1 Introduction

The pH, alkalinity and total inorganic carbon algorithms that are incorporated into WASP come directly from QUAL2K & QUAL2Kw (Chapra, Pelletier and Tao, 2008). Every effort was made to insure that the implementation of the pH calculation within WASP is consistent with QUAL2K/.

The following sections were mostly taken from the QUAL2K documentation and where appropriate the equations were modified to match the assumptions and kinetic implementations in WASP.

2 pH Calculation

The following equilibrium, mass balance and electroneutrality equations define a freshwater dominated by inorganic carbon (Stumm and Morgan 1996),

$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \tag{1}$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \tag{2}$$

$$K_w = [H^+][OH^-] \tag{3}$$

$$c_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{4}$$

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{5}$$

where K_1, K_2 and K_w are acidity constants, Alk = alkalinity [eq L^{-1}], $H_2CO_3^*$ = the sum of dissolved carbon dioxide and carbonic acid, HCO_3^- = bicarbonate ion, CO_3^{2-} = carbonate ion, H^+ = hydronium ion, OH^- = hydroxyl ion, and c_T = total inorganic carbon concentration [mole L^{-1}]. The brackets [ ] designate molar concentrations.

Note that the alkalinity is expressed in units of eq/L for the internal calculations. For input and output, it is expressed as mgCaCO$_3$/L. The two units are related by

$$Alk(\text{mgCaCO}_3/L) = 50{,}000 \times Alk(\text{eq/L}) \tag{6}$$

The equilibrium constants are corrected for temperature by

Harned and Hamer (1933):

$$pK_w = \frac{4787.3}{T_a} + 7.1321 \log_{10}(T_a) + 0.010365 T_a - 22.80 \tag{7}$$

Plummer and Busenberg (1982):

$$\log K_1 = -356.3094 - 0.06091964 T_a + 21834.37 / T_a \\ + 126.8339 \log T_a - 1{,}684{,}915 / T_a^2 \tag{8}$$

Plummer and Busenberg (1982):

$$\log K_2 = -107.8871 - 0.03252849 T_a + 5151.79 / T_a \\ + 38.92561 \log T_a - 563{,}713.9 / T_a^2 \tag{9}$$

The nonlinear system of five simultaneous equations (1 through 5) can be solved numerically for the five unknowns: $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[OH^-]$, and $\{H^+\}$. An efficient solution method can be derived by combining Eqs. (1), (2) and (4) to define the quantities (Stumm and Morgan 1996)

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \tag{10}$$

$$\alpha_1 = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2} \tag{11}$$

$$\alpha_2 = \frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \tag{12}$$

where α_0, α_1, and α_2 = the fraction of total inorganic carbon in carbon dioxide, bicarbonate, and carbonate, respectively. Equations (3), (11), and (12) can be substituted into Eq. (4) to yield,

$$Alk = (\alpha_1 + 2\alpha_2)c_T + \frac{K_w}{[H^+]} - [H^+] \tag{13}$$

Thus, solving for pH reduces to determining the root, $\{H^+\}$, of

$$f([H^+]) = (\alpha_1 + 2\alpha_2)c_T + \frac{K_w}{[H^+]} - [H^+] - Alk \tag{14}$$

where pH is then calculated with

$$pH = -\log_{10}[H^+]$$ (15)

The root of Eq. (14) is determined with a numerical method. The user can choose bisection, Newton-Raphson or Brent's method (Chapra and Canale 2006, Chapra 2007) as specified on the QUAL2K sheet. The Newton-Raphson is the fastest but can sometimes diverge. In contrast, the bisection method is slower, but more reliable. Because it balances speed with reliability, Brent's method is the default.

2.1 Total Inorganic Carbon (c_T)

Total inorganic carbon concentration increases due to fast carbon oxidation and plant respiration. It is lost via plant photosynthesis. Depending on whether the water is undersaturated or oversaturated with CO_2, it is gained or lost via reaeration,

$$S_{cT} = r_{cco}\text{FastCOxid} + r_{cca}\text{PhytoResp} + r_{cca}\frac{\text{BotAlgResp}}{H}$$
$$- r_{cca}\text{PhytoPhoto} - r_{cca}\frac{\text{BotAlgPhoto}}{H} + \text{CO2Reaer}$$ (16)

where

$$\text{CO2Reaer} = k_{ac}(T)\left([CO_2]_s - \alpha_0 c_T\right)$$ (17)

where $k_{ac}(T)$ = the temperature-dependent carbon dioxide reaeration coefficient [/d], and $[CO2]_s$ = the saturation concentration of carbon dioxide [mole/L].

The stoichiometric coefficients are computed as[1]

$$r_{cca} = r_{ca}\left(\frac{\text{gC}}{\text{mgA}}\right) \times \frac{\text{moleC}}{12\,\text{gC}} \times \frac{\text{m}^3}{1000\,\text{L}}$$ (18)

$$r_{cco} = \frac{1}{r_{oc}}\left(\frac{\text{gC}}{\text{gO}_2}\right)\frac{\text{moleC}}{12\,\text{gC}} \times \frac{\text{m}^3}{1000\,\text{L}}$$ (19)

2.2 Carbon Dioxide Saturation

The CO_2 saturation is computed with Henry's law,

$$[CO_2]_s = K_H p_{CO_2}$$ (20)

where K_H = Henry's constant [mole (L atm)$^{-1}$] and p_{CO_2} = the partial pressure of carbon dioxide in the atmosphere [atm]. Note that the partial pressure is input as a constant or as an

---

[1] The conversion, m^3 = 1000 L is included because all mass balances express volume in m^3, whereas total inorganic carbon is expressed as mole/L.

environmental time function in units of ppm. The program internally converts ppm to atm using the conversion: 10^{-6} atm/ppm.

The value of K_H can be computed as a function of temperature by (Edmond and Gieskes 1970)

$$pK_H = -\frac{2385.73}{T_a} - 0.0152642 T_a + 14.0184 \tag{21}$$

The partial pressure of CO_2 in the atmosphere has been increasing, largely due to the combustion of fossil fuels (Figure 1). Values in 2007 are approximately $10^{-3.416}$ atm (= 383.7 ppm).
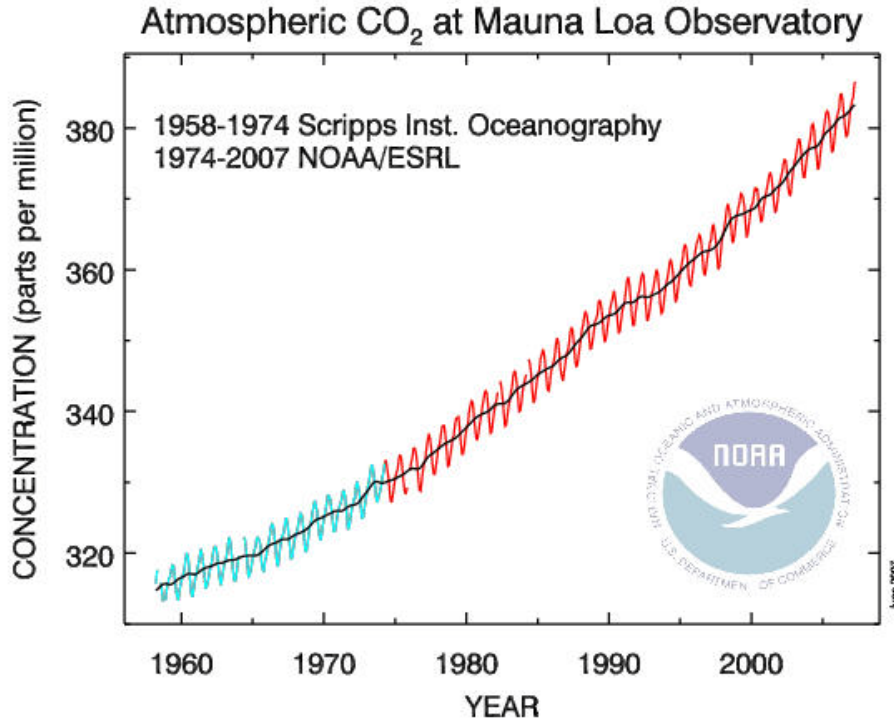
Figure 1 Concentration of carbon dioxide in the atmosphere as recorded at Mauna Loa Observatory, Hawaii.

The CO_2 reaeration coefficient can be computed from the oxygen reaeration rate by

$$k_{ac}(20) = \left(\frac{32}{44}\right)^{0.25} = 0.923\, k_a(20) \tag{22}$$

2.3 Effect of Control Structures: CO_2

As was the case for dissolved oxygen, carbon dioxide gas transfer in streams can be influenced by the presence of control structures. WASP assumes that carbon dioxide behaves similarly to dissolved oxygen. Thus, the inorganic carbon mass balance for the element immediately downstream of the structure is written as

$$\frac{dc_{T,i}}{dt} = \frac{Q_{i-1}}{V_i}c'_{T,i-1} - \frac{Q_i}{V_i}c_{T,i} - \frac{Q_{ab,i}}{V_i}c_{T,i} + \frac{E'_i}{V_i}\left(c_{T,i+1} - c_{T,i}\right) + \frac{W_{cT,i}}{V_i} + S_{cT,i} \tag{23}$$

where $c'_{T,i-1}$ = the concentration of inorganic carbon entering the element [mgO$_2$/L], where

$$c'_{T,i-1} = (\alpha_1 + \alpha_2)c_{T,i-1} + CO_{2,s,i-1} - \frac{CO_{2,s,i-1} - \alpha_2 c_{T,i-1}}{r_d} \tag{24}$$

where r_d is calculated from the dam reaeration algorithm for dissolved oxygen.

2.4 Alkalinity (Alk)

As summarized in the present model accounts for changes in alkalinity due to several mechanisms:

Table 1 Processes that effect alkalinity.

Process	Utilize	Create	Alkalinity change
Nitrif	NH4	NO3	Decrease
Denitr	NO3		Increase
OPHydr		SRP	Decrease
ONHydr		NH4	Increase
PhytoPhoto	NH4		Decrease
	NO3		Increase
	SRP		Increase
PhytoResp		NH4	Increase
		SRP	Decrease
PhytoUpN	NH4		Decrease
	NO3		Increase
PhytoUpP	SRP		Increase
PhytoExcrN		NH4	Increase
PhytoExcrP		SRP	Decrease
BotAlgUpN	NH4		Decrease
	NO3		Increase
BotAlgUpP	SRP		Increase

BotAlgExcrN		NH4	Increase
BotAlgExcrP		SRP	Decrease

It should be noted that the alkalinity calculations in advanced eutrophication module of WASP do not include the influences of metals.

2.5 Nitrification

Nitrification utilizes ammonium and creates nitrate. Hence, because a positive ion is taken up and a negative ion is created, the alkalinity is decreased by two equivalents. The change in alkalinity can be related to the nitrification rate by

$$S_{a,nitr} = -\frac{2\,\text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007\,\text{gN}} \frac{\text{gN}}{10^6\,\mu\text{gN}} \frac{50{,}000\,\text{mgCaCO}_3}{1\,\text{eq}} \text{Nitrif}\left(\frac{\mu\text{gN}}{\text{L d}}\right) \tag{25}$$

2.6 Denitrification

Denitrification utilizes nitrate and creates nitrogen gas. Hence, because a negative ion is taken up and a neutral compound is created, the alkalinity is increased by one equivalent. The change in alkalinity can be related to the denitrification rate by

$$S_{a,denitr} = \frac{1\,\text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007\,\text{gN}} \frac{\text{gN}}{10^6\,\mu\text{gN}} \frac{50{,}000\,\text{mgCaCO}_3}{1\,\text{eq}} \text{Denitr}\left(\frac{\mu\text{gN}}{\text{L d}}\right) \tag{26}$$

where the r's are ratios that translate the processes into the corresponding amount of alkalinity. The stoichiometric coefficients are derived from nutrient algorithms in WASP.

2.7 Organic P Hydrolysis

Hydrolysis of organic P results in the creation of inorganic phosphate. Depending on the pH, the phosphate will either have 1 (pH $\cong$ 2 to 7) or 2 (pH $\cong$ 7 to 12) negative charges. Hence, because negative ions are being created, the alkalinity is decreased by one or two equivalents, respectively. The change in alkalinity can be related to the P hydrolysis rate by[2],

$$S_{a,OPh} =$$

$$-(\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4})\frac{\text{eq}}{\text{moleP}} \frac{\text{moleP}}{30.974\,\text{gP}} \frac{\text{gP}}{10^6\,\mu\text{gP}} \frac{50{,}000\,\text{mgCaCO}_3}{1\,\text{eq}} \text{OPHydr}\left(\frac{\mu\text{gP}}{\text{L d}}\right) \tag{27}$$

where

$$\alpha_{H2PO4} = \frac{K_{p1}[\text{H}^+]^2}{[\text{H}^+]^3 + K_{p1}[\text{H}^+]^2 + K_{p1}K_{p2}[\text{H}^+] + K_{p1}K_{p2}K_{p3}} \tag{28}$$

---

[2] Note that although it will almost always be negligible, Eq. (193) PO_4^{3-} ☐ for completeness

$$\alpha_{HPO4} = \frac{K_{p1}K_{p2}[H^+]}{[H^+]^3 + K_{p1}[H^+]^2 + K_{p1}K_{p2}[H^+] + K_{p1}K_{p2}K_{p3}} \tag{29}$$

$$\alpha_{PO4} = \frac{K_{p1}K_{p2}K_{p3}}{[H^+]^3 + K_{p1}[H^+]^2 + K_{p1}K_{p2}[H^+] + K_{p1}K_{p2}K_{p3}} \tag{30}$$

where $K_{p1} = 10^{-2.15}$, $K_{p2} = 10^{-7.2}$, and $K_{p3} = 10^{-12.35}$.

2.8 Organic N Hydrolysis

Hydrolysis of organic N results in the creation of ammonia. Depending on the pH, the ammonia will either be in the form of ammonium ion with a single positive charge (pH < 9) or neutral ammonia gas (pH > 9). Hence, when the positive ions are created, the alkalinity is increased by one equivalent. The change in alkalinity can be related to the N hydrolysis rate by

$$S_{a,ONh} = F_i \frac{1\,eq}{moleN} \frac{moleN}{14.007\,gN} \frac{gN}{10^6\,\mu gN} \frac{50{,}000\,mgCaCO_3}{1\,eq} ONHydr\left(\frac{\mu gN}{L\,d}\right) \tag{31}$$

2.9 Phytoplankton Photosynthesis

Phytoplankton photosynthesis takes up nitrogen as either ammonia or nitrate and phosphorus as inorganic phosphate. If ammonia is the primary nitrogen source, this leads to a decrease in alkalinity because the uptake of the positively charged ammonium ions is much greater than the uptake of the negatively charged phosphate ions. If nitrate is the primary nitrogen source, this leads to an increase in alkalinity because both nitrate and phosphate are negatively charged.

The following representation relates the change in alkalinity to phytoplankton photosynthesis depending on the nutrient sources as well as their speciation as governed by the pH,

$$\begin{aligned}
S_{a,PhytP} = \frac{50{,}000\,mgCaCO_3}{1\,eq} \\
\left(-r_{na}P_{ap}F_i \frac{1\,eq}{moleN} \frac{moleN}{14.007\,gN} \frac{gN}{10^6\,\mu gN}\right. \\
+ r_{na}\left(1 - P_{ap}\right) \frac{1\,eq}{moleN} \frac{moleN}{14.007\,gN} \frac{gN}{10^6\,\mu gN} \\
\left.+ r_{pa}(\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4}) \frac{1\,eq}{moleP} \frac{moleP}{30.974\,gP} \frac{gP}{10^6\,\mu gP}\right) \\
\times PhytoPhoto\left(\frac{\mu gA}{L\,d}\right)
\end{aligned} \tag{32}$$

2.10 Phytoplankton Nutrient Uptake

Phytoplankton takes up nitrogen as either ammonia or nitrate and phosphorus as inorganic phosphate. The following representation relates the change in alkalinity to phytoplankton uptake rates depending on the nutrient sources as well as their speciation as governed by the pH,

$$S_{a,PUp} = \frac{50,000 \, \text{mgCaCO}_3}{1 \, \text{eq}}$$

$$\left(\left(-P_{ap}F_i + (1 - P_{ap}) \right) \frac{1 \, \text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007 \, \text{gN}} \frac{\text{gN}}{10^6 \, \mu\text{gN}} \times \frac{\text{PhytoUpN}(\mu\text{gN/L/d})}{H(\text{m})} \right. \tag{33}$$

$$\left. + (\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4}) \frac{1 \, \text{eq}}{\text{moleP}} \frac{\text{moleP}}{30.974 \, \text{gP}} \frac{\text{gP}}{10^6 \, \mu\text{gP}} \times \frac{\text{PhytoUpP}(\mu\text{gP/L/d})}{H(\text{m})} \right)$$

2.11 Phytoplankton Nutrient Excretion

Phytoplankton excretes ammonia and inorganic phosphate. The following representation relates the change in alkalinity to phytoplankton excretion rates including the effect of pH on the nutrient's speciation,

$$S_{a,PEx} = \frac{50,000 \, \text{mgCaCO}_3}{1 \, \text{eq}}$$

$$\left(F_i \frac{1 \, \text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007 \, \text{gN}} \frac{\text{gN}}{10^6 \, \mu\text{gN}} \times \frac{\text{PhytoExN}(\mu\text{gN/L/d})}{H(\text{m})} \right.$$

$$\left. - (\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4}) \frac{1 \, \text{eq}}{\text{moleP}} \frac{\text{moleP}}{30.974 \, \text{gP}} \frac{\text{gP}}{10^6 \, \mu\text{gP}} \times \frac{\text{PhytoExP}(\mu\text{gP/L/d})}{H(\text{m})} \right)$$

$$\tag{34}$$

2.12 Bottom Algae Nutrient Uptake

Bottom algae take up nitrogen as either ammonia or nitrate and phosphorus as inorganic phosphate. The following representation relates the change in alkalinity to bottom algae uptake rates depending on the nutrient sources as well as their speciation as governed by the pH,

$$S_{a,BAUp} = \frac{50,000 \, \text{mgCaCO}_3}{1 \, \text{eq}}$$

$$\left(\left(-P_{ab}F_i + (1 - P_{ab}) \right) \frac{1 \, \text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007 \, \text{gN}} \frac{\text{gN}}{10^6 \, \mu\text{gN}} \times \frac{\text{BotAlgUpN}(\text{mgN/m}^2/\text{d})}{H(\text{m})} \right.$$

$$\left. + (\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4}) \frac{1 \, \text{eq}}{\text{moleP}} \frac{\text{moleP}}{30.974 \, \text{gP}} \frac{\text{gP}}{10^6 \, \mu\text{gP}} \times \frac{\text{BotAlgUpP}(\text{mgP/m}^2/\text{d})}{H(\text{m})} \right)$$

$$\tag{35}$$

2.13 Bottom Algae Nutrient Excretion

Bottom algae excrete ammonia and inorganic phosphate. The following representation relates the change in alkalinity to bottom algae excretion rates including the effect of pH on the nutrient's speciation,
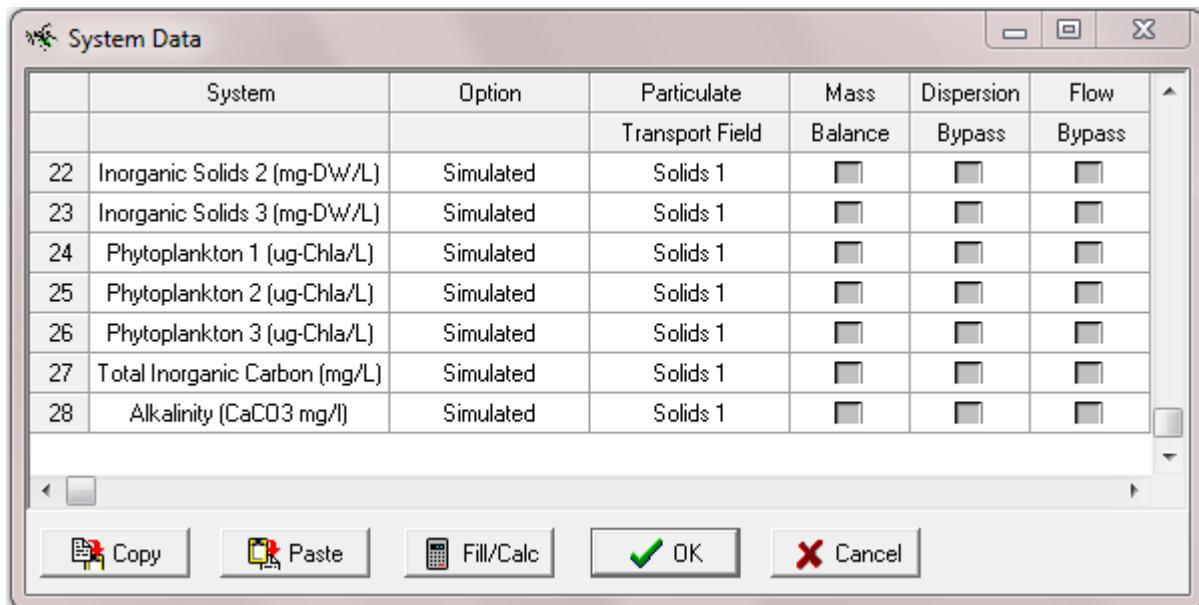
$$S_{a,BAEx} = \frac{50{,}000 \, \text{mgCaCO}_3}{1 \, \text{eq}}$$

$$\left(F_i \frac{1 \, \text{eq}}{\text{moleN}} \frac{\text{moleN}}{14.007 \, \text{gN}} \frac{\text{gN}}{10^6 \, \mu\text{gN}} \times \frac{\text{BotAlgExN(mgN/m}^2\text{/d)}}{H(\text{m})} \right.$$

$$\left. - (\alpha_{H2PO4} + 2\alpha_{HPO4} + 3\alpha_{PO4}) \frac{1 \, \text{eq}}{\text{moleP}} \frac{\text{moleP}}{30.974 \, \text{gP}} \frac{\text{gP}}{10^6 \, \mu\text{gP}} \times \frac{\text{BotAlgExP(mgP/m}^2\text{/d)}}{H(\text{m})} \right)$$

(36)

3 Model Input

The data required to support the application of the advanced eutrophication model to predict pH is described below.

3.1 Systems

For the inclusion of pH calculations within the WASP Framework two additional state variables (Total Inorganic Carbon and Alkalinity) were added to the advanced eutrophication model. The user would be advised to set their simulation option to By-Pass if pH calculations are not needed (Figure 2).

	System	Option	Particulate Transport Field	Mass Balance	Dispersion Bypass	Flow Bypass	
22	Inorganic Solids 2 (mg-DW/L)	Simulated	Solids 1	☐	☐	☐	
23	Inorganic Solids 3 (mg-DW/L)	Simulated	Solids 1	☐	☐	☐	
24	Phytoplankton 1 (ug-Chla/L)	Simulated	Solids 1	☐	☐	☐	
25	Phytoplankton 2 (ug-Chla/L)	Simulated	Solids 1	☐	☐	☐	
26	Phytoplankton 3 (ug-Chla/L)	Simulated	Solids 1	☐	☐	☐	
27	Total Inorganic Carbon (mg/L)	Simulated	Solids 1	☐	☐	☐	
28	Alkalinity (CaCO3 mg/l)	Simulated	Solids 1	☐	☐	☐	

Figure 2 WASP State Variables for pH Calculation

Note: If you are upgrading a previous advanced eutrophication WASP input file (WIF) to the new module there is several steps you will need to do.

➢ Set the Simulation Option on the System Screen (shown above to simulate)

➢ You will need to go into the Flow and Exchange screen and click okay (this causes the interface to add the new state variable (Total Inorganic Carbon and Alkalinity) to the boundary conditions screen.

➤ Go to the boundary conditions screen and set you pH and alkalinity concentrations coming into your model network.

➤ Complete the required information given below to calculate pH.

3.2 Time Functions

Figure 3 illustrates the new environmental time function to provide a time variable partial pressure for atmospheric CO2. If the user specifies a time function and constant as specified in Section 3.3, the environmental time function will be used. Note the user selects which time functions will be considered and must check the "used" radio button for the information to be passed to the model. For each time function being defined the user must provide a time series of data that consists of at least two points.

Figure 3 Time Function for CO2 Atmospheric Partial Pressure

3.3 Constants

Figure 4 illustrates where the user specifies the only constant needed for the pH calculation (if not specified as a time function). The CO_2 atmospheric partial pressure constant is specified in the advance eutrophication module by selecting Constants and the Global Constants group. To switch between the constant groups, chose using the drop down picklist. Note the user is specifies the values for the constants, but also needs to check the "Used" radio button. Failing to check this box will keep the interface for sending this information to the model. If a time

function as described in Section 3.2 provides data for CO_2 atmospheric partial pressure it supersedes the value specified here.


Figure 4 Constant Atmospheric Partial Pressure for CO2

3.4 Output Variables

Output variables from the pH/alkalinity and total inorganic carbon calculation in the advanced eutrophication module are listed in Figure 5. An output variable for total inorganic carbon (state variable), Alkalinity (state variable), pH (calculated) and unionized ammonia (calculated) have been added as output. Variables checked in the "Output" box will be available to the WASP graphical post-processing software. For each variable with a checked "CSV" box, WASP will produce a separate comma-delimited file containing output for all segments and all output times. In this example, checked CSV output variables are related directly or indirectly to the benthic algal simulation.
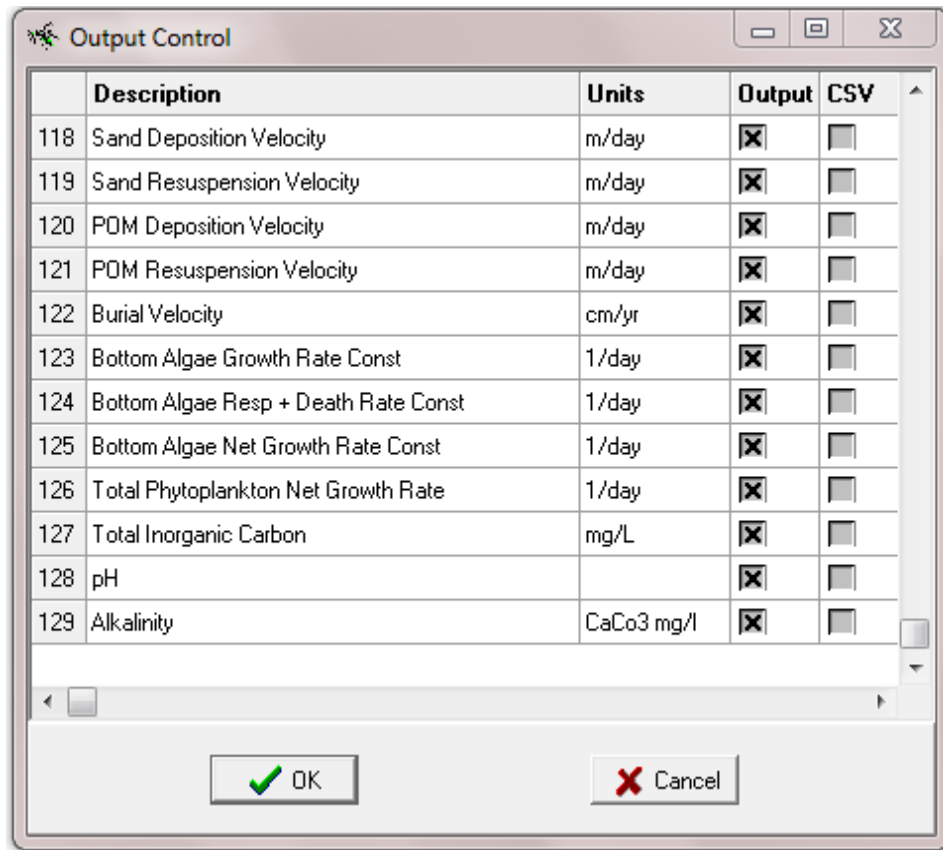
Figure 5 WASP Output Variables for pH Calculation

4 References

Chapra, S.C., Pelletier, G.J. and Tao, H. 2008. QUAL2K: A Modeling Framework for Simulating River and Stream Water Quality, Version 2.11: Documentation and Users Manual. Civil and Environmental Engineering Dept., Tufts University, Medford, MA., Steven.Chapra@tufts.edu