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Technical Memorandum #8: Klamath River pH Model

Date: January 6, 2004 (revised 9-27-04)

Abstract:

This technical memorandum describes the construction and application of a pH model for the Klamath River in the vicinity of the Klamath Hydroelectric Project (Project). Estimates are made by application of two pH models used in conjunction. For run-of-river sections of the Klamath River, a pH model was constructed and applied as described in this technical memorandum. Reservoir sections were modeled with the CE-QUAL-W2 simulation model as described in this memorandum. To create a contiguous simulation, results from one model were passed to the next at shared boundaries. The models were calibrated for pH. These model runs produced simulated pH values that generally stay within a range of 8-10 pH units along the river, but may fall slightly outside this range under some conditions (but still within range of conditions found in the Klamath basin). The pH model results should be viewed with some uncertainty given the limited available data that is available to construct and calibrate the model

1. Introduction

pH of the Klamath River has been estimated in a series of continuous reaches from Link Dam to Seiad Valley for both Existing Conditions (EC) and Without Project (WOP) configurations under May-Sep 2000 environmental conditions. Originally, a pH model developed by Oregon Department of Environmental Quality (ODEQ) was chosen for this modeling work. This model is referred to as the "Little River pH Model" in spreadsheets containing its calculations. Upon review, the ODEQ model was found to have limitations that precluded its use on the Klamath River[1]. Instead, CE-QUAL-W2 was used to model pH in reservoirs and the Watercourse pH Model was developed to model pH in river sections of the Klamath River. Under Existing Conditions, simulated reaches include sections of river, modeled for pH by the Watercourse pH Model (pH Model) and sections of reservoir, modeled for pH by CE-QUAL-W2. Under Without Project conditions, there are no reservoirs and only the pH Model system will be used. The two modeling systems are distinct and, to model the entire river from Link Dam to Seiad Valley, results were passed from one section of the river to the next at common boundaries.

Modeling approach, state variables, boundary conditions, model application, results, and pertinent regulatory statistics are discussed in the following sections.

2. Approach

The pH Model estimates pH along a specified river reach at hourly intervals over the course of a specified simulation period. Estimates of pH and TIC are made for each node of the reach, typically laid out in equal intervals, assuming a laterally- and vertically-

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[1] Complete description of the ODEQ model and associated limitations for application to the Klamath River in the Project area are outlined in Technical Memorandum 5.

averaged water column. CE-QUAL-W2 estimates hourly pH in laterally-averaged compartments representing reservoir sections of the river.

The pH model uses a Lagrangian scheme to make its estimates. In this approach, water is released at the top of the reach and tracked as it travels downriver undergoing interaction with the environment. Initial conditions are applied to the water "parcel" at the first node of the reach and pH is estimated at each subsequent node based on the flux of carbon dioxide into or out of the parcel during travel between nodes. While pH may be affected by dissolution of bedrock minerals, geologic sources were not simulated in this version of the model. In the Watercourse pH Model, alkalinity of a parcel of water is conserved and changes to pH result solely from carbon dioxide (CO_2) addition and removal by algae respiration and growth, and exchange with the atmosphere.

Carbon dioxide loss and gain are calculated for the periods of time spent traveling between nodes, in reach subsections. At the head of each subsection, pH is determined from alkalinity and total inorganic carbon (TIC) using water temperature and chemical equilibrium constants. Within each subsection, alkalinity is conserved and flux of carbon dioxide is calculated from estimated atmospheric CO_2 transfer rates and net algae growth. At the end of each subsection, a new concentration of TIC in the water parcel is calculated as the sum of initial TIC and carbon associated with CO_2 flux during residence time in the subsection. From this new TIC concentration, a new pH is determined for the water parcel as it enters the next subsection. In this fashion the pH of the parcel changes with addition or removal of CO_2 through each subsection of the reach.

CE-QUAL-W2 is a finite difference model using implicit numerical solutions to estimate pH, alkalinity, TIC, temperature and a number of other water quality constituent concentrations within reservoir reaches of the river. Detailed descriptions of CE-QUAL-W2 construction and application to this system may be found in Cole and Wells (2002) and PacifiCorp (2004a).

3. State Variables

Within any reach subsection, CO_2 flux at any particular time or location depends upon the environmental state of the system. For example, atmospheric flux of CO_2 depends upon water temperature, speed, and depth of flow. CE-QUAL-W2 calculates a full suite of environmental state variables (including those needed specifically to determine pH) during the course of its simulation. On the other hand, the pH Model uses state variables that are pre-determined for each node at each hour of the simulation by results of detailed hydrodynamic and water quality simulations of the river. In this application, these detailed simulations have been made with Resource Management Associates' RMA-2 and RMA-11 models. Results of these simulations have been presented in PacifiCorp (2004b).

In the pH Model, each subsection is described by state variables that include water temperature, velocity, depth, change in water column algae, and change in bed algae. These variables are used to determine residence time, CO_2 transfer rate coefficient, CO_2

saturation concentration, net total algae growth, and ionization fractions for chemical equilibrium calculations. Values for state variables within a subsection are assumed equal to their values at the head of the subsection for the hour just prior to the time the water parcel enters the subsection. These values are assumed to be constant during the time the parcel resides in the subsection.

4. Boundary Conditions

Boundary conditions for pH modeling describe the flow, pH, alkalinity, and total inorganic carbon (TIC) at points of inflow into the system. Headwater boundary conditions for the pH Model are defined by hourly values of flow, pH, and alkalinity. Hourly TIC at the headwater is calculated from pH and alkalinity (Snoeyink and Jenkins, 1980). Tributary boundary conditions in the pH Model are defined by flow, alkalinity, and TIC. These values are used in a mass balance at the tributary junction to determine mixed (tributary and river) concentrations of alkalinity and TIC from which the model calculates pH. CE-QUAL-W2 requires both headwater and tributary alkalinity and TIC for its pH calculations.

In this section, all water quality boundary values for pH, alkalinity, and TIC are described for EC and WOP 2000 simulations. Other input values, including flows, are described in detail by PacifiCorp (2004a).

4.1.   Link River

The Link River section of the Klamath River extends from Link Dam to the headwaters of Lake Ewauna and is modeled as a river reach using the pH Model. Link River boundary conditions include headwaters at Link Dam and tributary East and West Side Powerhouse returns.

4.1.1. Link Dam

Establishing the headwater boundary conditions at Link Dam is especially important because these conditions set the stage for down river reaches. As shown in results of these simulations, inflow boundary conditions appear to determine, or strongly influence, the magnitide of pH calculated the length of the study area (Link Dam (RM 255) to Seiad Valley (RM 129)).

pH

Using data from the Klamath Tribes Natural Resources Department (Kann, 2001) and US Bureau of Reclamation (USBR) monitoring program data, pH values for Link Dam were estimated for 2000. For lack of sufficient hourly USBR data, semi-monthly Klamath Tribes data were selected to represent Link Dam conditions. Of two Klamath Tribes sites in the vicinity, Fremont Bridge is closer to Link Dam and possibly more representative of conditions at the dam release. But there are insufficient data from the Fremont Bridge site for the period in question, so the Pelican Marina site was chosen to represent Link Dam. The following comparison of the different data sets supports this selection.

A comparison of available USBR water quality probe data and semi-monthly depth-averaged Pelican Marina pH[2] for 2001 is shown in Figure 1. Although hourly data at Link Dam tend to be equal to or less than the semimonthly trace by about one-half of a pH unit for much of July, the two data series approximately track similar trends.
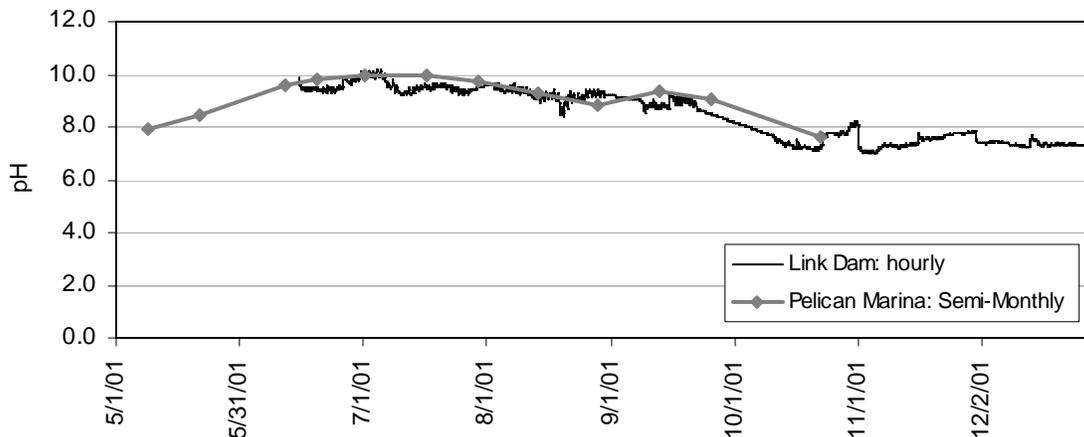

Figure 1. Comparison of observed hourly pH at Link Dam (USBR) and observed semimonthly pH at Pelican Bay (Klamath Tribes)

Comparison of available Fremont Bridge and Pelican Marina data shows no significant spatial variations in observed pH. Although data from the two sites are generally not available at coincident time periods, values are similar when there is overlap (between April 1994 and March 1995). Available data from 1994 to 1999 for Pelican Marina and Fremont Bridge are shown in Figure 2.
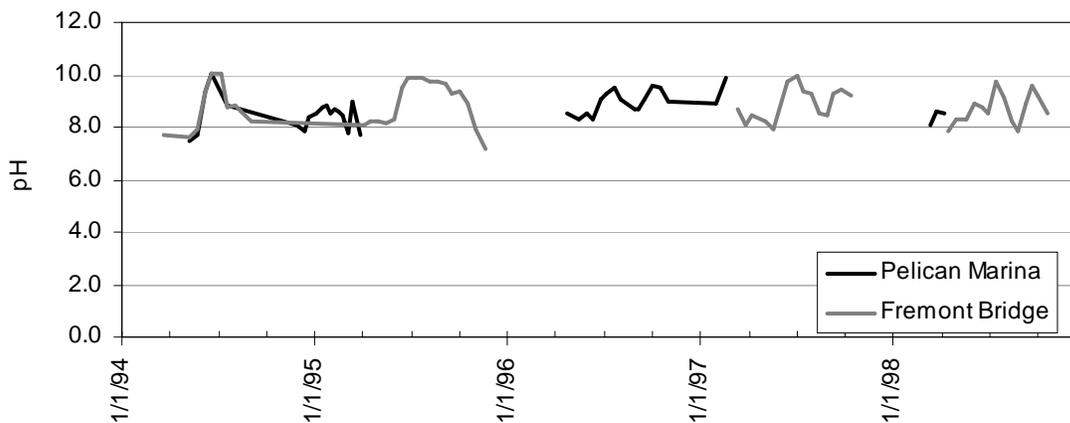

Figure 2. Comparison of semimonthly observed pH at Freemont Bridge and Pelican Marina (Klamath Tribes): 1993-1997

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[2] All semi-monthly data are depth-averaged. To compute depth-averaged pH, values from individual depths were converted to H^+ concentrations, averaged, then converted back to logarithmic pH values. In averaging, depth-associated values were given equal weight (i.e. not volume-weighted), a simplification considered appropriate for this study. Maximum top to bottom deviation in 2000 and 2001 was 0.26 pH units.

Considering the approximate agreement of seasonal pH trends at Link Dam, Fremont
Bridge, and Pelican Marina, and lacking additional data, Pelican Marina data were used
to represent the Link Dam boundary condition for pH for 2000. These data are shown
graphically in Figure 3 and tabulated in Table 1. Intermediate hourly values of pH were
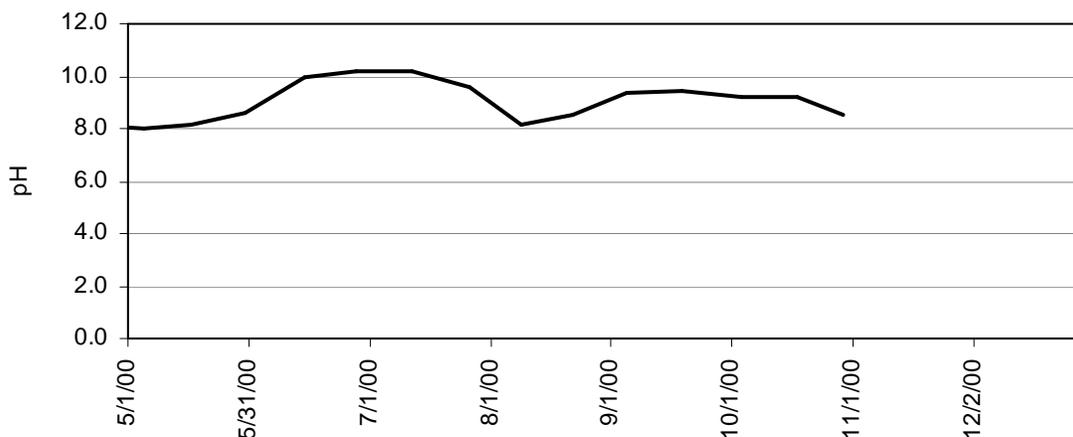interpolated from these data.

Figure 3. Depth-averaged pH at Pelican Bay: 2000 (Klamath Tribes)

Table 1. Depth-averaged pH at Pelican Bay: 2000 (Klamath Tribes)

DATE	Julian Day	Depth Averaged pH
12-Apr-00	103	8.20
5-May-00	126	8.02
17-May-00	138	8.18
31-May-00	152	8.62
15-Jun-00	167	9.99
28-Jun-00	180	10.17
12-Jul-00	194	10.18
27-Jul-00	209	9.59
9-Aug-00	222	8.13
22-Aug-00	235	8.56
5-Sep-00	249	9.34
19-Sep-00	263	9.44
4-Oct-00	278	9.22
18-Oct-00	292	9.17
30-Oct-00	304	8.50

Alkalinity and TIC

Alkalinity appears to be relatively consistent from year to year and throughout the year in
the vicinity of Link Dam. Based on averaged observed concentrations, inflow alkalinity
concentration was set to a constant 57 mg/L as CaCO3 for the simulation period of May-

Oct 2000. Hourly total inorganic carbon concentrations were calculated from water temperature, alkalinity, and pH.

4.1.2. East Side and West Side Powerhouse

Because of their proximity, East Side and West Side Powerhouses boundary conditions were set equal to Link Dam.

4.2.   Lake Ewauna – Keno Reservoir

Boundary conditions for the Lake Ewauna – Keno Reservoir reach include South Suburban Sanitation District, Klamath Falls Water Treatment Plan, Lost River Diversion Channel, Klamath Straits Drain, and both storm water and agricultural return flows.

4.2.1. South Suburban Sanitation District

South Suburban Sanitation District (SSSD) reports pH among other water quality data such as dissolved oxygen, BOD, TSS, total phosphorus, ammonia and nitrate, to Oregon Department of Environmental Quality (ODEQ). Reported with a frequency of 5 times a week, pH and temperature values were converted to monthly averages for use in simulations. Monthly values for alkalinity and TIC were estimated from these pH and temperature averages assuming atmospheric equilibrium (Snoeyink and Jenkins, 1980). For lack of sufficient data, monthly average pH for 2001 was used as a surrogate for 2000 pH. Values of pH, TIC, and alkalinity used are shown in Table 2 and Table 3.

Table 2. pH at South Suburban Sanitation District: 2000 (from 2001 data)

DATE	Julian Day	pH
1-Jan-00	1	8.20
15-Jan-00	15	8.13
15-Feb-00	46	8.08
15-Mar-00	74	7.86
15-Apr-00	105	7.46
15-May-00	135	7.61
15-Jun-00	166	7.50
15-Jul-00	196	7.60
15-Aug-00	227	8.20
15-Sep-00	258	8.43
15-Oct-00	288	8.40
15-Nov-00	319	8.09
15-Dec-00	349	8.34
1-Jan-01	366	8.00

Table 3. Alkalinity and total inorganic carbon (TIC) at South Suburban Sanitation District: 2000

DATE	Julian Day	Alkalinity	TIC
1-Jan-00	1	24.28	6.07
15-Jan-00	15	13.41	3.35
15-Feb-00	46	26.46	6.62
15-Mar-00	75	29.01	7.25
15-Apr-00	106	8.55	2.14
15-May-00	136	12.36	3.09
15-Jun-00	167	10.79	2.70
15-Jul-00	197	9.82	2.45
15-Aug-00	228	11.35	2.84
15-Sep-00	259	9.03	2.26
15-Oct-00	289	8.66	2.16
15-Nov-00	320	23.85	5.96
15-Dec-00	350	48.64	12.16
1-Jan-01	367	24.28	6.07

4.2.2. Klamath Falls Water Treatment Plant

Monthly average pH of water discharged by Klamath Falls Water Treatment Plant were determined from ODEQ reports and is shown in Table 4. Alkalinity and TIC were set to 50 mg/l and 14 mg/l, respectively, throughout the year of 2000 based on ODEQ (1995).

Table 4. pH at Klamath Falls Water Treatment Plan: 2000

DATE	Julian Day	pH
1-Jan-00	1	7.4
15-Jan-00	15	7.3
15-Feb-00	46	7.3
15-Mar-00	75	7.3
15-Apr-00	106	7.4
15-May-00	136	7.5
15-Jun-00	167	7.5
15-Jul-00	197	7.5
15-Aug-00	228	7.6
15-Sep-00	259	7.5
15-Oct-00	289	7.6
15-Nov-00	320	7.6
15-Dec-00	350	7.6
1-Jan-01	367	7.6

4.2.3. Klamath Straits Drain

Klamath Straits Drain pH, TIC and alkalinity data (shown in Table 5 and Table 6) were estimated from bimonthly data collected by USBR at Klamath Straits Drain at Highway 97 (KSD97) in 2000.

Table 5. pH at Klamath Strains Drain: 2000

DATE	Julian Day	pH
1-Jan-00	1	8.38
15-Jan-00	15	8.38
15-Feb-00	46	8.38
15-Mar-00	75	8.38
15-Apr-00	106	8.38
15-May-00	136	8.62
15-Jun-00	167	8.35
15-Jul-00	197	8.34
15-Aug-00	228	8.18
15-Sep-00	259	8.87
15-Oct-00	289	7.60
15-Nov-00	320	8.49
15-Dec-00	350	7.86
1-Jan-01	367	7.50

Table 6. Alkalinity and total inorganic carbon (TIC) at Klamath Straits Drain: 2000

DATE	Julian Day	Alkalinity	TIC
1-Jan-00	1	236.00	59.00
15-Jan-00	15	236.00	59.00
15-Feb-00	46	236.00	59.00
15-Mar-00	75	236.00	59.00
15-Apr-00	106	236.00	59.00
15-May-00	136	278.00	69.50
15-Jun-00	167	241.43	60.36
15-Jul-00	197	174.14	43.54
15-Aug-00	228	193.50	48.38
15-Sep-00	259	206.36	51.59
15-Oct-00	289	339.38	84.85
15-Nov-00	320	240.79	60.20
15-Dec-00	350	144.54	36.14
1-Jan-01	367	90.00	22.50

4.2.4. Lost River Diversion Channel

Inflow values for pH, TIC and alkalinity from Lost River Diversion Channel were based on those reported for Klamath Straits Drain for the year 2000. Values of pH, TIC and alkalinity for the Lost River Diversion Channel are presented in Table 7 and Table 8.

Table 7. pH at Lost River Diversion Channel: 2000

DATE	Julian Day	pH
1-Jan-00	1	8.38
13-Jan-00	13	8.38
25-Jan-00	25	8.38
10-Feb-00	41	8.38
2-Mar-00	62	8.38
15-Mar-00	75	8.38
29-Mar-00	89	8.38
12-Apr-00	103	8.38
27-Apr-00	118	8.48
10-May-00	131	8.58
24-May-00	145	8.54
17-Jul-00	199	8.33
11-Aug-00	224	8.20
15-Sep-00	259	8.87
10-Oct-00	284	7.81
24-Oct-00	298	7.86
7-Nov-00	312	8.26
21-Nov-00	326	8.36
5-Dec-00	340	8.07
18-Dec-00	353	7.80
1-Jan-01	367	7.50

Table 8. Alkalinity and total inorganic carbon (TIC) at Lost River Diversion Channel: 2000

DATE	Julian Day	Alkalinity	TIC
1-Jan-00	1	236.00	59.00
13-Jan-00	13	236.00	59.00
25-Jan-00	25	236.00	59.00
10-Feb-00	41	236.00	59.00
2-Mar-00	62	236.00	59.00
15-Mar-00	75	236.00	59.00
29-Mar-00	89	236.00	59.00
12-Apr-00	103	236.00	59.00
27-Apr-00	118	236.00	59.00
10-May-00	131	243.00	60.75
24-May-00	145	328.86	82.22
17-Jul-00	199	167.71	41.93
11-Aug-00	224	185.79	46.45
15-Sep-00	259	206.36	51.59
10-Oct-00	284	315.33	78.83
24-Oct-00	298	291.50	72.88
7-Nov-00	312	239.00	59.75
21-Nov-00	326	244.00	61.00
5-Dec-00	340	244.00	61.00
18-Dec-00	353	244.00	61.00
1-Jan-01	367	244.00	61.00

4.2.5. Storm-Water Runoff

Inflow values for pH, TIC and alkalinity from storm water and agricultural runoff were assumed equal to those of Klamath Straits Drain for the year 2000. Values of pH, TIC and alkalinity for the storm water and agricultural runoff are presented in Table 9 and Table 10.

Table 9. pH at for Storm Water Runoffs: 2000

DATE	Julian Day	pH
1-Jan-00	1	7.4
15-Jan-00	15	7.3
15-Feb-00	46	7.3
15-Mar-00	75	7.3
15-Apr-00	106	7.4
15-May-00	136	7.5
15-Jun-00	167	7.5
15-Jul-00	197	7.5
15-Aug-00	228	7.6
15-Sep-00	259	7.5
15-Oct-00	289	7.6
15-Nov-00	320	7.6
15-Dec-00	350	7.6
1-Jan-01	367	7.6

Table 10. Alkalinity and total inorganic carbon (TIC) for Storm Water runoffs: 2000

DATE	Julian Day	Alkalinity	TIC
1-Jan-00	1	236.00	59.00
15-Jan-00	15	236.00	59.00
15-Feb-00	46	236.00	59.00
15-Mar-00	75	236.00	59.00
15-Apr-00	106	236.00	59.00
15-May-00	136	278.00	69.50
15-Jun-00	167	241.43	60.36
15-Jul-00	197	174.14	43.54
15-Aug-00	228	193.50	48.38
15-Sep-00	259	206.36	51.59
15-Oct-00	289	339.38	84.85
15-Nov-00	320	240.79	60.20
15-Dec-00	350	144.54	36.14
1-Jan-01	367	90.00	22.50

4.2.6. Columbia Plywood

Average monthly pH of Columbia Plywood discharge was calculated from monthly monitoring reports submitted by Columbia Plywood to ODEQ. TIC and alkalinity were set to 52 mg/l and 15.8 mg/l, respectively, throughout the year of 2000 as determined by ODEQ (1995). Monthly average pH values used for Columbia Plywood inflows are presented in Table 11.

Table 11. pH at Columbia Plywood: 2000

DATE	Julian Day	pH
1-Jan-00	1	7.15
15-Jan-00	15	7.15
15-Feb-00	46	7.16
15-Mar-00	75	7.27
15-Apr-00	106	7.10
15-May-00	136	7.10
15-Jun-00	167	7.06
15-Jul-00	197	6.90
15-Aug-00	228	7.43
15-Sep-00	259	7.43
15-Oct-00	289	7.49
15-Nov-00	320	7.17
15-Dec-00	350	7.24
1-Jan-01	367	7.24

4.2.7. Collins Forest Products #1 and #2

Values of pH for Collins Forest Products #1 and #2 discharges were estimated from the monthly water quality reports submitted to ODEQ. Estimated monthly pH values for discharges #1 and #2 are shown in Table 12 and Table 13, respectively. Estimates of TIC and alkalinity for both discharges were taken from ODEQ (1995). Based on that report, alkalinity and TIC were set to 50 mg/l and 12.22 mg/l, respectively, throughout the year of 2000 for discharge #1. Alkalinity and TIC were set to 50 mg/l and 11.88 mg/l, respectively, throughout the year of 2000 for discharge #2.

Table 12. pH at Collins Forest Products #1: 2000

Date	Julian Day	pH
1-Jan-00	1	8.1
15-Jan-00	15	7.7
15-Feb-00	46	7.5
15-Mar-00	75	7.5
15-Apr-00	106	7.5
15-May-00	136	8.0
15-Jun-00	167	7.9
15-Jul-00	197	7.9
15-Aug-00	228	7.8
15-Sep-00	259	7.9
15-Oct-00	289	7.4
15-Nov-00	320	7.5
15-Dec-00	350	7.6
1-Jan-01	367	7.8

Table 13. pH at Collins Forest Products #2: 2000

Date	Julian Day	pH
1-Jan-00	1	9.2
15-Jan-00	15	8.8
15-Feb-00	46	9.2
15-Mar-00	75	9.3
15-Apr-00	106	9.1
15-May-00	136	9.0
15-Jun-00	167	9.1
15-Jul-00	197	8.9
15-Aug-00	228	8.0
15-Sep-00	259	7.4
15-Oct-00	289	7.3
15-Nov-00	320	7.6
15-Dec-00	350	8.1
1-Jan-01	367	9.6

4.3. Klamath River – Keno Dam to JC Boyle Reservoir

In EC simulations, flow and water quality into the Klamath River reach between Keno Dam and JC Boyle Reservoir is determined by simulated outflow from Lake Ewauna. There are no appreciable accretions within this reach.

4.4. J.C. Boyle Reservoir

Except for Spencer Creek, there are no tributary inflows to J.C. Boyle Reservoir. In EC simulations, Spencer Creek inflow is added to headwater inflow and assigned the headwater quality as determined by upstream simulation.

4.5. Klamath River – J.C. Boyle Dam to Copco Reservoir

In EC simulations, flow and water quality into the Klamath River reach that runs between J.C. Boyle Dam and Copco Reservoir are determined by simulated outflow from JC Boyle Reservoir. This reach was modeled with two significant sources of inflow: springs (which are distributed as three point sources distributed over about a one-quarter mile reach) and the powerhouse return.

4.5.1. Springs

Based on a general review of water quality in the area and considering an annual mass balance in the river, alkalinity of spring flow was set at a constant 68 mg/l for the duration of the simulation. Using this value, an assumed constant temperature of 12 degrees C, and an assumption of atmospheric equilibrium, corresponding constant values for TIC and pH were calculated as 16 mg/l and 8.4, respectively. These constant values for alkalinity, TIC, and pH were used to represent spring inflow water quality.

4.5.2. Powerhouse Return

Under existing conditions (EC), water is diverted from the river at J.C. Boyle Dam to turbines and re-enters the river at the Powerhouse return. As modeled in EC simulations, powerhouse return water quality is assumed equal to headwater quality.

4.6. Copco Reservoir

There are no major tributaries to Copco reservoir and any assigned accretions within the Copco Reservoir reach are assumed to have the same quality as ambient inflowing Klamath River water.

4.7. Iron Gate Reservoir

Within Iron Gate Reservoir the accretion/depletion is applied at Jenny Creek, the major tributary to the reservoir. In these simulations, TIC and alkalinity concentrations for Jenny Creek were assumed to be constant at 13.8 mg/l and 58 mg/l, respectively, throughout the year.

4.8. Iron Gate Dam to Seiad

The Klamath River is modeled with the pH Model between Iron Gate Dam and Seiad. Seven creeks and two rivers contribute to Klamath River flow in this reach. Alkalinity, pH, and water temperature for the Scott and Shasta Rivers are average values calculated from bi-monthly observations reported by Watercourse (2002). Tributary creeks in this reach were assigned pH and water temperature equal to those of the Scott River due to lack of available data. Because the creeks are free of agricultural discharges and the Scott River is not, alkalinity in the creeks has been assumed to be much lower than that in the Scott River. Alkalinity in the creeks has been set to 30 mg/l for these simulations. For both rivers and creeks, TIC has been calculated from alkalinity, pH, and water temperature using instantaneous equilibrium equations (Snoeyink and Jenkins, 1980). Tributaries to the Iron Gate-Seiad reach are listed in Table 14 along with associated alkalinity, pH, water temperature (Tw), and calculated TIC.

Table 14. pH for modeled tributaries of the Klamath River from Iron Gate Dam to Seiad Valley2000

Tributary	Alkalinity	pH	Tw	TIC[1]
Bogus Creek	30	7.71	13.2	7.6
Willow Creek	30	7.71	13.2	7.6
Cottonwood Creek	30	7.71	13.2	7.6
Shasta River	323	8.51	17.7	77.1
Humbug Creek	30	7.71	13.2	7.6
Beaver Creek	30	7.71	13.2	7.6
Horse Creek	30	7.71	13.2	7.6
Scott River	130	7.71	13.2	32.8
Grider Creek	30	7.71	13.2	7.6

[1] calculated from alkalinity, pH, and water temperature (Tw)

5. Model Sensitivity

As described in model documentation (see Appendix: Watercourse pH Model Documentation), two biogeochemical processes determine pH in these simulations. These processes are atmospheric exchange and algal growth. Each of these processes transports CO_2 either into or out of the water column, causing pH to adjust to a temporary equilibrium value. Transfer of CO_2 across the air-water interface is governed by the CO_2 transfer rate coefficient, KCO2. Within the water column, CO_2 is exchanged with organic matter through algal growth and decomposition. Factors in this exchange include

the assumed carbon content of algae and simulated rates of algae growth and mortality. If all else is constant and pH is within the range of pH found in natural waters, CO_2 increases will lower pH and decreases will raise pH.

Beside these two biogeochemical processes, alkalinity can significantly influence pH. Alkalinity is a measure of the capacity for waters to neutralize strong acids and is a principle component in the calculation of pH. All else constant, an increase in alkalinity will increase pH and a decrease in alkalinity will decrease pH. In these models, alkalinity is conservative. Therefore, alkalinity concentrations at the upstream boundary and in tributaries can have a large influence on pH values in the system.

Several simulations were made to test the sensitivity of the model to CO_2 transfer, algal growth, and alkalinity. To test sensitivity to CO_2 transfer, algal carbon content, and alkalinity, a model of the Keno reach (Klamath River from Keno Dam to the JC Boyle headwaters) was run under June 2000 conditions. Results of simulations on the Peaking reach under July 2000 conditions demonstrate the models sensitivity to algal growth and decay.

The Keno reach has no tributary inflow and, therefore, instream alkalinity is constant and equal to the alkalinity of inflow at the upstream boundary. Simulated algae growth and water temperature for the period are shown in Figure 4 and Figure 5 respectively. Simulated pH for an alkalinity of 20 mg/L as CaCO3 (0.4 meq/L) is depicted in Figure 6. Simulated pH for an alkalinity of 100 mg/L as CaCO3 (2.0 meq/L) is depicted in Figure 7. These simulations indicate that the model responds strongly to changes in alkalinity within a range of alkalinities found in natural waters. An increase in alkalinity from 20 to 100 mg/L as CaCO3 significantly reduced the range of simulated pH from 2.2 to 0.7 pH units and slightly changed the monthly average pH from 8.8 to 9.0 pH units. These results also suggest that, particularly at reduced levels of alkalinity, that pH responds strongly to changes in algae concentration while changes in temperature (affecting reaction rates) do not impose significant differences. Statistics for pH concentrations from these two simulations are presented in Table 15.

Table 15. Statistical comparison of pH sensitivity to alkalinity.

Alkalinity (mg/L as CaCO3)	min	max	range	mean	CV
20	7.5	9.7	2.2	8.8	0.04
100	8.6	9.3	0.7	9.0	0.01
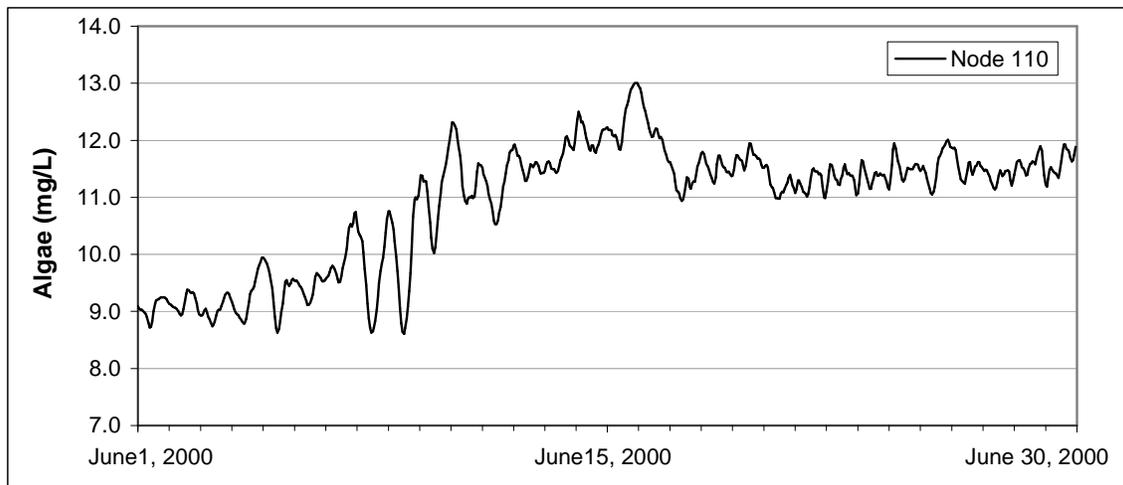
Figure 4. Simulated algae concentrations for Keno reach, June 2000
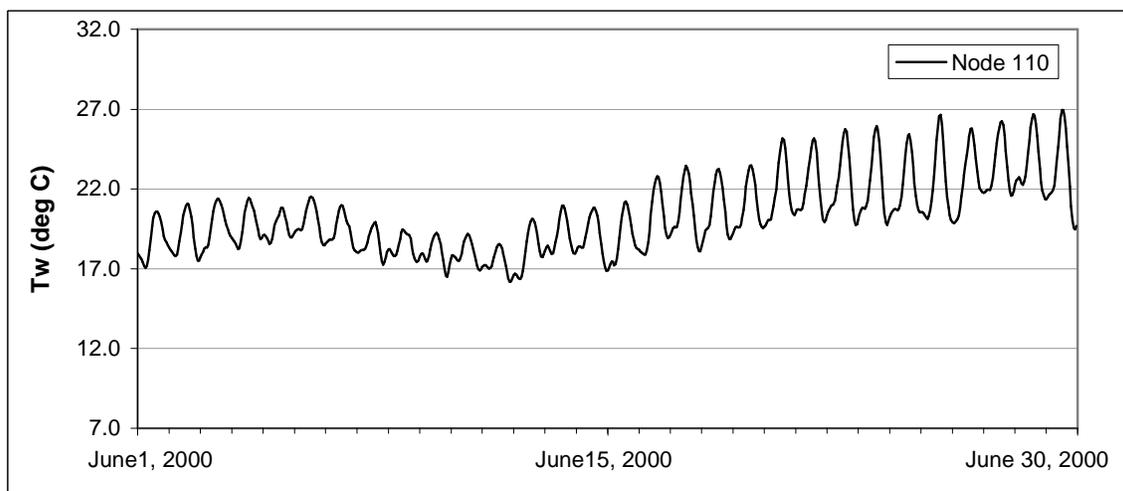
Figure 5. Simulated water temperature for Keno reach, June 2000
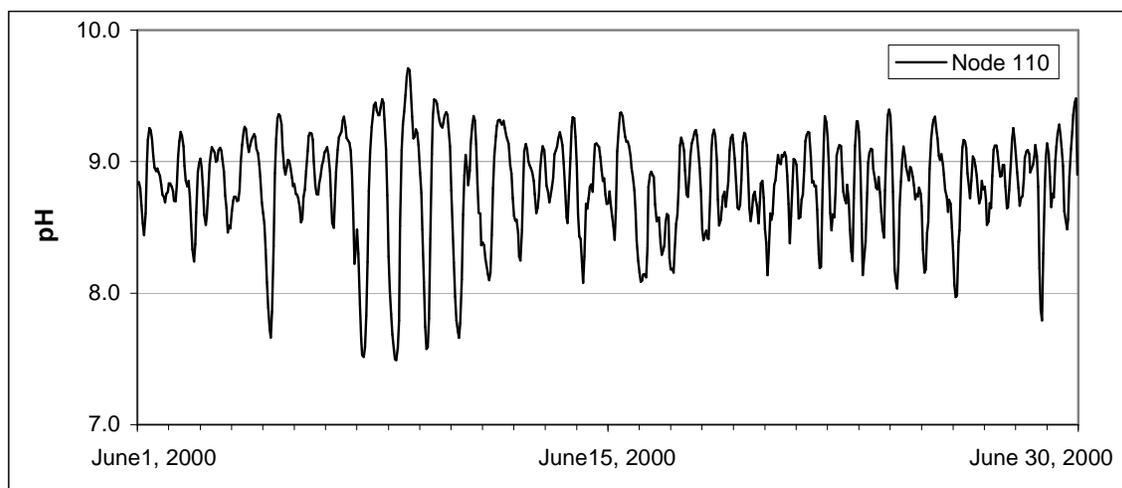
Figure 6. Simulated pH for Keno reach, June 2000 (Alkalinity=20 mg/L as CaCO3)
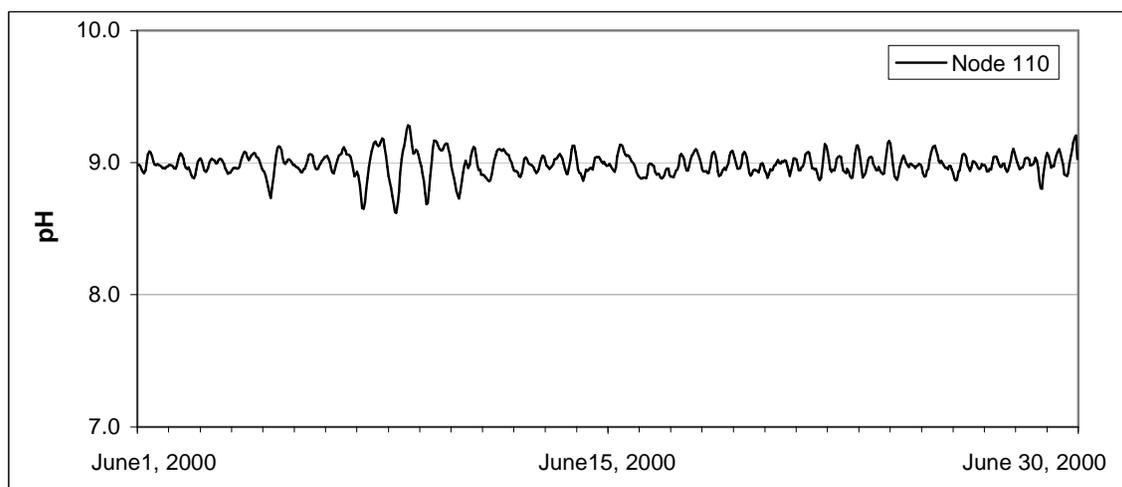

Figure 7. Simulated pH for Keno reach, June 2000 (Alkalinity=100 mg/L as CaCO3)

Three more simulations illustrate the sensitivity of the pH model to changes in CO_2 transfer rate and type of algae (as expressed by algae carbon content). These simulations were also made under June 2000 conditions for the Keno River reach. The simulations represent a base case, a case in which CO_2 transfer rate was effectively tripled, and a case in which the carbon content (and, therefore, the amount of CO_2 released or consumed in death and growth) of the modeled algae species was reduced by approximately 50 percent. In the model, CO_2 transfer rate is a linear function of oxygen transfer rate (i.e $KCO2= a*Ka$), and the CO_2 transfer rate was increased by increasing the factor, a, relating the two. To better illustrate variations, only the first two weeks of June 2000 are analyzed.

As depicted in Figure 8 and Figure 9, the model is fairly insensitive to CO_2 transfer rate and type of algae. Statistics of pH concentrations from the three simulations are presented in Table 16. Tripling the KCO2 transfer rate from 0.92*Ka to 2.8*Ka did not

change the range significantly and lowered the mean only slightly. Reducing algal carbon content by 40% from 5E-5 to 3E-5 mol CO_2/mg algae lowered the range of pH values somewhat but did not affect the mean pH significantly.

Table 16. Statistical comparison of pH sensitivity to CO_2 transfer rate and Algal carbon content.

Simulation	min	max	range	mean	CV
Base	7.9	9.5	1.5	8.8	0.03
KCO2 tripled	8.0	9.4	1.5	8.7	0.03
Algae carbon reduced 40%	8.2	9.3	1.1	8.8	0.02
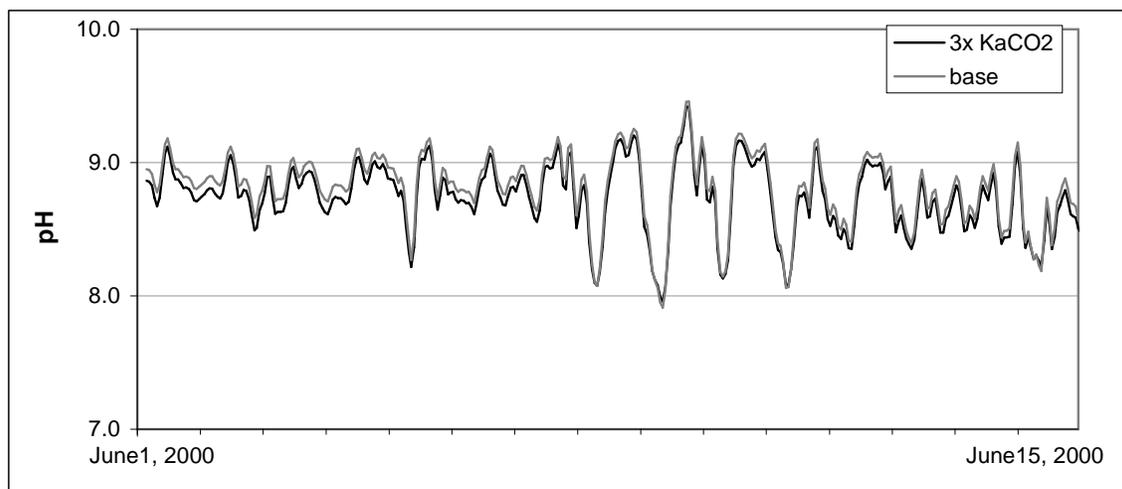
Figure 8. Simulated pH for Keno reach, June 2000. Rate of CO_2 exchange increased.
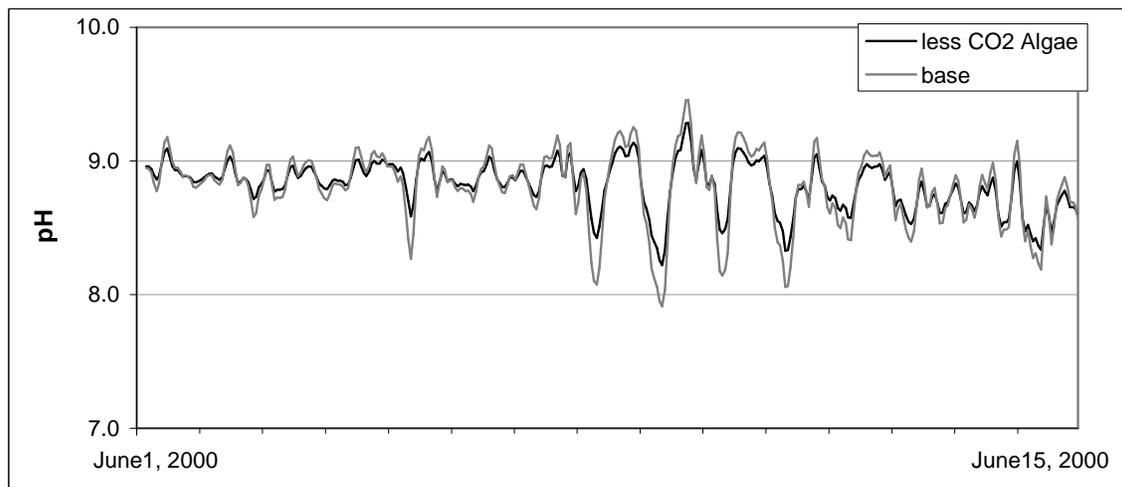
Figure 9. Simulated pH for Keno reach, June 2000. CO_2 from algae decreased.

Finally, two simulations of the Peaking reach illustrate the model's sensitivity to algal growth and decay rates. The simulations were made under July 2000 climatic conditions when simulated phytoplankton concentrations are nearing their peak. In one simulation, phytoplankton concentration was assumed to be zero (i.e., no growth or decay). In a second simulation, phytoplankton growth was modeled. Concentrations are relatively

high, with inflowing phytoplankton concentrations for the month of July averaging 10.3 mg/L (this concentration is derived from upstream model simulation). As shown in Figure 10, allowing growth and decay can have impacts on the diurnal variation in pH. Statistics for these two simulations are summarized in Table 17. In this example, phytoplankton growth and death raised the mean pH slightly (from 9.0 to 9.2) while increasing the range of pH significantly (from 1.0 to 5.0 pH units). Comparing the diurnal range in simulated pH under the "no phytoplankton" condition (Figure 10) with field observations of pH (Figure 23) suggests that there may be little phytoplankton production within this steep turbulent river reach.

Table 17. Statistical comparison of pH sensitivity to phytoplankton growth and decay.

Simulation	min	max	range	mean	CV
With phytoplankton	6.8	11.8	5.0	9.2	0.17
No phytoplankton	8.6	9.6	1.0	9.0	0.03
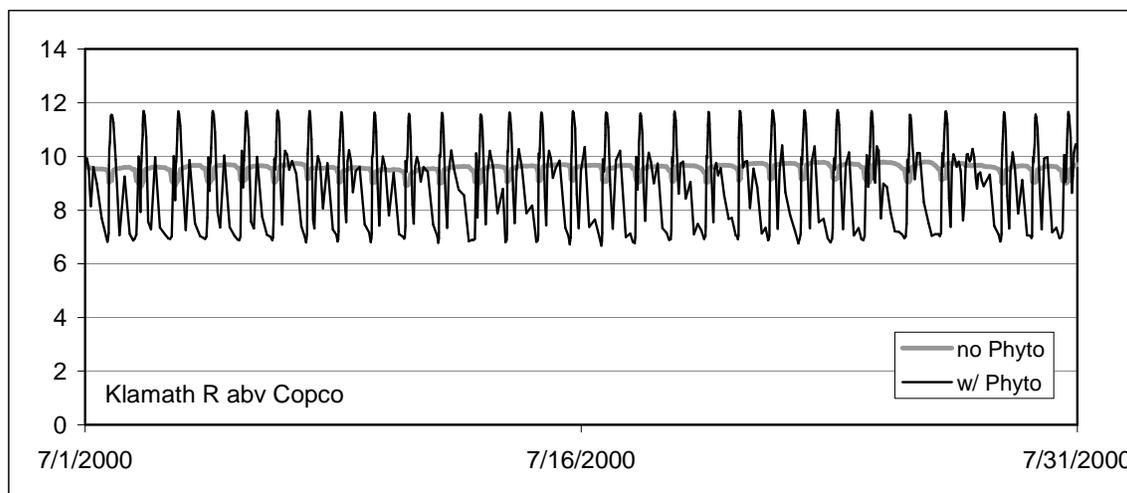
Figure 10. Simulated pH for Keno reach, June 2000. CO$_2$ from algae decreased.

In general, the pH model is sensitive to changes in algal concentrations and to alkalinity. The model does not seem to be sensitive to changes in atmospheric transfer of CO$_2$ (or, consequently, reaeration rate). The model is slightly sensitive to carbon content of algae.

6. Model Testing

In this section, the models are tested against reported pH at three locations along the Klamath River. Limited time series and grab sample pH data exist for the calibration period (year 2000); however, sufficient information exists in Keno Reservoir near Miller Island and near Keno, and for the Klamath River above Copco Reservoir.

The Klamath River from Link Dam to Seiad Valley was represented in several reaches. Under existing conditions, these reaches include sections of river, modeled for pH by the pH Model, and sections of reservoir, modeled for pH by CE-QUAL-W2. There are four river sections (Link River, Keno, Bypass, and Iron Gate-Seiad) and three reservoir sections (Lake Ewauna, J.C. Boyle, and Copco-Iron Gate).

Monitoring sites reporting pH in the Klamath River are sparse, but available data allowed comparison at several sites: three sites had good records of pH during the simulation period of May-Sep 2000. The sites include Klamath River at Miller Island, Klamath River at Keno, and Klamath River above Copco. The Miller Island and Keno sites are located in Lake Ewauna, the reservoir behind Keno Dam. Data from these sites are compared to simulation results from CEQUAL-W2. The "above Copco" site is at the downstream end of the Peaking reach, above Copco reservoir. Data from this site is compared to simulation results from the pH Model.

Simulation results and observed pH for Miller Island are presented in Figure 11 through Figure 15 and summarized in Table 18. Simulated pH compares well to observed pH at Miller Island from May 1 to the middle of June. After mid-June, simulated results diverge higher and stay between 1-2 pH units higher through July. Diurnal variation in simulated pH is similar to that reported and peaks of both simulated and observed pH coincide. Trends are matched reasonably well.

Simulation results and observed pH for Klamath River at Keno are presented in Figure 16 through Figure 20 and summarized in Table 19. Simulated pH compares similarly well to observed pH at Keno. Again, the correspondence is good until mid-June. As at Miller Island, after mid-June simulated results diverge higher and stay between 1-2 pH units higher through July. Diurnal variation in simulated pH is similar to that reported until mid-June when simulated results lose nearly all diurnal variation. Peaks of both simulated and observed pH seem to coincide. Trends are matched reasonably well, except that simulated results do not experience the week-long decline in pH that measured data show in early July – typically corresponding with widespread low DO conditions in the reservoir.

Simulation results and observed pH at Klamath River above Copco are presented in Figure 21 through Figure 25 and summarized in Table 20. Simulated pH compares reasonably well to observed pH at Klamath River above Copco from May 1 to the middle of May. After this time, simulated pH values rise about 1 pH unit above measured values and remain about this much higher through July. Diurnal variation in simulated pH is similar to that reported. Phase of simulated pH peaks do not always correspond to measured data. There is little or no trend (increasing or decreasing through time) in the measured data during this period and simulated results also show little trend.

Table 18. Comparison of simulated to observed pH, May-Sep 2000 (Klamath River at Miller Island)

Summary statistics	mean	COV	n
Measured pH	7.95	0.100	3604
Simulated pH	8.95	0.084	3604

Comparison statistics	Avg bias	Avg absolute bias	RMS
Measured vs simulated pH	-1.00	1.04	1.44

Table 19. Comparison of simulated to observed pH, May-Sep 2000 (Klamath River at Keno)

Summary statistics	mean	COV	n
Measured pH	7.78	0.074	3215
Simulated pH	9.20	0.053	3215

Comparison statistics	Avg bias	Avg absolute bias	RMS
Measured vs simulated pH	-1.42	1.43	2.53

Table 20. Comparison of simulated to observed pH, May-Sep 2000 (Klamath River abv Copco)

Summary statistics	mean	COV	n
Measured pH	7.96	0.044	3580
Simulated pH	9.04	0.044	3580

Comparison statistics	Avg bias	Avg absolute bias	RMS
Measured vs simulated pH	-1.08	1.08	1.43
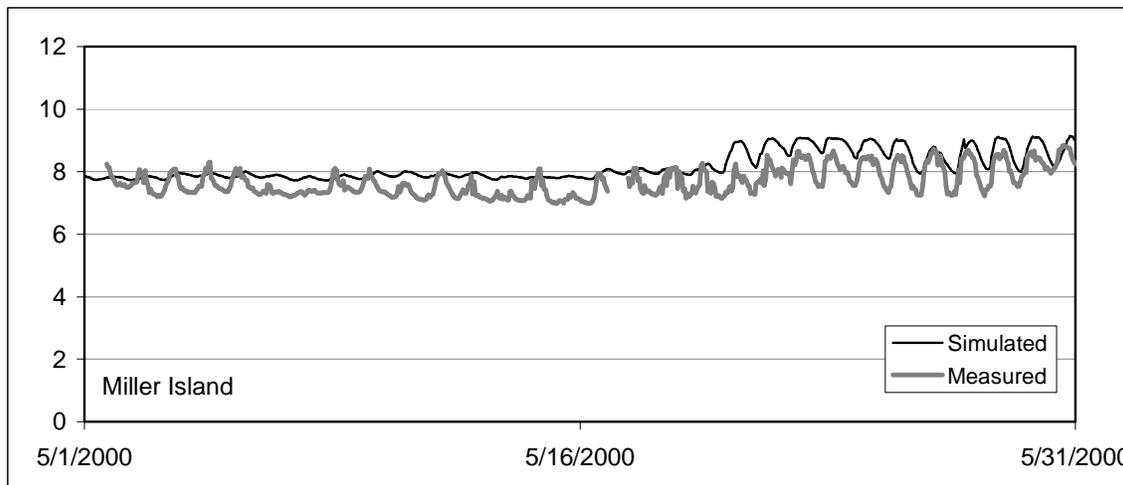
Figure 11. Simulated vs measured pH at Miller Island, May 2000.
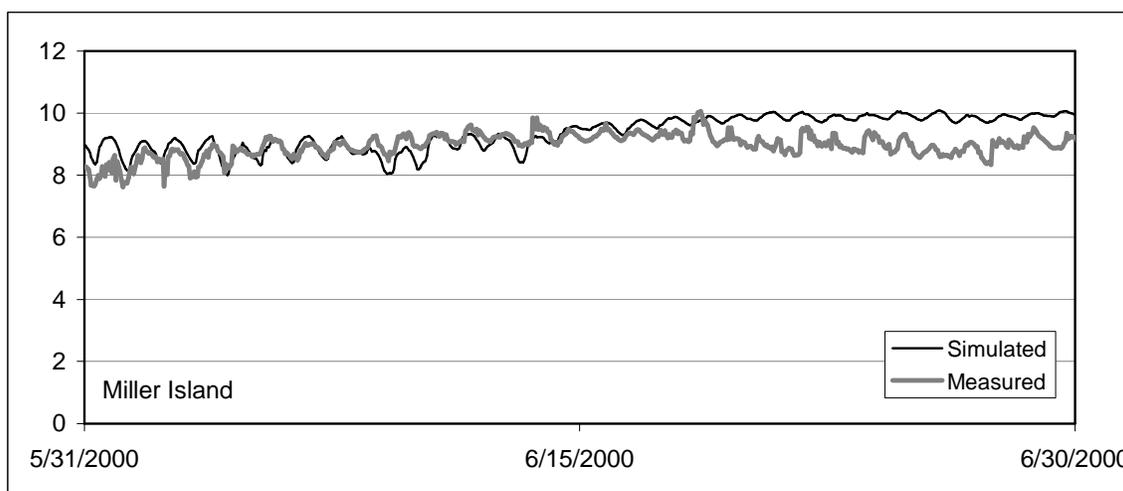
Figure 12. Simulated vs measured pH at Miller Island, June 2000.
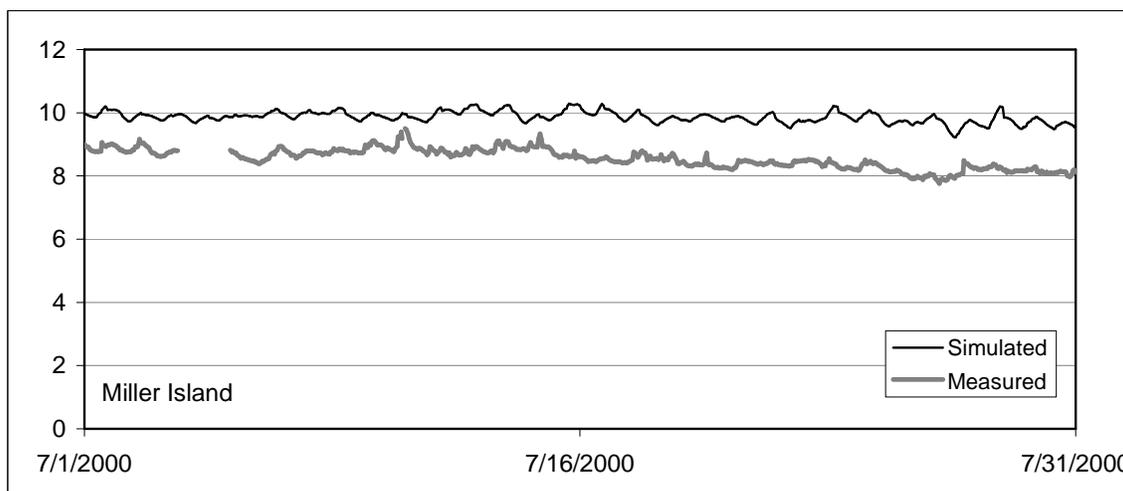
Figure 13. Simulated vs measured pH at Miller Island, July 2000.
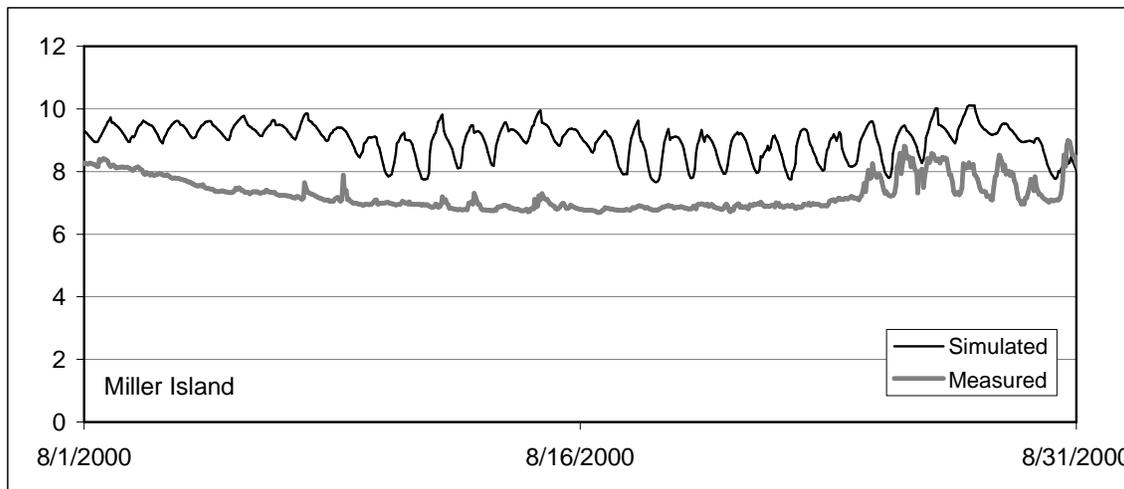
Figure 14. Simulated vs measured pH at Miller Island, August 2000.
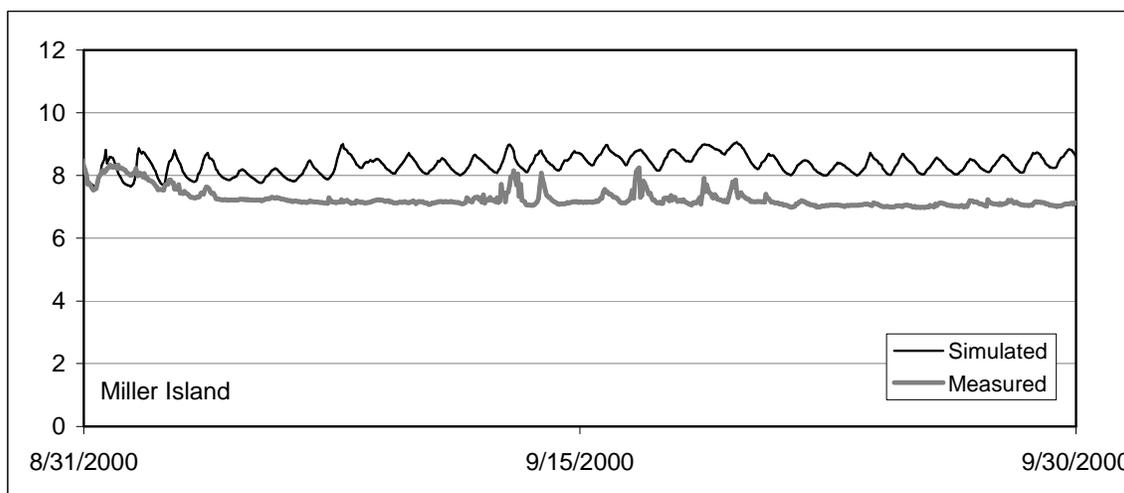
Figure 15. Simulated vs measured pH at Miller Island, September 2000.
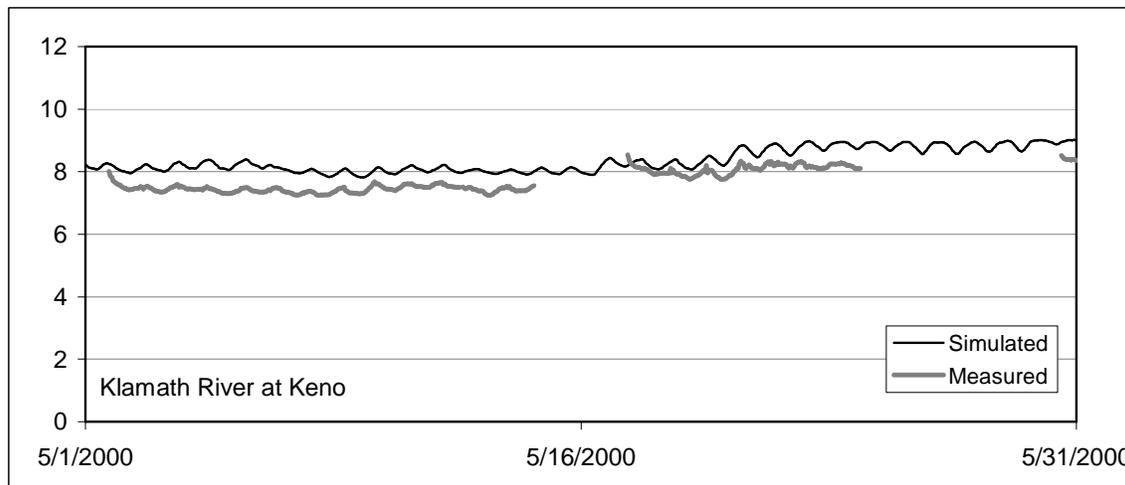
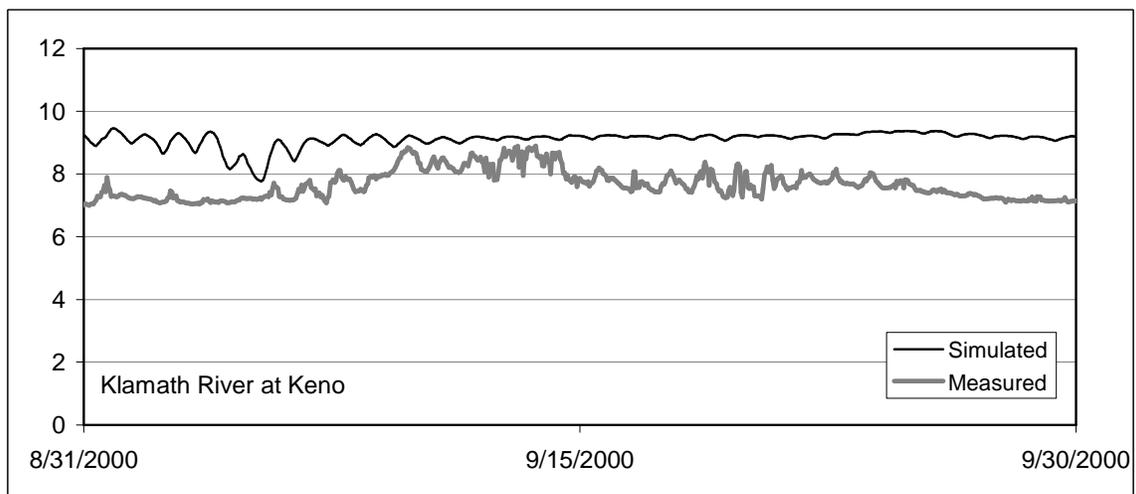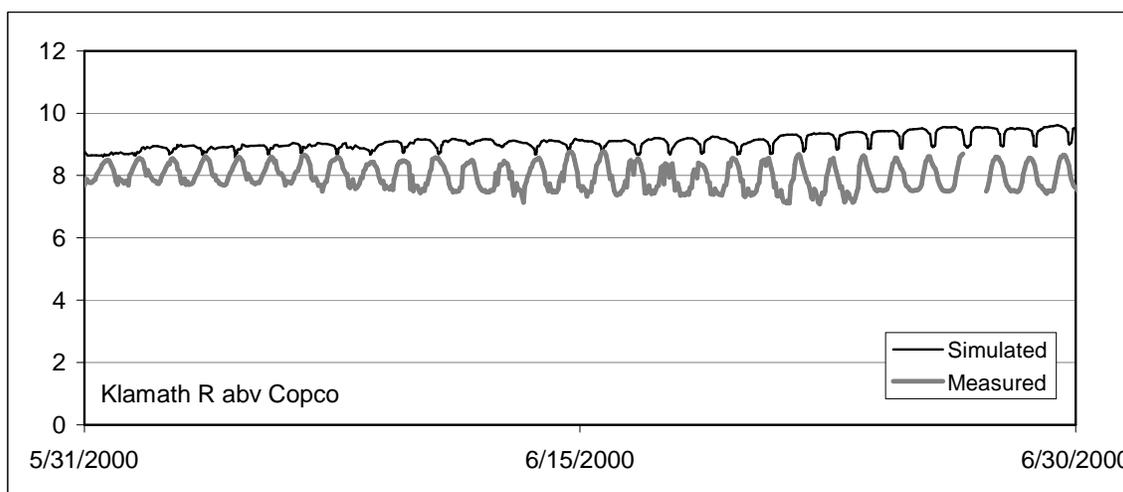**Figure 16. Simulated vs measured pH at Klamath River at Keno, May 2000.**
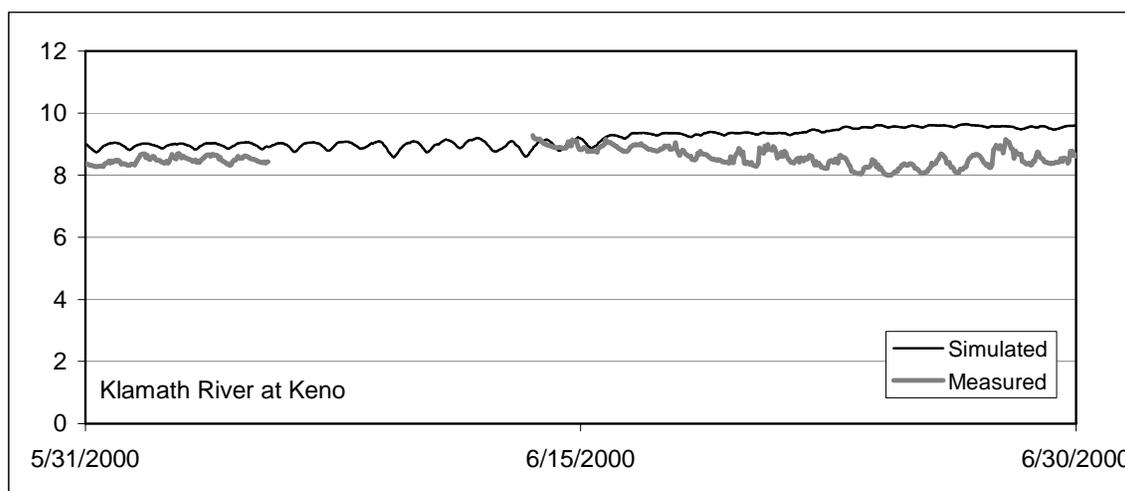
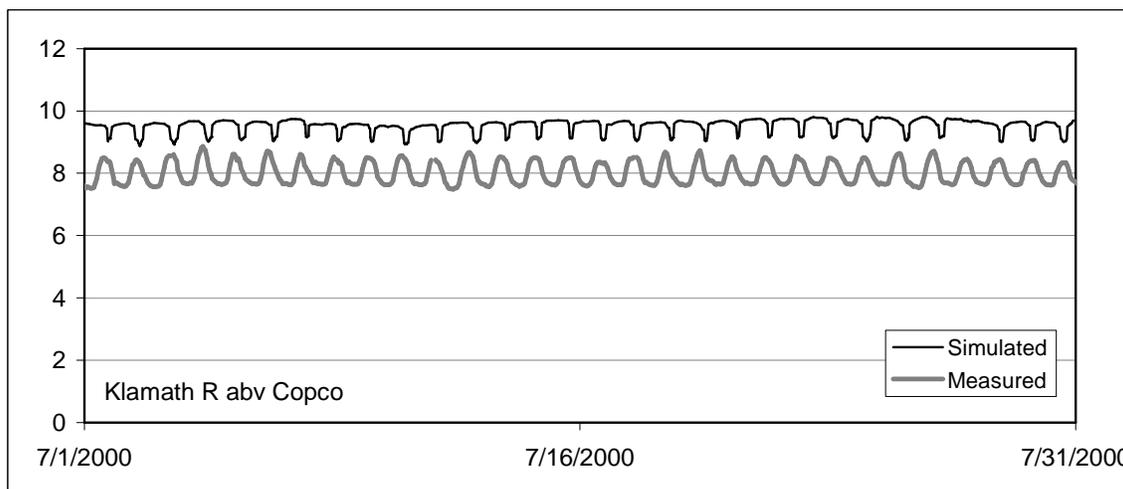**Figure 17. Simulated vs measured pH at Klamath River at Keno, June 2000.**
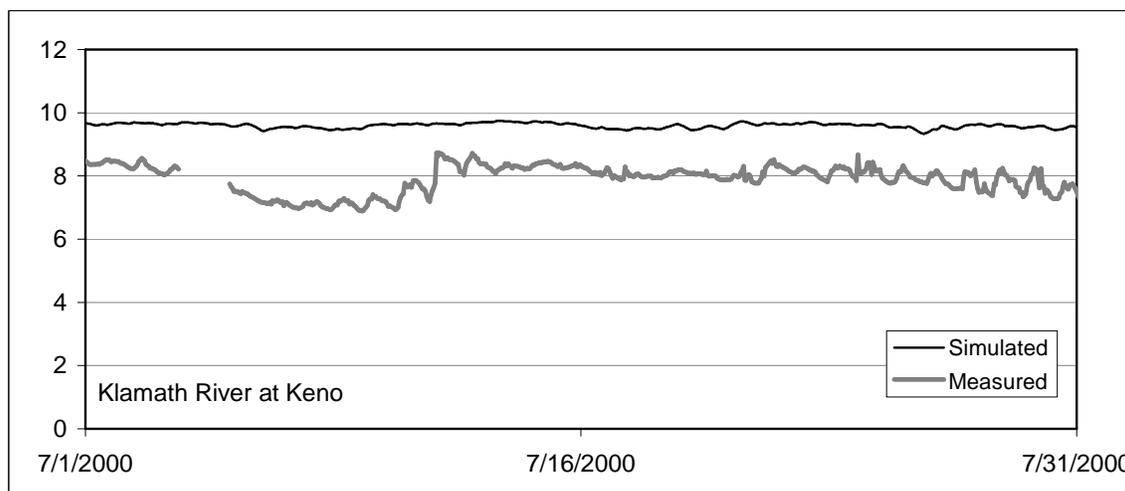
Figure 18. Simulated vs measured pH at Klamath River at Keno, July 2000.
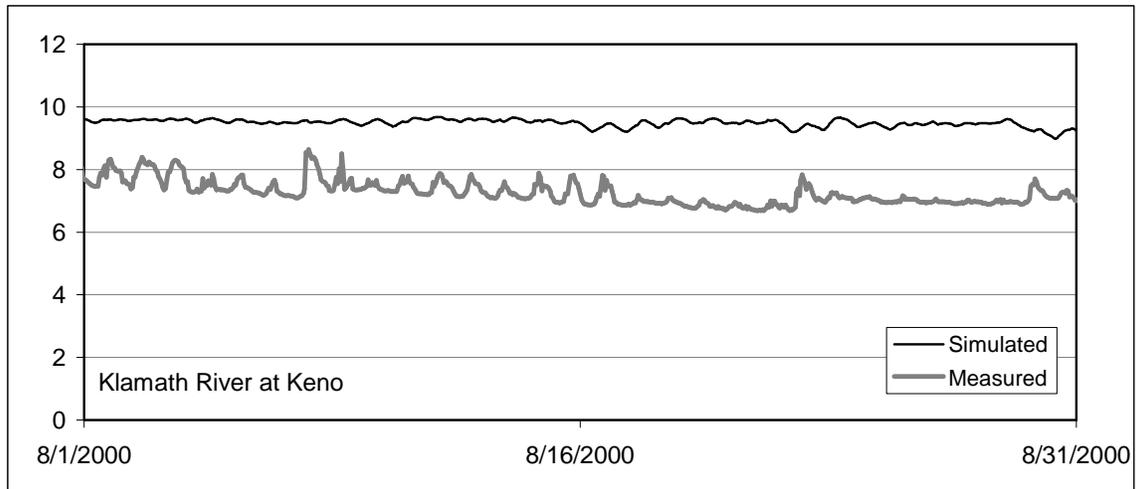
Figure 19. Simulated vs measured pH at Klamath River at Keno, August 2000.

Figure 20. Simulated vs measured pH at Klamath River at Keno, September 2000.
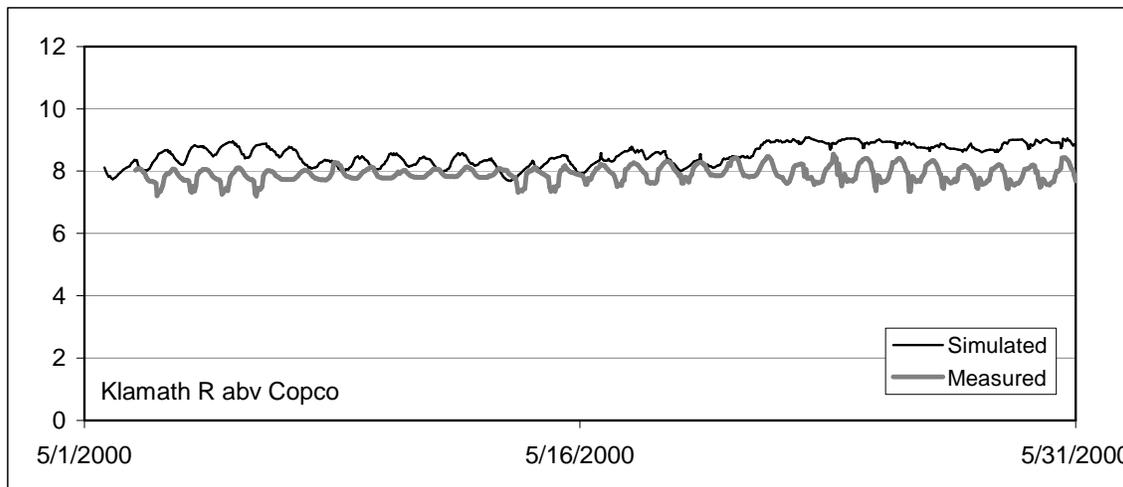
Figure 21. Simulated vs measured pH at Klamath River above Copco, May 2000.

Figure 22. Simulated vs measured pH at Klamath River above Copco, June 2000.

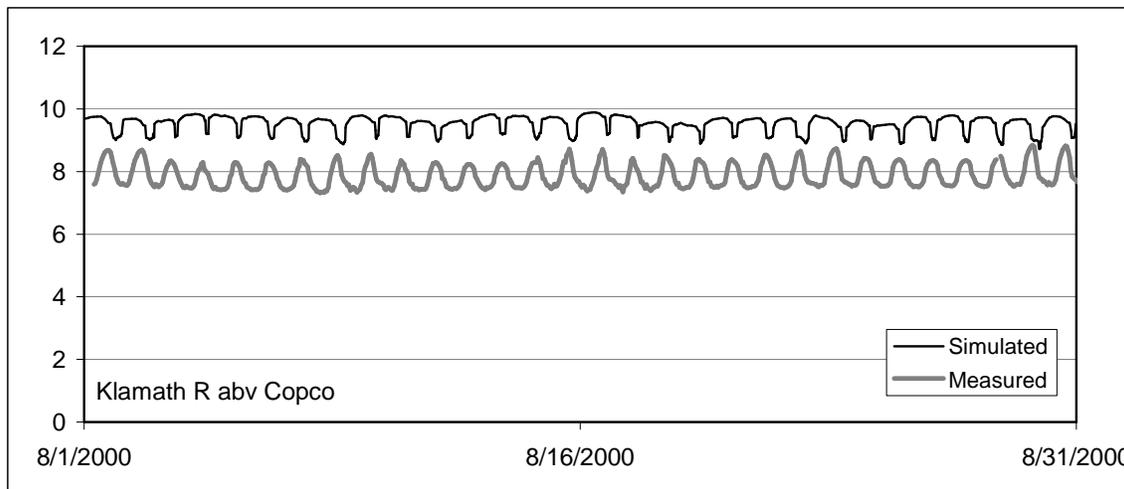**Figure 23. Simulated vs measured pH at Klamath River above Copco, July 2000.**

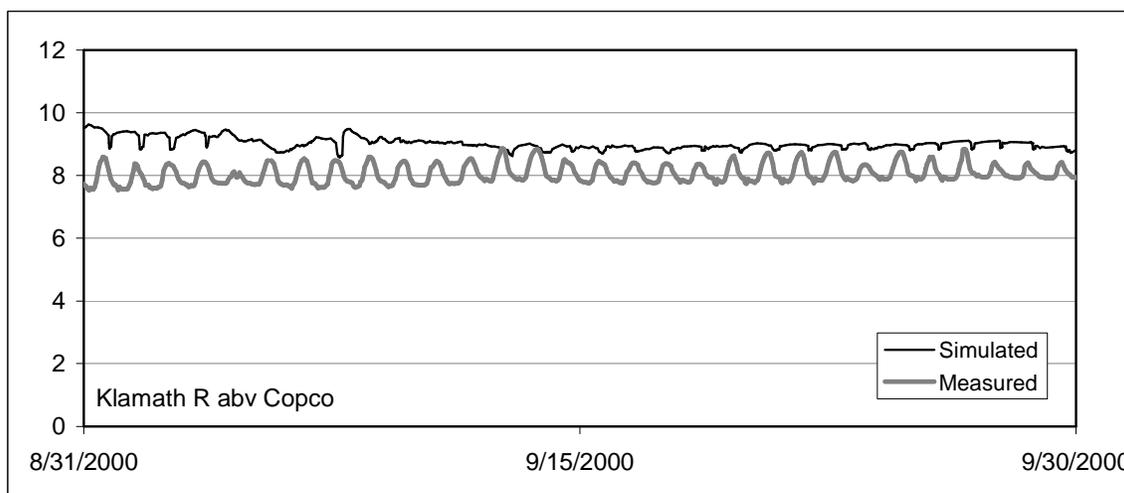**Figure 24. Simulated vs measured pH at Klamath River above Copco, August 2000.**

Figure 25. Simulated vs measured pH at Klamath River above Copco, September 2000.

7. References

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Appendix: Watercourse pH Model Documentation

The Watercourse pH model is designed to estimate pH and total inorganic carbon (TIC) along a river reach at hourly intervals. The reach is defined by nodal points at which key water-quality parameters are specified. In-stream boundary conditions required for the Watercourse pH model include water temperature, speed, depth, algae concentration, and benthic algae concentration. These five state variables are defined for each node of the reach and each hour of the simulation and provide the means for estimating TIC and pH along the reach over time. Assuming that pH, alkalinity, and TIC do not affect other simulated water quality constituents, values for these state variables are taken from hourly results of more detailed hydrodynamic and water quality simulations. Headwater boundary conditions for the pH Model are defined by hourly values of flow, pH, and alkalinity. Hourly TIC at the headwater is calculated from pH and alkalinity. Tributary boundary conditions in the pH Model are defined by flow, alkalinity, and TIC.

The Watercourse model is designed as a Lagrangian simulation wherein one parcel of water is tracked the length of the system. Parcels are released at the head of the reach each hour and allowed to react with the environment as they travel from node to node downstream through changing water conditions.

The parcel starts out at the upstream boundary at time t_0 with initial conditions of pH, alkalinity, and total inorganic carbon (initial total inorganic carbon is calculated from pH and alkalinity assuming instantaneous equilibrium). In-stream boundary conditions for the first segment of the reach are temperature, speed, depth, and calculated change in algae and benthic algae concentrations in time (dAlg/dt and dBalg/dt) associated with the upstream node. These conditions are applied as the parcel travels from upstream to downstream node with a travel (or, residence) time of "delt."

1. Total inorganic carbon (C_t)

As the parcel travels through the system, alkalinity is conserved but total inorganic carbon is added to the parcel through two mechanisms: atmospheric transfer and net algal respiration. At the end of each segment (i.e. at each node), total inorganic carbon is calculated as

$$Ct = Ct' + delCO2atm + delCO2algae$$

where Ct' is the total inorganic carbon at the top of the segment, delCO2atm is the change in Ct due to atmospheric transfer, and delCO2algae is the change in Ct due to net algal respiration.

1.1.   *Atmospheric transfer, delCO2atm*

Atmospheric transfer is modeled like reaeration, using a CO_2 transfer rate coefficient, KCO2, derived from an estimated oxygen transfer rate coefficient, Ka, and a factor accounting for molecular size differences. The CO_2 transfer equation is:

$$delCO2 = KCO2*(CO2s-CO2)*delt$$

where

KCO2 = ACO2*Ka (/day)

Ka = oxygen transfer rate coefficient (/day)

= $5.026*u^{0.969}*d^{-1.673}$

u = average speed (m/s) of river in segment (approximated by u at node 1)

d = average depth (m) of river in segment (approximated by d at node 1)

ACO2 = Factor to convert reaeration coefficient to air-water CO_2 transfer coefficient

= $(32/44)^{0.25} = 0.92$

CO2s = CO_2 saturation

CO2 = aqueous CO_2 ($H2CO_3$*)

delt = residence time in segment (day)

Aqueous CO_2 ($H2CO_3$*) can be calculated from Ct, pH, and equilibrium constants. First an intermediate value, ALPHA, is calculated

$$ALPHA = [H^+]^2 / ([H^+]^2 + K_1*[H^+] + K_1*K_2)$$

Aqueous CO_2 is then calculated as the product of ALPHA and total inorganic carbon, Ct:

$$CO2 = ALPHA*Ct$$

Now the equation for mass transfer of CO_2 becomes

$$delCO2 = KCO2*(CO2s-ALPHA*Ct)*delt$$

where Ct is the average Ct in the segment (approximated here by Ct at the upstream node).

For this equation, CO_2 saturation is calculated using Henry's Law:

$$CO2s = K_h*pCO2$$

where K_h is Henry's constant and pCO_2 is the local partial pressure of CO_2.

K_h can be approximated by $10^{-1.5}$ or it can be calculated from

$$K_h = 44000*10^{\wedge}(2385.73/Tk-0.0152642*Tk+14.0184)$$

where Tk is temperature (deg K).

pCO_2 is given as $10^{-3.5}$ and may be adjusted for elevation (meters above MSL) by:

$$pCO_2 = 10^{-3.5} * exp((-0.03418*elevation)/(288.0-0.006496*elevation)$$

1.2.   *Algae contribution, delCO2algae*

Contribution of CO_2 to the system by algal respiration is governed by stoichiometry. A simple stoichiometry of algal growth and respiration is given (Chapra, 1997) as:

$$6CO_2 + 6H_2O <-> C(6)H(12)O(6) + 6O_2$$

This relationship states that 6 molecules of CO_2 are used in making 1 molecule of algal material. This algal material weighs 180 grams/mol. So, the number of moles of CO_2 consumed per mg of algae produced is:

$$6/(180*1000) = 3.3E-5 \text{ mol } CO_2/\text{mg Algae}$$

We use this factor to calculate the contribution of algae growth and respiration to concentrations of Ct so that:

$$delCO2algae = -3.3E-5*delAlgae*delt$$

where delCO2algae is the change in total inorganic carbon (mol/l) due to algae growth as the parcel travels through the segment, and delAlgae is the net growth rate of algae in that segment.

1.3. Calculating pH

Once Ct (the total inorganic carbon in the system at the downstream end of the segment) is calculated, the model estimates pH using an iterative numerical method (in this case, the Excel "Goal Seek" function). The model estimates pH (i.e. $-\log[H^+]$) from alkalinity, total inorganic carbon, and carbonate equilibrium constants by locating $[H^+]$ such that:

$$\text{Alkalinity} = TIC*(a_1 + 2a_2) + K_w / [H^+] - [H^+]$$

where

$a_1 = [H^+]*K_1 / E$
$a_2 = K_1*K_2 / E$
$E = [H^+]^2 + [H^+]*K_1 + K_1*K_2$

and equilibrium constants K_1, K_2, and K_w are calculated from:

$pK_1 = $ -1.0E-6*(Tw**3)+2E-4*(Tw**2)-0.0145*Tw+6.5857
$pK_2 = $ -1.0E-6*(Tw**3)+2E-4*(Tw**2)-0.0167*Tw+10.638
$pK_w = $ 9.0E-7*(Tw**3)+9.0E-5*(Tw**2)-0.0402*Tw+14.931
$Tw = $ water temperature

Equilibrium constants are updated for each segment of river based on water temperature of the upstream node. With pH in the segment calculated, the process is repeated in the next segment, following the parcel of water through all segments of the river and leaving a record of pH for each node.