

## Klamath River Technical Memorandum 5

Topic: Oregon Department of Environmental Quality pH model review

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Abstract: The Oregon Department of Environmental Quality (ODEQ) pH model, which has been applied to the Little River and the Sprague River, was examined for application to the Klamath River. The model is not well-documented and there seem to be several faults with the construction of the model. The ODEQ pH model is not recommended for the Klamath River because of fundamental flaws associated with the model and its assumptions.

### Introduction

The Klamath River, beginning at Link Dam, Upper Klamath Lake, and ending at the Pacific Ocean, runs through both Oregon and California. Because both states have an interest in the water quality of the Klamath River, the Oregon Department of Environmental Quality (ODEQ) requested that Watercourse Engineering, Inc. (Watercourse) apply an in-house model, which had been applied to both the Little River and the Sprague River by ODEQ, to simulate pH in the Oregon portion of the Klamath River. The following is a review of the pH model provided to Watercourse by ODEQ.

### Description of pH model

The ODEQ pH model is constructed in an Excel workbook and is comprised of four calculation worksheets: Oxygen Production, Carbon Mass Balance, Temperature and pHdiurnal. Each of the first three worksheets calculates time-constant information that links with the final worksheet, pHdiurnal, which is the actual time-varying model. Overall, oxygen production due to algae, fast pH reactions (the carbonate system), and some temperature corrections are calculated and fed into time varying calculations of slow pH reactions (algal effects on pH and atmospheric carbon dioxide (CO<sub>2</sub>) effects) to determine the ultimate pH of the river. The contents of each worksheet are discussed below.

### ***Oxygen Production***

The “Oxygen Production” worksheet calculates average daily areal production of oxygen (O<sub>2</sub>) by phytoplankton,  $P_{aO_2}$ , over an entire reach of river as a function of reaeration rate, observed diurnal change in DO, and depth (Thomann & Mueller p. 290). This O<sub>2</sub> production rate is used to estimate CO<sub>2</sub> consumption via stoichiometry. The formula describing O<sub>2</sub> production is given as:

$$P_{aO_2} = \left( \frac{0.5K_{aO_2} (1 - e^{-K_{aO_2}})}{(1 - e^{-0.5K_{aO_2}})^2} \right) (\Delta_{DO}) (H) \quad (1)$$

Where:

- $P_{aO_2}$  = average daily areal oxygen production by phytoplankton, g DO/m<sup>2</sup>-day
- $K_a$  = reaeration rate, 1/day = 0.88US<sub>e</sub>
- $U$  = velocity (ft/sec)
- $S_e$  = slope, ft/mi
- $\Delta_{DO}$  = observed diurnal change in DO (mg/l)
- $H$  = depth (m)

Each of these parameters is set up to be calculated as an average, weighted by river length over which they apply. In fact, constant values are used for velocity (1.07 ft/sec), depth (2.80 ft), and slope (52.8 ft/mile) over the reach.

$K_a$  is calculated using Tsivogloy and Wallace @ 20°C (Thomann & Mueller p 281). The formula assumes a steep friction slope ( $S_e = 52.8$  ft/mile (0.01 ft/ft)) and flow between 10 and 300 cfs. Contrary to notes presented in the Oxygen Production sheet,  $K_a$  is not corrected for temperature within this sheet. This value of  $K_a$  is also used in the pH model to estimate,  $K_{aCO_2}$ , mass transfer of CO<sub>2</sub> across the air-water interface.

### Issues within the “Oxygen Production” sheet

The estimate used for bed channel slope appears to be quite high, considering the given depths and velocities. From given depths, velocities, and an estimated Manning’s n of 0.045 (which is a common value for the roughness coefficient in natural streams with rough beds) an estimate of the friction slope can be calculated using Manning’s Equation (Thomann and Muller p 48):

$$U = \frac{1.49}{n} R_h^{2/3} S_0^{1/2} \quad (2)$$

Where:

- $U$  = average velocity, ft/sec
- $n$  = Manning’s Roughness coefficient
- $R_h$  = hydraulic radius, ft = A/P
- $A$  = cross-sectional area, ft<sup>2</sup>
- $P$  = wetted perimeter in cross section, ft
- $S_0$  = slope of the channel bed, ft/ft

The hydraulic radius, expressed as a function of depth and width (assuming a rectangular cross section) is defined as:

$$R = \frac{dw}{w + 2d} \quad (3)$$

Where:  $d$  = depth of river, ft  
 $w$  = width of river, ft

In most river systems, the channel is assumed relatively wide compared to depth, so that  $w \gg 2d$  and  $w+2d$  is approximately equal to  $w$ . Therefore  $R$  is approximated as:

$$R = \frac{dw}{w} = d \quad (4)$$

Manning's Equation can be written to solve for friction slope as:

$$S_0 = \left( \frac{u \cdot n}{1.49d^{2/3}} \right)^2 \quad (5)$$

Using equation ( 5 ) with  $n = 0.045$  and  $d = 2.80$  ft, the friction slope is calculated as 0.0003 ft/ft. The assumed slope factor of 0.01 ft/ft used to calculate  $K_a$  is more than 30 times larger than the estimated slope factor for the depth and velocity specified in the model. Because rates for both  $P_{aO_2}$  and  $CO_2$  air-water transfer are based on  $K_a$ , which depends on the slope estimate, values for these rates appear to be too large as well.

### **Carbon Mass Balance**

The "Carbon Mass Balance" sheet calculates the concentrations of  $H_2CO_3^*$  ( $CO_2(aq)$ ) resulting from mixing river water and wastewater effluent (labeled "Meacham") based on a mass balance of alkalinity and  $C_{iCO_3}$ . The Excel "Goal Seek" function is then used to find a pH such that both alkalinity and  $C_{iCO_3}$  meet requirements of the equilibrium equation:

$$Alkalinity = C_{iCO_3}(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+] \quad (6)$$

Equilibrium constants are adjusted for temperature.

Together with mass-balance calculated alkalinity and  $C_{iCO_3}$ , resulting pH was probably meant to calculate an "equilibrium"  $H_2CO_3^*$  that is achieved relatively quickly after mixing. This is a "fast reaction" calculation and does not take into account slower transfer rates due to atmospheric  $CO_2$  transfer or algal effects. In fact, the calculated pH is not used anywhere in the model and "equilibrium" values are actually just "mixed" values with no reactions. The "initial mixed" value of  $H_2CO_3^*$  and the "equilibrium" values of  $H_2CO_3^*$ ,  $C_{iCO_3}$ , and  $K_{a1}$  are used in pH model calculations.

## Issues within the “Carbon Mass Balance” Sheet

In the model as given to Watercourse Engineering, Inc., all “equilibrium” values are set equal to “initial mixed” values and not derived from the calculated pH as seems intended. The calculated pH of the mixed water is never used and these equilibrium values are, therefore, not true “fast-reaction” equilibrium values.

The worksheet contains confusing labels: some values labeled “initial mixed” are not calculated using a mass balance, but are hardwired. Also, within the spreadsheet, there is a small error in calculating  $C_{iCO_3}$ , which affects results noticeably only if pH outside the range  $6 < \text{pH} < 9$ .

## Temperature

The “Temperature” sheet calculates CO<sub>2</sub> saturation values using:

$$\text{CO}_2 \text{ Saturation} = 10^{\left(\frac{-2385.73}{\text{Temp}} + 14.01884 - 0.0152642 * \text{Temp}\right)} * 3.162 * 10^{-4} * e^{\frac{(-0.03418 * \text{Elevation})}{(288.0 - 0.006496 * \text{Elevation})}} * 44000 \quad (7)$$

Units for CO<sub>2</sub> saturation (CO<sub>2s</sub>) are not specified. While the reference to this formula is given as “USEPA 1985 and Caupp et al., 1997” a list of references is not provided with the model, so the formula could not be checked completely. Part of the formula does appear as given in “Rates Constants, and Kinetics Formulations in Surface Water Quality Modeling” (USEPA, 1985).

The sheet estimates a “CO<sub>2</sub> saturation factor” as CO<sub>2s</sub> at “predicted” temperature divided by CO<sub>2s</sub> at “measured” temperature. Calculated “equilibrium” H<sub>2</sub>CO<sub>3</sub>\* from the “Carbon Mass Balance” worksheet is multiplied by this factor and the product is the saturation value used to drive CO<sub>2</sub> gas transfer in the pH model.

The worksheet also calculates a temperature-correction for  $K_{aCO_2}$  and maximum algal growth in a similar way: a factor is derived by dividing the given rate at an “initial” or “predicted” temperature by the rate at a “measured” temperature. In the worksheet, “predicted” and “measured” temperatures are set equal, so the factor is unity for both  $K_{aCO_2}$  and maximum algal growth rate.

## Issues within the “Temperature” Sheet

There is no evident basis for the “predicted” or “measured” temperatures used to calculate these factors. The temperatures do not correspond to the temperatures of the river or wastewater (at Meachum) given in the “Carbon Mass Balance” sheet.

Because elevation is a constant (2300 meters), the difference in calculated CO<sub>2</sub> saturation values is due entirely to the difference in temperature, so this factor would appear to represent a temperature adjustment of some kind. But the use of this factor with the “equilibrium” H<sub>2</sub>CO<sub>3</sub>\* calculated in the “Carbon Mass Balance” sheet for use in the “pHdiurnal” sheet does not make sense. Using CO<sub>2s</sub> (as calculated by equation ( 7 ) for

the predicted temperature) for the long-term equilibrium concentration of  $H_2CO_3^*$  would make more sense.

All of these factors seem to be used as extra calibration factors to adjust (predicted) model results to observed (measured) values.

### **pH diurnal**

The “pHdiurnal” sheet copies “initial mixed” and “equilibrium” values for  $H_2CO_3^*$  and  $C_{iCO_3}$ , and the “equilibrium” value of  $K_{a1}$ , from the “Carbon Mass Balance” sheet to calculate air-water transfer of  $H_2CO_3^*$ . Before use in the model, “equilibrium”  $H_2CO_3^*$  is multiplied by the “CO<sub>2</sub> saturation factor” from the “Temperature” sheet

The pH model is set up as a Lagrangian structure in which reaches are defined by travel time through them. In this model, pH is estimated at the end of each time step from transient concentrations of  $H_2CO_3^*$  and  $C_{iCO_3}$ . Carbonate concentrations are estimated from a mass balance around  $H_2CO_3^*$  accounting for net algal consumption of CO<sub>2</sub> and estimated mass transfer across the air-water interface.

Algal consumption of CO<sub>2</sub> is calculated as the product of estimated algal oxygen production and a stoichiometric conversion from oxygen to carbon dioxide production. Algal oxygen production is represented as the product of average daily oxygen production rate and the minimum of orthophosphate and light limitations on growth:

$$O_2 \text{ production} = P_{aO_2} * \min(\text{orthophosphate limit, light limit})$$

where  $P_{aO_2}$  is the oxygen production rate calculated in the “Oxygen Production” sheet and modified by the temperature factor for algal growth from the “Temperature” sheet, the orthophosphate limit is derived from a Monod limiting formula using the current orthophosphate concentration and a user-specified Michaelis-Menton 1/2 saturation constant, and the light limit is given by the following formula attributed to Simonsen and Harremost (exact reference unspecified):

$$Limit_{light} = Maximum \left( 0, \cos \left( \frac{2\pi \cdot (t - 0.5)}{\alpha} \right) \right) \quad (8)$$

Where:

$$\alpha = 2f$$

$$f = \text{fraction of day in light} = 16/24$$

$$t = \text{fraction of day that has passed since the previous midnight}$$

To calculate time-dependant orthophosphate limitations, the model simulates orthophosphate concentrations based on initial value, uptake rates, and recycling. Uptake is modeled like oxygen production and is calculated as the product of a user-specified maximum uptake and the minimum of algal growth limitations. (Additionally, the model assumes phosphorous and light limitation.)

In effect, recycling reduces orthophosphate uptake by 1/3. The recycling calculations are somewhat convoluted but, ultimately, these calculations state the following:

$$[\text{ortho P}] \text{ uptake after recycling} = ([\text{ortho P}] \text{ uptake})/\text{recycleF} \quad (9)$$

and

$$[\text{ortho P}]' = [\text{ortho P}] - ([\text{ortho P}] \text{ uptake})/\text{recycleF} \quad (10)$$

Where: recycleF = recycle factor = 1.5  
 [ortho P]' = concentration of ortho P in the next downstream section or time step

$H_2CO_3^*$  transfer from atmosphere is modeled as a linear function of reaeration. The factor, c, relating  $H_2CO_3^*$  transfer rate,  $K_{aCO_2}$ , to reaeration rate changes along the simulated reach by river mile and is defined as a calibration factor. The  $CO_2/O_2$  calibration factor used in this model ranges from 1.6-3.2, and seems high compared to a value of 0.92 as calculated from Chapra (1997; p 688), using the following equation:

$$c = \left( \frac{32}{M} \right)^{0.25} \quad (11)$$

Where: M = the molecular mass of carbon dioxide = 44

This calibration factor is applied by river mile (as listed in a small table within the “pHdiurnal” sheet) except in the most upstream portion of the river where a different factor was manually entered into the cells. “Calibrated”  $K_{aCO_2}$  is adjusted for temperature using the factor from the “Temperature” sheet. As described above, this temperature adjustment factor is equal to 1 and represents no change in  $K_{aCO_2}$ .

Reaeration itself is a linear function of the product of velocity and friction slope as described by Tsivoglou and Wallace (see earlier discussion and Thomann and Mueller, pg 281). As noted earlier, the authors have apparently assumed a steep friction slope (Se = 0.01 ft/ft) and flows in the range  $10 < Q < 300$  cfs, so calculated reaeration seems to be higher than what would be expected from the actual system.

The model calculates an  $H_2CO_3^*$  “loss from respiration,”  $H_2CO_3^*_{resp}$ , which represents the net loss of  $H_2CO_3^*$  resulting from algal growth and respiration. The method of calculation is:

$$H_2CO_3^*_{resp} = \left( 1 - e^{-K_{aCO_2}\Delta t} \right) \left( \frac{CO_2 \text{ consumption}}{K_{aCO_2}} \right) \quad (12)$$

It is unclear if this equation is being used in an appropriate manner, and a reference for the equation is not given.

Atmospheric transfer of  $H_2CO_3^*$  in the pH model is based on a DO sag model, using the formula:

$$\frac{d(H_2CO_3^*)}{dt} = K_{aCO_2} (H_2CO_{3sat}^* - H_2CO_3^*) \quad (13)$$

The pH model integrates over a time step,  $\Delta t$ , to get a new value of  $H_2CO_3^*$  due to atmospheric transfer,  $H_2CO_{3atm}^*$ :

$$H_2CO_{3atm}^* = H_2CO_{3sat}^* - (H_2CO_{3sat}^* - initialH_2CO_3^*)e^{-K_{aCO_2}\Delta t} \quad (14)$$

Where:  $initialH_2CO_3^*$  =  $H_2CO_3^*$  at the beginning of the time step and is taken from the previous river section

The model calculates a resulting  $H_2CO_3^*$  as the sum of the newly estimated  $H_2CO_3^*$  concentration (i.e.,  $H_2CO_{3atm}^*$ ) and net algae-associated loss.

Then, the model calculates  $C_{iCO_3}$  as:

$$C_{iCO_3} = initC_{iCO_3} - (H_2CO_{3sat}^* - initH_2CO_3^*)e^{-K_{aCO_2}\Delta t} - H_2CO_{3resp}^* \quad (15)$$

Where:  $initC_{iCO_3}$  = the equilibrium  $C_{iCO_3}$  calculated in the “Carbon Mass Balance” sheet

Which can be shown to be equivalent to:

$$C_{iCO_3} = initC_{iCO_3} + \Delta H_2CO_3^* - H_2CO_{3resp}^* \quad (16)$$

Equation ( 16 ) states that total carbonate carbon in the system is the sum of an initial  $C_{iCO_3}$ , the change in  $H_2CO_3^*$  due to atmospheric transfer ( $\Delta H_2CO_3^*$ ), and loss due to respiration. If carbon stayed in the  $H_2CO_3^*$  compartment, this would be a reasonable calculation.

Finally, the model calculates instantaneous pH as:

$$pH = Min \left( 9.5, \left| \log \left( \frac{K_{a1} H_2CO_3^*}{C_{iCO_3}} \right) \right| \right) \quad (17)$$

Equation ( 17 ) is derived from the equation used to calculate the  $H_2CO_3^*$  in the “Carbon Mass Balance” sheet:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \quad (18)$$

The calculation of pH using equation ( 17 ) assumes a system open to the atmosphere with a pH between approximately 6 and 10, such that approximately all carbonate is in the  $HCO_3^-$  form.

### Issues within the “pHdiurnal” sheet

There are several specific issues within the “pHdiurnal” sheet.

Because of the way “equilibrium” values are calculated on the “Carbon Mass Balance” sheet, the only difference between “initial mixed” and “equilibrium” values for  $H_2CO_3^*$  is the temperature correction applied to the “equilibrium” value.

As mentioned earlier, using the instantaneously mixed “equilibrium”  $H_2CO_3^*$  to represent  $H_2CO_3^*_{sat}$  is incorrect because the “equilibrium” concentration as calculated is not a saturation value. The appropriate value would be calculated from equation ( 7 ). We note that the second part of the right-hand side of the atmospheric transfer equation ( 14 ) is calculated under a column mislabeled “addition due to aeration.”

The model calculates a resulting  $H_2CO_3^*$  as either very small (0.00001) or the sum of  $H_2CO_3^*_{atm}$  and “respiration loss.” This calculation is not correct because, although atmospheric transfer does go into the  $H_2CO_3^*$  compartment,  $H_2CO_3^*$  is immediately redistributed among the other carbonate-system compartments. So the calculated value of  $H_2CO_3^*$  stays artificially high and the resulting driving force for atmospheric transfer is artificially low.

### Overall Comments

The spreadsheets are not clearly set-up and columns and values are mislabeled, so it was a difficult task to follow the intended logic of the authors. There are several fundamental flaws with the way in which this model is set up and implemented, as well as several aspects to the model which make use difficult. Generally, the main comments are:

- 1) Model is hardwired to calculate a maximum pH of 9.5, but this is not stated anywhere. Klamath River pH alues have exceeded this value.
- 2) Numbers which should be calculated are hardwired and it is difficult to establish their origins.
- 3) Numbers which are hardwired have no references attached to them.
- 4) Reaeration rates seem to be miscalculated resulting in high values of  $CO_2$  consumption and  $CO_2$  transfer rates.
- 5) The formula for calculating loss of  $CO_2$  due to respiration does not appear to use the correct logic.

- 6) CO<sub>2</sub> transfer from the atmosphere does not appear to be modeled correctly in many separate aspects.
- 7) There is no list of references attached to the pH model.
- 8) The model is piece-wise calibrated to fit observed data. There are no physical justifications given for setting calibration parameters as they have been set, and there is no indication that the model is applicable outside of the narrow conditions for which it is calibrated. The reliability of this calibration should therefore be held in question.
- 9) The model assumes only phosphorous limitation with respect to nutrients in the algal growth dynamics: a condition which may not occur at all times in the Klamath River basin.

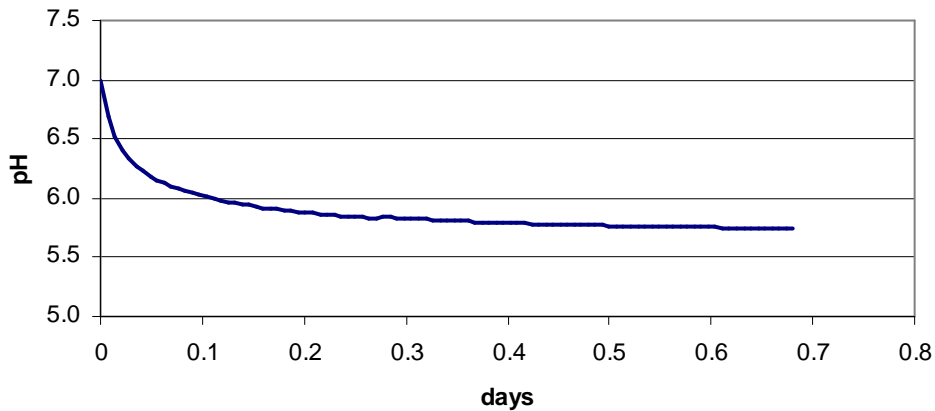
Hardwired numbers appear in all worksheets supporting the pH model. As a result, it is not clear that either oxygen production or temperature corrections are correctly modeled.

Reaeration rates are derived from an assumption of a high friction slope (0.01 ft/ft) resulting in values of CO<sub>2</sub> consumption and CO<sub>2</sub> transfer rates that may be on the order of 30 times too high. Also, the calibration factors relating reaeration rates to  $K_{aCO_2}$  are all higher than the value estimated from Chapra (1997) and referenced in other ODEQ documents (ODEQ, 2000).

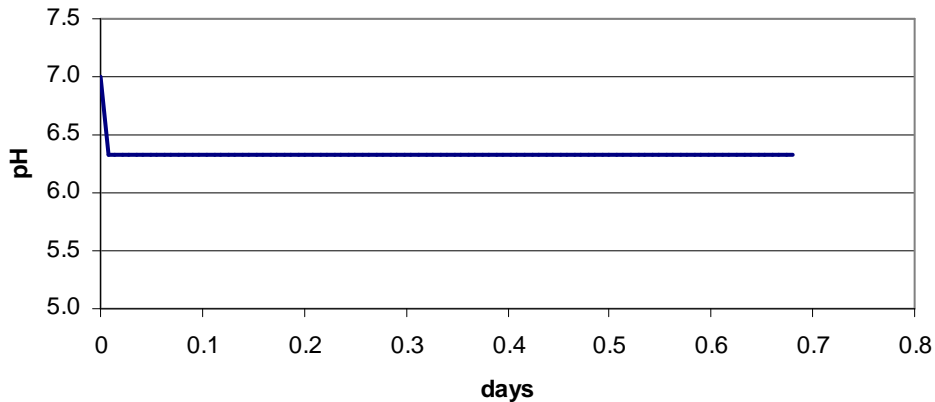
The formula for calculating net loss of CO<sub>2</sub> due to algal activity is unclear. In the formula, respiration loss is related to both  $K_{aCO_2}$  and CO<sub>2</sub> consumption.

Many aspects of the transfer of CO<sub>2</sub> from the atmosphere into the water column seem to be incorrect. First, the  $H_2CO_3^*_{sat}$  value used to calculate the  $H_2CO_3^*$  difference ( $H_2CO_3^*_{equilibrium} - H_2CO_3^*$ ) that drives atmospheric CO<sub>2</sub> transfer in the pH diurnal model is derived from the “equilibrium” value of  $H_2CO_3^*$  from the “Carbon Mass Balance” worksheet. This makes little sense because the value for  $H_2CO_3^*_{equilibrium}$  is actually just the initial mixed river concentration and not a true equilibrium value. Even more importantly, the equilibrium value (even assuming it were calculated from the estimated pH of the mixed river and wastewater) is the “fast reaction” equilibrium (modified by a temperature correction from the “Temperature” sheet) and has nothing to do with atmospheric concentrations. The value of  $H_2CO_3^*_{sat}$  should be calculated from an formula such as equation ( 7 ).

Just as importantly, the model does not attempt to distribute carbonate from  $H_2CO_3^*$  to other carbonate compartments. In actuality, atmospherically transferred CO<sub>2</sub> does initially go into the  $H_2CO_3^*$  compartment. But  $H_2CO_3^*$  is immediately redistributed among the other carbonate-system compartments, lowering the resulting  $H_2CO_3^*$  concentration. In the existing model formulation, the calculated value of  $H_2CO_3^*$  is not transferred, staying artificially high, and the resulting driving force for atmospheric transfer is artificially low. A small test of the correct formulation (which requires a numeric or iterative solution) indicates that redistribution is important and necessary. The results of a pH calculation using carbonate redistribution and a calculation without carbonate redistribution are presented in Figure 1 and Figure 2, respectively.



**Figure 1 pH calculation with carbonate distribution included:  $H_2CO_3^*$  concentration equals  $10^{-5}$  M, partial pressure of  $CO_2$  equals  $10^{-3.5}$  atm.**



**Figure 2 pH calculation without carbonate distribution included:  $H_2CO_3^*$  concentration equals  $10^{-5}$  M, partial pressure of  $CO_2$  equals  $10^{-3.5}$  atm.**

Finally, the pH model uses a DO sag model to calculate atmospheric transfer of  $H_2CO_3^*$ , integrating over a time step to get a new value of  $H_2CO_3^*$ , as shown in equation ( 14 ).

By this equation, atmospheric transfer equals:

$$\Delta H_2CO_3^* = \left( H_2CO_{3sat}^* - initH_2CO_3^* \right) e^{-K_{aCO_2}\Delta t} \quad (19)$$

and represents the change in  $H_2CO_3^*$  from  $H_2CO_{3sat}^*$  over a time step,  $\Delta t$ , and where  $initH_2CO_3^*$  is taken from previous river section. This is the amount of  $H_2CO_3^*$  transferred in one time step. That would be correct if  $H_2CO_3^*$  were like oxygen, for which this equation was developed (see Thomann & Mueller, pg 279). But  $H_2CO_3^*$  is immediately redistributed to other  $CO_3$  species, so the change in  $H_2CO_3^*$  isn't solely dependent on its concentration, and this exponential model is not correct. The error produced by using this formulation is most likely very small because it is just applied over one time step, but it seems better to use a differential value, not an analytic value,

because the differential value assumes a constant concentration while the analytic (exponential) solution does not.

## Conclusions

The ODEQ pH model is not recommended for application to the Klamath River because of fundamental flaws associated with the model and because of the upper pH limit of 9.5 imposed by the model and its assumptions. Lake Ewauna, a portion of the Klamath River near Klamath Falls, Oregon, has historically had pH values greater than 9.5.

## References

- Chapra, S.C. (1997) *Surface Water Quality Modeling*, McGraw-Hill Companies, Inc., San Francisco.
- ODEQ (2000) The Periphyton Control Model and its Application to the Grande Ronde River, Oregon. State of Oregon Department of Environmental Quality. April, 2000.
- Thomann, R.V. and Mueller, J.A. (1987) *Principles of Surface Water Quality Modeling and Control*, HarperCollins Publishers Inc., New York.
- USEPA (1985) Rates Constants, and Kinetics Formulations in Surface Water Quality Modeling. Second edition. EPA Number: 600/3-85/040 (June, 1985)