{photosynthesis}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

**Equation 1**

Periphyton obtains energy from the sun for this daytime process. Instream dissolved oxygen is produced by the removal of hydrogen atoms from the water. The photosynthesis process consumes dissolved forms of carbon during the production of plant cells. Periphyton requires oxygen for respiration, which can be considered to proceed throughout the day and night (Thomann and Mueller, 1987). Carbon dioxide ($\text{CO}_2$) is produced during the respiration process as represented by the following equation:

$$6 \text{CO}_2 + 6\text{H}_2\text{O} \xleftarrow{\text{Respiration}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

**Equation 2**

The consumption of $\text{CO}_2$ during photosynthesis and $\text{CO}_2$ production during respiration has no direct influence on alkalinity. Since alkalinity is associated with a charge balance, changes in $\text{CO}_2$ concentrations result in a shift of the carbon equilibrium proton balance and the pH of the solution. (The pH of a solution is defined as an expression of hydrogen-ion concentration in terms of its negative logarithm (Sawyer and McCarty, 1978.)) However, it can be shown that photosynthesis would result in limited alkalinity changes through the uptake of charge ions, such as ortho-phosphorus (PO$_4^-$), nitrate (NO$_3^-$), and ammonia (NH$_3^+$).

Carbon dioxide is very soluble in water, some 200 times greater than oxygen, and obeys normal solubility laws within the conditions of temperatures and pressures encountered in fresh water ecosystems (Wetzel, 1983). Dissolved CO$_2$ hydrates to yield carbonic acid (CO$_2$ + H$_2$O $\Leftrightarrow$ H$_2$CO$_3$). The concentration of hydrated carbon dioxide ($\text{CO}_2{\text{aq}}$) predominates over carbonic acid in natural waters and it is assumed that carbonic acid is largely equivalent to hydrated carbon dioxide (e.g. [H$_2$CO$_3$] $\approx$ [CO$_2{\text{aq}}$]) (Snoeyink and Jenkins, 1980).

Carbonic acid dissociates rapidly relative to the hydration reaction to form bicarbonate (H$_2$CO$_3^*$ $\Leftrightarrow$ H$^+$ + HCO$_3^-$). In addition, bicarbonate dissociates to form carbonate ions (HCO$_3^-$ $\Leftrightarrow$ H$^+$ + CO$_3^{2-}$). The various components of the carbonate equilibria are interrelated by temperature dependent constants (i.e. $pK_{a1}$ and $pK_{a2}$, respectively) which establishes an equilibrium between H$_2$CO$_3^*$, HCO$_3^-$, and CO$_3^{2-}$:

$$\text{HCO}_3^- + \text{H}_2\text{O} \Leftrightarrow \text{H}_2\text{CO}_3^* + \text{OH}^-$$
$$\text{CO}_3^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{HCO}_3^- + \text{OH}^-$$
$$\text{H}_2\text{CO}_3^* \Leftrightarrow \text{H}_2\text{O} + \text{CO}_2$$

**Equation 3**
From these dissociation relationships, the proportions of $H_2CO_3^*$, $HCO_3^-$, and $CO_3^{2-}$ at various pH values indicate that $H_2CO_3^*$ dominates in waters at pH 5 and below. Above pH of 9.5 $CO_3^{2-}$ is quantitatively significant. Between a pH of 7 and 9.5 $HCO_3^-$ predominates (Wetzel, 1983).

Alkalinity is defined as a measure of the capacity of a water solution to neutralize a strong acid (Snoeyink and Jenkins, 1980). In natural water this capacity is attributable to bases associated with the carbonate buffering system ($HCO_3^-, CO_3^{2-}$ and $OH^-\) \). The carbonate equilibria reactions given above result in solution buffering. Any solution will resist change in pH as long as these equilibria are operational.

Photosynthesis and respiration are the two major biologically mediated processes that influence the amount of available $CO_2(aq)$ in fresh water systems. Accordingly, the pH of the solution will fluctuate diurnally and seasonally in accordance with a change of charge balance resulting from the production and/or consumption of $CO_2(aq)$ during these respective processes. Thus, an estimation of $CO_2(aq)$ will provide a method to determine pH levels in relation to the carbonate equilibrium proton balance within the solution. The concentration of $CO_2(aq)$ (e.g. $H_2CO_3$) in solution can be determined as:

$$[H_2CO_3^*] = \alpha_0 C_{CO_3}$$

Equation 4

where $\alpha_0$ is mathematically defined as (Chapra, 1997):

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

Equation 5

where $K_{a1}$ and $K_{a2}$ are equilibrium constants for carbonic acid and bicarbonate ions, respectively, and where the amount of total inorganic carbon ($C_{tCO_3}$) in natural waters is defined as:

$$C_{CO_3} = \frac{Alkalinity - \frac{K_W}{[H^+]} + [H^+]}{(\alpha_1 + 2\alpha_2)}$$

Equation 6

The “Alkalinity” component of Equation 6 is expressed in milliequivalents (meq). The “Kw” term is a temperature-dependent equilibrium constant for water and can be defined as:

$$K_w = [H^+][OH^-]$$

Equation 7

The “$\alpha_1$” and “$\alpha_2$” terms in Equation 6 are mathematical definitions of ionization fractions (Chapra, 1997):

$$\alpha_1 = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

Equation 8

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

Equation 9
An increase in instream CO$_2$ results in a lower pH. Conversely, a decrease in CO$_2$ results in a higher pH. The consumption of CO$_2$ during periphyton photosynthesis causes elevated pH levels between the Little River at rivermile 14.7, 8.0 and 0.6 monitoring sites.

**PH MODEL**

The impact of algal production on pH can be determined by a mass balance of the carbonate species. Assuming that the consumption of carbon is consistent along the river bottom, the change in total carbonate species can be estimated as the amount of CO$_2$(aq) plus the amount brought in by aeration and production, minus the amount of carbon dioxide consumed over time:

\[
C_{CO2(aq)T} = C_{CO2(aq)E} - ([C_{CO2(aq)E} - C_{CO2(aq)T}]e^{-K_{aCO2}T}) + ([1 - e^{-K_{aCO2}T}][P_{aCO2}])
\]

Equation 10

where:

- $C_{CO2(aq)}$ = Dissolved CO$_2$ (e.g. [CO$_2$]$_{aq}$) $\approx$ [H$_2$CO$_3$] (mmoles/l); and
- $E$ = Equilibrium Condition @ Time = 0;
- $T$ = Time (day);
- $K_{aCO2}$ = Inorganic carbon gas transfer rate from the atmosphere (day$^{-1}$);
- $P_{aCO2}$ = Periphyton consumption of CO$_2$ (mmoles CO$_2$/mg O$_2$/l * day).

Periphyton oxygen production is developed through an analytical formula developed by Di Torro (1981) that relates the observed range of diurnal dissolved oxygen ($\Delta$DO), depth (H), and aeration coefficient ($K_{aO2}$) to a measure of maximum potential benthic oxygen production ($P_{aO2}$):

\[
P_{aO2} = \left(0.5K_{aO2}[1 - e^{-K_{aO2}}] \right) \left(\Delta_{DO} \right)(H)
\]

Equation 11

Equation 11 is a method to calculate the amount of oxygen produced by periphyton per bottom area normalized by depth (mg/l-day). The stoichiometric equivalent of carbon consumed during the photosynthetic process was determined by a simple mass balance relationship which defines the amount of oxygen produced during photosynthesis to the amount of carbon consumed (Equation 1). Specifically, $P_{aO2}$ (Equation 11) was converted to carbon consumed during the photosynthetic process (Chapra, 1997) and incorporated into the model:

\[
\text{Oxygen to Carbon Conversion} = \frac{6 \text{ mmole CO}_2}{6 \times 32 \text{ mgO}_2} = 0.03125 \frac{\text{mmole CO}_2}{\text{mgO}_2}
\]

Equation 12

Equation 10 is analogous to classical dissolved oxygen balances, with the exception that only the free carbon ([CO$_2$]$_{aq}$)$\approx$ [H$_2$CO$_3$] portion of the total carbonate concentration is involved in the aeration equilibrium calculations. Neglecting the influence of buffers other than the carbonate system, and assuming that total alkalinity does not change, the pH can then be estimated from the application of these equations. Changes in free carbon (e.g. [CO$_2$]$_{aq}$)$\approx$ [H$_2$CO$_3$]) and total carbonate species (e.g. [CtCO$_3$]) due to photosynthesis and respiration were calculated through the application of Equation 10. At the range of pH found in Little River (approximately 6.5-9.0), it can be assumed that most of the carbonate buffers are in the form of bicarbonate HCO$_3^-$ (e.g. C$_2$CO$_3$ $\approx$ HCO$_3^-$). The temperature dependent equilibrium constant for bicarbonate ($K_{a1}$) is defined as:
\[
K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^+]} \]

Equation 13

Through substitution and rearrangement, pH can be defined as the negative logarithm of \([H^+]:\)

\[
[H^+] = \frac{K_{a1}[CO_{2(aq)}]}{[C_tCO_3]} \]

Equation 14

where \([C_tCO_3]\) and \([CO_{2(aq)}]\) are determined through the application of Equation 10.

The carbon balance presented in Equation 10 is expressed in terms of a deficit, and is defined as the difference between saturation and existing concentrations. The carbon deficit will increase due to carbon uptake from periphyton and decrease from gas exchange (Chapra, 1997). The carbon equilibrium level in water is defined as saturation, at which point no net diffusion exchange of carbon between air and the water will occur. The carbon exchange rate between air and water depends on both the differences between existing carbon concentrations and saturation, as well as water turbulence. For example, carbon diffusion rates will increase at a greater carbon deficit and water turbulence levels. This process is similar to re-aeration in streams.

It is assumed that the dominant carbon balance processes are photosynthetic uptake (i.e. periphyton uptake) and carbon re-areation (i.e. gas exchange). By assuming that the uptake of carbon and equilibrium reactions occur at a greater rate than replacement of carbon through aeration, the response of pH to reduced carbon concentration can be modeled. Accordingly, the carbon balance accounts for the current deficit, the amount of carbon brought in through aeration due to that deficit, the amount of carbon lost due to photosynthesis and the amount of carbon brought in through aeration due to the increase deficit resulting from photosynthesis.

The impact of algal production on pH was determined by solving the inorganic carbon mass balance up to a pH of 9.5. Above 9.5, the solution was assumed to be simply greater than 9.5 in order to simplify the calculations (e.g. available inorganic carbon is significantly curtailed at pH values equal or above 9.5.).

**APPLICATION OF THE MODEL**

**Model Time Step**

A simple steady state analysis does not provide information on how effective nutrient control may be downstream of the nutrient source because uptake from benthic algae reduces the available nutrient supply. Accordingly, a time dependent solution of the inorganic carbon balance was used to assess the potential influence of diurnal pattern of photosynthetic activity. A time dependent determination of total carbonate \((C_tCO_3)\) and hydrated carbon dioxide \((CO_{2(aq)})\) provided a method to estimate in-stream pH levels resulting from increased periphyton production rates downstream of a source of pollution. The time step was modeled at a ten-minute interval.

**CO\(_2\) and O\(_2\) Aeration Rate**

The carbon mass balance equations in this model are extremely sensitive to the estimated, or assumed, ratios between aeration \((K_{aCO_2})\) and production \((P_a)\) rates. It can be shown that a decreased gas transfer or increased benthic consumption rate would increase the rate which the \(CO_{2(aq)}\) deficit develops, and therefore result in an increase in-stream pH. In addition, increased depths would decrease the relative impact from periphyton production rates \((P_a)\). The distance or
the time required to exceed water quality standards is dependent on the availability of inorganic carbon concentrations of the water entering the section of the river, or from other sources such as tributaries, groundwater, or atmospheric aeration of CO₂.

Aeration rates ($K_{aO2}$) were estimated through the use of the Tsivoglou and Wallace (1972) formula. The formula was developed using a database of direct measurement of re-aeration:

$$K_{aO2} = 0.88 \frac{US}{S}$$

Equation 15

Where $K_{aO2}$ is in day⁻¹ at 20°C, $S$ is the slope in feet/mile, and $U$ is the velocity in feet per second. More recent comparisons by Grant and Skavroneck (1980) indicated that this expression is most accurate for small shallow streams (Thomann and Mueller, 1987).

There is little literature describing aeration rates for inorganic carbon ($K_{aCO2}$). Tsivoglou (1967) found during a series of laboratory tests that the mean ratio for dissolved oxygen ($K_{aO2}$) and inorganic carbon aeration rates ($K_{aCO2}$) to be 0.894 with a range of 0.845 to 0.940 and a standard deviation of 0.034. Simonsen and Harremoest (1978) determined aeration rates in a river using a twin curve method for both carbon and oxygen and found that the $K_{aCO2}$ averaged 0.57 $K_{aO2}$. It was assumed that the aeration rates for inorganic carbon followed the relationship presented by Simonsen and Harremoest (1978).

Periphyton Growth

The rate of periphyton growth is limited by the availability of light, nutrients, and water temperature. In a situation where the available light for periphyton growth is at an optimum level and nutrients are plentiful, then the growth of periphyton will be dependent on the temperature effect (Thomann and Mueller, 1987). If all of these are available in excess (i.e. non limiting condition), then dense mats of periphyton will grow and the algal mass will then be regulated by grazing by macro-invertebrates, grazer predation, substrate characteristics, and hydraulic sloughing.

Potential periphyton growth was assumed to occur proportional to the calculated growth rate from light availability ($G_L$) and the calculated growth rate from nutrient ($G_N$) concentration, whichever rate is lowest. It was assumed that the calculated production rate of oxygen ($P_{AO2}$) (see Equation 11) was proportionately reduced by these periphyton growth rate functions:

$$\text{Potential Periphyton Growth} = \text{Minimum (} G_N \text{ or } G_L \text{)} \times P_{AO2}$$

Equation 16

In addition, a component to estimate periphyton growth response to changes in stream temperature ($G_T$) was used to estimate the instream pH in Little River from rivermile 26.0 to the mouth given instream temperatures ranging from 15 to 22 degrees C.

Algal Growth Factor - Availability of Light ($G_L$)

Increased Solar Radiation has been shown to increase pH by encouraging photosynthetic chemical reactions associated with primary production (DeNicola et al., 1992). Increased algal productivity in response to increased solar exposure has been well documented (Gregory et al., 1987; DeNicola et al, 1992). In addition, it has been shown that photosynthesis of benthic algal communities in streams reaches a maximum at low light intensities (Gregory et al., 1987; Powell, 1996).

The effect of solar radiation on periphyton productivity ($G_L$) was added to model calculations, and was assumed to follow a sinusoidal curve described by Simonsen and Harremoest (1978):

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where alpha is the length of day (assumed 16 hours/day) and t is the time of day and is represented in Figure 4.

![Figure 4: Algal Growth Rate due to Solar Radiation (GL)](image)

**Algal Growth Factor - Nutrients (G_N)**

Algae (periphyton) production due to phosphorus concentrations, as well as periphyton nutrient uptake, was assumed to follow the Michaelis-Menton model of enzyme kinetics: Algae production and nutrient uptake due to available nutrients (G_N) was assumed to be relative to the availability of in-stream dissolved orthophosphorus (Figure 5).

![Figure 5: Algal Growth rate due to instream nutrient concentration (G_N)](image)

A conservative 0.004 mg/l Michaelis-Menton half saturation constant (K_S) was used in the model to calculate G_N. This value corresponds to an algal growth rate which is one half (0.5) the maximum rate. Typical phosphorus half saturation constants found in literature for benthic algae range from 0.004 to 0.008 mg/l.
If a nutrient control program is initiated, but the reduction in input load only reduces the nutrient concentration to a level of about two to three times the Michaelis constant, then there will be no effect on the algal growth. This is equivalent to the notion of the limiting nutrient. Removing a nutrient that is in excess will not have any effect on growth until lower concentrations are reached. The treatment program may then be ineffective. The nutrient effect on algal growth, therefore, is a marked contrast to other types of water quality problems where reductions in input load (as in biochemical oxygen demand reduction) can generally be considered as being advantageous (Thomann and Meuller, 1987).

Horner et al. (1990), conducting research in laboratory streams, observed that nutrient uptake by filamentous algae increased most dramatically as Soluble Reactive Phosphorus (SRP) concentrations increased up to 0.015 mg/l, and decreased beyond 0.025 mg/l. The author noted that this information corroborates results presented in Horner et al. (1983): Working with the attached filamentous green algae Mougeotia sp., Horner et al. (1983) reported that algal accrual increased in proportion to increased SRP up to about 0.025 mg/l, but further increases were not as pronounced above that concentration, presumably due to a saturation of uptake rates.

Bothwell (1989) reported that maximum algal growth occurred at ortho-phosphorus concentration of 0.028 mg/l. However, this author reported that there appears to be differences between saturation growth rates and biomass accrual rates, with algal cellular requirements saturated at ambient phosphorus levels between 0.003 - 0.004 mg/l (Bothwell, 1992). However, many researchers have found that much higher levels of phosphorus are required to produce algal bloom problems in streams and rivers (Horner et al., 1990; Horner et al., 1983; Welch et al., 1989). Discrepancies may arise because of species differences, differing physical factors, the influences of algal mat thickness and community nutrient requirements, and the dynamics of nutrient spiraling. Accordingly, it was assumed that the algal growth, and subsequently the phosphorus uptake rate, was saturated at in-stream concentrations greater than 0.025 mg/l.

It is important to note that Bothwell (1985) observed that additions of multiple nutrients have a greater stimulatory effect on periphyton than estimated from single nutrients as assumed in this modeling work. Accordingly, pH modeling simulations may underestimate the actual production rates resulting from nutrient additions (G_{N}) that would be observed in the river.

**Algal Growth Factor - Temperature (G_{T})**

The assimilative capacity of a water body is often proportional to temperature because of its influence on equilibrium conditions and several biological and chemical reaction rates. In a review of laboratory studies, field studies and mathematical models, O’Connor (1998) demonstrated that the gas transfer rate between the water surface and overlying atmosphere, rather than the carbonate equilibrium reaction rate, was the controlling mechanism for pH change resulting from temperature changes. Therefore the analysis of assimilative capacity at different temperatures focuses on factors influencing CO₂ exchange and not the carbonate equilibrium reaction.

Specific temperature dependent functions affecting CO₂ exchange include in this model are: 1) CO₂ saturation; 2) maximum algal growth rate (expressed as the photosynthetic demand of carbon); and 3) CO₂ aeration. Temperature influences were estimated by multiplying the ratio between the estimated rate at predicted temperatures and the calculated rate at initial conditions, which was calibrated using observed field temperature data.

The saturation level of carbon dioxide is related to temperature through Henry’s law and is calculated as a function of temperature and altitude according to USEPA (1986); and as expressed by Caupp et al. (1997):

\[
\text{CO}_2 \text{ Saturation} = 10^{\left(-2385.73 \times \frac{14.01884 \times \text{Temp} + 0.0152642}{\text{Temp}} + 0.152642 \times \text{Temp} + \text{Elevation} + 44000 \times \text{Temp} - 2385.73\right) + 0.006496 \times \text{Elevation}}
\]

Equation 18
where Temp is water temperature in Kelvin, and Elevation is elevation in meters.

The influence of temperature on the CO$_2$ aeration rate is modified using the Arrhenius relationship with a standard reference to 20 °C. The USEPA Document (1985) identified a typical range of theta values between 1.022 and 1.024, with a reported range of 1.008 to 1.047. This range was developed for the simulation of dissolved oxygen. A theta value of 1.02 identified by O’Connor (1998) for CO$_2$ was used:

$$K_t = K_{20} \theta (\text{Temp} \text{°C} - 20 \text{ °C})$$

Equation 19

where $K_t$ is the CO$_2$ aeration rate at temperature (t), and $K_{20}$ is the CO$_2$ aeration rate at 20 °C.

Temperature effects on the algal growth rate were related directly to maximum production rate ($P_{A02}$) (Equation 11). Algal growth rate, expressed as photosynthetic demand of carbon, was adjusted for temperature using the equations presented by the USEPA (1986):

$$\text{Algal Growth} (\text{Temperature}) = \theta (\text{Temperature} \text{ °C} - 20 \text{ °C})$$

Equation 20

Typical theta values were reported by USEPA to range between 1.01 and 1.2. Epply (1972) reported a theta of 1.066. This value was used in the model.

**Initial Buffering Capacity**

Initial alkalinity, pH and temperature of Little River were included in the carbon balance calculations in the model.

**Algal Biomass Accrual**

Results obtained from the application of this model do not simulate algal biomass accrual, but it provides a method to calculate an assumed diel production ($\approx$ growth) pattern. A simple procedure proposed by Horner et al. (1983) and discussed by Welch et al. (1989) provides a steady state kinetic prediction of the potential periphyton biomass accrual based on physical and chemical characteristics of the river and their influence on algae growth rates and accumulation. The model was originally calibrated against the growth of filamentous green algae in artificial channels over a range of velocities and phosphorus concentrations. Application of the model with site specific data from the Spokane River, Washington (Welch et al., 1989) and the Coast Fork Willamette River, Oregon (DEQ 1995-b) indicated that the rate of biomass accumulation reduced proportionally to that of in-stream limiting nutrient concentrations, and that the rate of bioaccumulation was expected to decrease downstream as uptake removed the limiting nutrient. In addition, it was also hypothesized that periphyton biomass will eventually approach maximum levels even at low in-stream nutrient concentrations following a sufficiently long growing season.

**Invertebrate Grazing**

The pH model described above does not estimate the potential effects of grazing by macroinvertebrate on the standing crops and net production of the periphyton community. Grazing may influence not only standing crop, but also nutrient uptake and recycle rates, as well as species distribution within the benthic algal mat. Grazing generally results in lower periphyton biomass (Lamberti et al., 1987 and; Welch et al., 1989), a simplified algal community, lower rates
of carbon production, and a constraint nutrient cycling (Mulholland et al., 1991). Reduced production rates anticipated under a nutrient control strategy would likely increase the relative influence of grazing as a controlling mechanism on periphyton. Hence, periphyton biomass accrual rates in Little River may be lower than predicted by the model as a result of a relative increased invertebrate grazing pressure at the anticipated reduced periphyton growth rates.

**Model Calibration**

The model was calibrated using streamflow and continuous pH data collected during August, 2000. The streamflow measured during the survey was 13 cubic feet per second, which is near the historic 7Q10. As can be seen in Figures 6 and 7 below, the model-calculated pH was very close to the observed pH.

![Figure 6: Little River pH Model Output](image-url)
The temperature model of the Little River was used to predict current management potential maximum temperatures at rivermiles 21.0, 14.7 and 8.0 of 16.0, 17.0, and 17.0 degrees F, respectively. The pH model predicts that the maximum instream pH at rivermile 14.7 will be 8.3 SU with the river achieving current management potential temperatures (see model output in Figure 8). The pH predicted at current management potential temperature near the mouth of Little River is 8.4 SU. The loading capacities for periphyton are the current management potential stream temperatures discussed above.
SECTION REFERENCES


