

WASP7 pH-Alkalinity - Model Theory and User's Guide

Supplement to Water Quality Analysis Simulation Program (WASP) User Documentation

by

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NOTICE

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Abstract

The WASP7 pH algorithms are linked within the Advanced Eutrophication module, and provide calculations of pH, alkalinity, and total inorganic carbon throughout a specified computational network. This supplemental user manual documents the pH algorithms, including the alkalinity and TIC equations, the model input and output, and a series of model verification tests.

To run the WASP7 pH-alkalinity module, the user must select the Advanced Eutrophication module and enable the pH and the alkalinity state variables. In addition, the user should select the “supplemental” variables that might significantly influence pH and alkalinity in the water body, such as CBOD, dissolved organic nitrogen and phosphorus, ammonia, nitrate, phosphate, phytoplankton, and benthic algae. Atmospheric concentration of CO₂ can be specified as a constant or time function. Water temperature must be specified using segment parameters and time functions. Rate constants and coefficients and environmental parameters controlling the supplemental variables should be specified (see supplemental user manuals for nutrient cycling, phytoplankton, and benthic algae). Initial conditions by segment and boundary conditions by inflow for pH and alkalinity must be specified for pH and alkalinity. External loadings can be specified for alkalinity and for total inorganic carbon.

Standard output for the advanced eutrophication module includes segment pH, total inorganic carbon, and alkalinity, as well as concentrations of NH₄⁺ and NH₃.

Acknowledgment

The pH, alkalinity and total inorganic carbon algorithms that are incorporated into WASP were adapted from QUAL2Kw and extended to saline systems with routines adapted from CO2SYS. Much of Chapter 3, Development of Equations, was adapted from the QUAL2K documentation to match the assumptions and kinetic implementations in WASP. We gratefully acknowledge the software, documentation, and technical consultations with Dr. Steve Chapra, Tufts University, and Dr. Greg Pelletier, Washington Ecology.

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1 Introduction

The relative acidity or alkalinity of a water body is an important component of its general health. Water weakly dissociates to yield a hydrogen ion, H^+ , and a hydroxyl ion, OH^- . The product of their molar concentrations, K_w , is approximately 10^{-14} . In pure water, equal amounts of H^+ and OH^- are formed, yielding molar concentrations of 10^{-7} . The molar concentration of hydrogen ions in a water body, $[H^+]$, is the result of several speciation reactions that balance its electrical charge. Acid that is added to water ionizes, increasing $[H^+]$ and forcing a decline in the molar concentration of hydroxyl ions $[OH^-]$. The negative log (base 10) of $[H^+]$ is $p[H]$.

Due to interactions between H^+ and other ions in solution, measured pH differs slightly from $p[H]$. Values for pH are calculated as $p[H]$ times an activity coefficient divided by water density. For fresh waters with low total dissolved solids, ionic strength is low and activity coefficients are close to 1.0. For temperatures close to 20 C, the density of fresh water is close to 1.0. For salt water systems, the activity and density corrections to pH can be significant.

pH is a convenient indicator of the general health of a water body, measuring the intensity of its acidity or alkalinity. pH is expressed on a scale from 0 to 14, where a value of 7 represents neutral conditions. Lower pH values indicate higher concentrations of H^+ characteristic of acidic waters. Conversely, higher values of pH indicate lower concentrations of H^+ characteristic of alkaline waters. In natural water bodies, pH values can range from a low of 1.7 for volcanic lakes to a high of 12.0 for closed alkaline systems (Hutchinson, 1957). Stream waters typically range from 6 to 8, while marine systems are generally constricted to values from 7.5 to 8.5. Chronic standards for pH are 6.5 to 9.0 for fresh water and 6.5 to 8.5 for salt water (U.S. EPA, 1986).

In most water bodies, pH levels are controlled by total inorganic carbon (TIC) and alkalinity. TIC is the sum of the inorganic carbon species in water [moles C/L], including dissolved carbon dioxide and carbonic acid, bicarbonate anion, and carbonate anion. TIC is often expressed in mass units of [mgC/L]. Values for TIC in seawater range between 22 and 27 [mgC/L]. Alkalinity is the stoichiometric sum of bases in solution [equivalents/L], measuring its ability to neutralize acids to the equivalence point of bicarbonate (around pH 4.5). Since carbonate alkalinity is the most important component, total alkalinity is often expressed in mass units of [mgCaCO₃/L]. Most of the carbonate in natural waters comes from the dissolution of carbonate rock and exchange with carbon dioxide in the atmosphere. Other natural components of alkalinity include borate, hydroxide, phosphate, silicate, nitrate, and ammonia. Values for alkalinity in seawater range between 2.25 and 2.5 [eq/L], or 110 to 130 [mgCaCO₃/L].

The pH, alkalinity and total inorganic carbon algorithms that are incorporated into WASP were adapted from QUAL2Kw (Chapra, Pelletier and Tao, 2008) and extended to saline systems with routines adapted from CO2SYS (Lewis and Wallace, 1998, Pierrot, et al., 2006). QUAL2K is a steady flow stream water quality model that is implemented within Excel. This model handles branching one-dimensional, steady flow stream and river systems with diurnal kinetics. QUAL2K includes the standard stream water quality processes from QUAL2E (Brown and

Barnwell, 1987) with improvements in model segmentation, forms of carbonaceous BOD evaluated, particulate organic matter simulation, anoxia and denitrification modeling, sediment-water dissolved oxygen and nutrient fluxes, explicit simulation of attached bottom algae, light extinction calculation, enhanced pH simulation, and pathogen removal functions.

CO2SYS is an Excel spreadsheet that performs calculations relating parameters of the carbon dioxide system in seawater and freshwater. The program addresses the four measurable parameters of the CO₂ system – total alkalinity, total inorganic CO₂ (i.e., the sum of the dissolved CO₂, carbonate, and bicarbonate), pH, and either fugacity or partial pressure of CO₂. The program uses two of these four parameters to calculate the other two parameters at a set of input conditions (temperature and pressure) and a set of output conditions chosen by the user. CO2SYS was written in Microsoft QuickBasic for batch operations in DOS, and a later version is implemented within Excel for operation in Windows.

2 Background

The new pH algorithms are incorporated into the WASP7 advanced eutrophication module, which includes the following state variables (new or revised variables shown in bold):

1. Ammonia nitrogen [mg N/L]
2. Nitrate nitrogen [mg N/L]
3. Dissolved organic nitrogen [mg N/L]
4. Orthophosphate phosphorus [mg P/L]
5. Dissolved organic phosphorus [mg P/L]
6. Inorganic silicon [mg Si/L]
7. Dissolved organic silicon [mg Si/L]
8. CBOD type 1 [mg O₂/L]
9. CBOD type 2 [mg O₂/L]
10. CBOD type 3 [mg O₂/L]
11. Dissolved oxygen [mg O₂/L]
12. Detrital carbon [mg C/L]
13. Detrital nitrogen [mg N/L]
14. Detrital phosphorus [mg P/L]
15. Detrital silicon [mg Si/L]
16. Total detritus [mg D/L]
- 17. Salinity [psu] or TDS [mg/L]**
18. Bottom algae total biomass [g D/m²]
19. Bottom algae cell nitrogen [mg N/g D]
20. Bottom algae cell phosphorus [mg P/g D]
21. Solids 1 (silt) [mg D/L]
22. Solids 2 (sand) [mg D/L]
23. Solids 3 (fines) [mg D/L]
24. Phytoplankton 1 [mg C/L]
25. Phytoplankton 2 [mg C/L]
26. Phytoplankton 3 [mg C/L]

- 27. Total inorganic carbon [mg C/L]
- 28. Total alkalinity [mg CaCO₃/L]

The relationship between WASP state variables is illustrated in Figure 1.

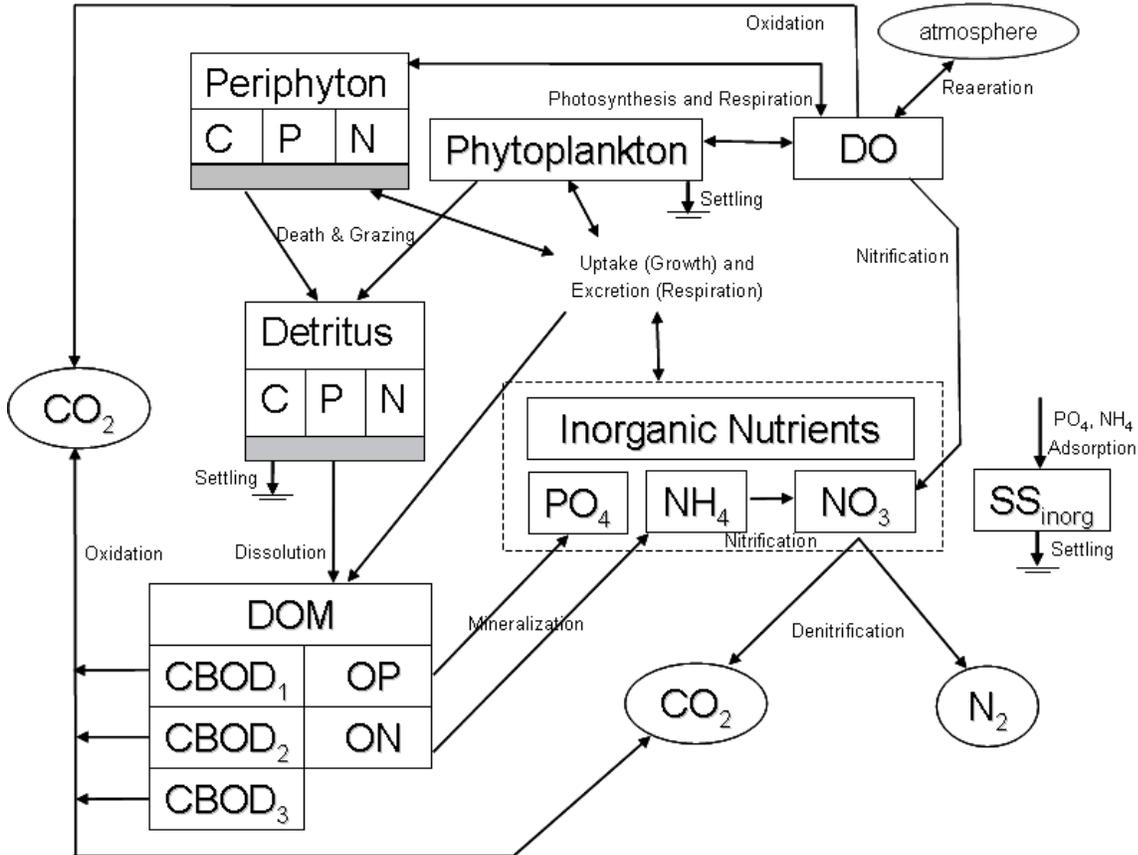


Figure 1 WASP Version 7 Eutrophication Kinetics

Each of the above state variables is represented using a general mass balance equation around an infinitesimally small fluid volume is given by:

Equation 1

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(u_x \cdot C) - \frac{\partial}{\partial y}(u_y \cdot C) - \frac{\partial}{\partial z}(u_z \cdot C) + \frac{\partial}{\partial x}\left(E_x \cdot \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \cdot \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \cdot \frac{\partial C}{\partial z}\right) + S$$

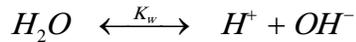
where C is the concentration of the water quality constituent [mg/L, or g/m³], t is time [days], u_x , u_y and u_z are longitudinal, lateral, and vertical velocities [m/day], E_x , E_y and E_z are longitudinal, lateral, and vertical diffusion coefficients [m²/day], and S is the total source-sink rate [g/m³-day]. Sources and sinks result from physical, biochemical, and biological reactions and transfer

mechanisms. In this documentation, volumetric source/sink terms are denoted by S , and are in units of $[\text{g}/\text{m}^3\text{-day}]$. Rate constants are denoted by k and are in units of $[\text{day}^{-1}]$. Units are qualified by subscripts D, C, N, P, Si, and A, which refer to dry weight, carbon, nitrogen, phosphorus, silicon, and chlorophyll a , respectively.

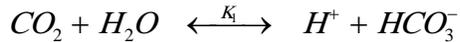
2.1.1 Chemical Speciation Reactions

In freshwater systems dominated by inorganic carbon, the primary dissociation reactions include water and carbonic acid (Stumm and Morgan 1996):

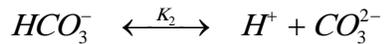
Equation 2



Equation 3

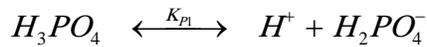


Equation 4

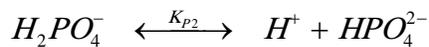


Additional speciation reactions that can affect biogeochemical kinetics include phosphate and ammonia:

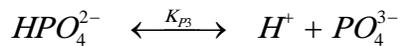
Equation 5



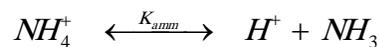
Equation 6



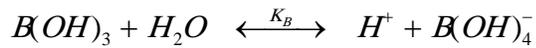
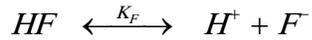
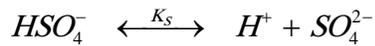
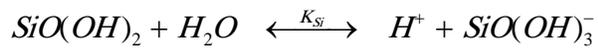
Equation 7



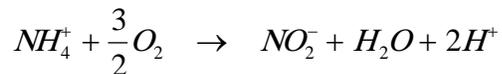
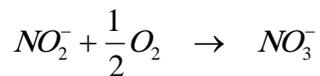
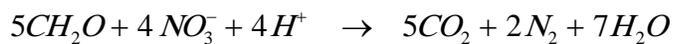
Equation 8



In marine systems, additional dissociation reactions with boric acid, hydrogen fluoride, bisulfate, and silicic acid can affect pH (Lewis and Wallace, 1998):

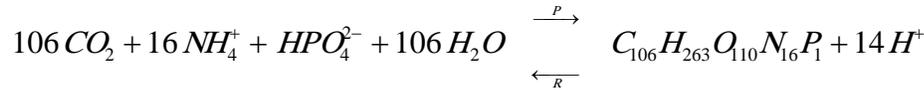
Equation 9**Equation 10****Equation 11****Equation 12****2.1.2 Biochemical Reactions**

The following chemical equations are used to represent the major biochemical reactions that take place in the model (Stumm and Morgan 1996):

Nitrification:**Equation 13****Equation 14****Denitrification:****Equation 15****Plant Photosynthesis and Respiration:**

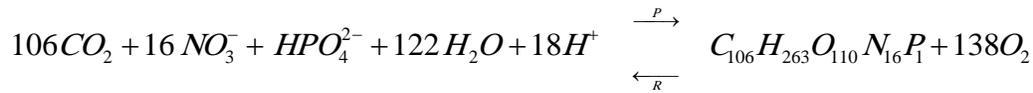
Ammonium as substrate:

Equation 16



Nitrate as substrate:

Equation 17



Note that a number of additional reactions are used in the model such as those involved with simulating pH and unionized ammonia. These will be outlined when these topics are discussed later in this document.

3 Development of Equations

3.1 pH Equilibrium Calculations

In WASP, pH calculations are conducted using molar concentrations of all constituents. The resulting value of $[H^+]$ is then used to calculate $p[H]$ as well as pH in one of four scales selected by the user:

1. Total scale [mol/kg-SW]
2. Seawater scale [mol/kg-SW]
3. Free scale [mol/kg-SW]
4. NBS scale [mol/kg-H₂O]

The default option is 2, seawater scale.

3.1.1 Freshwater Systems

A set of equilibrium, mass balance and electroneutrality equations define a freshwater system dominated by inorganic carbon (Stumm and Morgan 1996). From the first set of chemical reactions depicted in Section 2.1.1, the following equilibrium equations are derived:

Equation 18

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

Equation 19

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]}$$

Equation 20

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

where K_w , K_1 , and K_2 are acidity constants from **Equation 2**, **Equation 3**, and **Equation 4**, H_2CO_3^* is the sum of dissolved carbon dioxide and carbonic acid [mole/L], HCO_3^- is bicarbonate ion [mole/L], CO_3^{2-} is carbonate ion [mole/L], H^+ = hydronium ion [mole/L], and OH^- = hydroxyl ion [mole/L].

From **Equation 18**, the hydroxyl ion concentration is given by:

Equation 21

$$[\text{OH}^-] = K_w / [\text{H}^+]$$

Carbonate species concentrations can be derived from their speciation equations along with the following carbonate mass balance:

Equation 22

$$\text{TIC}_{mol} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

where TIC_{mol} is the total inorganic carbon concentration [mole/L].

Combining **Equation 19**, **Equation 20**, and **Equation 22**, the equilibrium concentrations of inorganic carbon species are given by:

Equation 23

$$[\text{H}_2\text{CO}_3^*] = \text{TIC}_{mol} \times \alpha_0 = \text{TIC}_{mol} \left(\frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \right)$$

Equation 24

$$[\text{HCO}_3^-] = \text{TIC}_{mol} \times \alpha_1 = \text{TIC}_{mol} \left(\frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \right)$$

Equation 25

$$[CO_3^{2-}] = TIC_{mol} \times \alpha_2 = TIC_{mol} \left(\frac{K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \right)$$

where α_0 , α_1 , and α_2 are the fractions of total inorganic carbon in carbon dioxide, bicarbonate, and carbonate, respectively.

While phosphorus speciation does not significantly affect the ion balance in most freshwater systems, these reactions are included here for completeness. Phosphate species concentrations can be derived from their speciation equations along with the following phosphate mass balance:

Equation 26

$$TIP_{mol} = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

where TIP_{mol} is the total inorganic phosphorus concentration [mole/L]. From this mass balance equation and the speciation equations (not shown), the equilibrium concentrations of inorganic phosphate species are given by:

Equation 27

$$[H_2PO_4^-] = TIP_{mol} \times \alpha_{H_2PO_4} = TIP_{mol} \left(\frac{K_{p1} [H^+]^2}{[H^+]^3 + K_{p1} [H^+]^2 + K_{p1} K_{p2} [H^+] + K_{p1} K_{p2} K_{p3}} \right)$$

Equation 28

$$[HPO_4^{2-}] = TIP_{mol} \times \alpha_{HPO_4} = TIP_{mol} \left(\frac{K_{p1} K_{p2} [H^+]}{[H^+]^3 + K_{p1} [H^+]^2 + K_{p1} K_{p2} [H^+] + K_{p1} K_{p2} K_{p3}} \right)$$

Equation 29

$$[PO_4^{3-}] = TIP_{mol} \times \alpha_{PO_4} = TIP_{mol} \left(\frac{K_{p1} K_{p2} K_{p3}}{[H^+]^3 + K_{p1} [H^+]^2 + K_{p1} K_{p2} [H^+] + K_{p1} K_{p2} K_{p3}} \right)$$

where K_{p1} , K_{p2} , and K_{p3} are acidity constants from Equation 5, Equation 6, and Equation 7, respectively, and $\alpha_{H_2PO_4}$, α_{HPO_4} , and α_{PO_4} are the fractions of total inorganic phosphate as $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} , respectively. Values for $K_{p1} = 10^{-2.15}$, $K_{p2} = 10^{-7.2}$, and $K_{p3} = 10^{-12.35}$.

While ammonia dissociation does not significantly affect the ion balance in most aquatic systems, this reaction can be important in modifying biogeochemical and biological reactions. From its speciation reaction, Equation 8, and a total ammonia mass balance, the fraction in ionized form is calculated by:

Equation 30

$$f_{NH4} = \frac{[H^+]}{[H^+] + K_{amm}}$$

where K_{amm} is the equilibrium coefficient for the ammonia dissociation reaction, which is related to temperature by:

Equation 31

$$pK_a = 0.09018 + \frac{2729.92}{T_a}$$

where T_a is absolute temperature [K] and $pK_a = -\log_{10}(K_{amm})$.

Following QUAL2K, the default equilibrium constants for fresh water systems are calculated from water temperature (Harned and Hamer, 1933 for K_w and Plummer and Busenberg, 1982 for K_1 and K_2). The user can choose alternate formulas for calculating these equilibrium constants, as defined and implemented in CO2SYS. The formulas published by Millero (1979) and by Millero et al. (2006) are appropriate for freshwater systems (see Section 4.3 for implementation of these options).

Finally, the electroneutrality equation for freshwater, carbonate-dominated systems is given by:

Equation 32

$$Alk_{eq} = \left\{ [OH^-] - [H^+] \right\} + \left\{ [HCO_3^-] + 2[CO_3^{2-}] \right\} + \left\{ [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] \right\}$$

where Alk_{eq} is total alkalinity [eq/L], and the terms in braces represent water alkalinity Alk_{water} , carbonate alkalinity Alk_{CO_3} , and phosphate alkalinity Alk_{PO_4} , respectively. Note that alkalinity is expressed in units of eq/L for the internal calculations. For input of initial and boundary conditions, and for output of simulated concentrations, alkalinity is expressed in mass units [mg CaCO₃/L]. The two units are related by the molar ratio of 50450 [mg CaCO₃/eq].

Species concentrations in Equation 32 are determined from $[H^+]$, along with their equilibrium constants, TIC_{eq} , and TIP_{eq} . Thus, solving for pH reduces to determining the root, $\{H^+\}$, of

Equation 33

$$f([H^+]) = Alk_{water} + Alk_{CO_3} + Alk_{PO_4} - Alk_{eq}$$

The root of Equation 33 is determined with the Newton-Raphson numerical method.

3.1.2 Marine Systems

In addition to carbonate and phosphate, marine systems are influenced by the speciation of borate, silicate, sulfate, and fluoride. While carbonate, phosphate, and silicate are simulated variables in WASP7, concentrations of borate, sulfate, and fluoride are calculated from salinity.

The electroneutrality equation for marine systems is given by:

Equation 34

$$Alk_{eq} = \left\{ [OH^-] - [H^+] \right\} + \left\{ [HCO_3^-] + 2[CO_3^{2-}] \right\} + \left\{ [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] \right\} + \left\{ [B(OH)_4^-] \right\} + \left\{ [Si(OH)_3^-] \right\} - [HSO_4^-] - [HF]$$

where Alk_{eq} is total alkalinity [eq/L], and the terms in braces represent water alkalinity Alk_{water} , carbonate alkalinity Alk_{CO_3} , phosphate alkalinity Alk_{PO_4} , borate alkalinity Alk_B , and silicate alkalinity Alk_{Si} , respectively. Note that alkalinity is expressed in units of eq/L for the internal calculations. For input of initial and boundary conditions, and for output of simulated concentrations, alkalinity is expressed in mass units [mg CaCO₃/L]. The two units are related by the molar ratio of 50450 [mg CaCO₃/eq].

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

Equation 35

$$f([H^+]) = Alk_{water} + Alk_{CO_3} + Alk_{PO_4} + Alk_B + Alk_{Si} - Alk_{eq} - [HSO_4^-] - [HF]$$

3.1.3 Output pH

The calculated value of $[H^+]$ is used to calculate p[H]:

Equation 36

$$p[H] = -\log_{10}[H^+]$$

where p[H] is based on the molar scale. This scale does not exactly conform to pH measurements, which take into account ionic interactions among constituents. Different pH scales are being used. WASP allows the user to select one of four scales for input and output of pH:

1. Total scale [mol/kg-SW]
2. Seawater scale [mol/kg-SW]
3. Free scale [mol/kg-SW]
4. NBS scale [mol/kg-H₂O]

To calculate pH at the selected scale, the molar concentration of H^+ is first converted to moles/kg solution (water plus solutes):

Equation 37

$$\{H\} = [H^+] / \rho_w$$

Note that this is not the same as molal concentration, which has units of moles/kg solvent (water excluding solutes). Different expressions for H^+ are given by:

Equation 38

$$H_{\text{total}} = \{H\} \times \left(\frac{1 + TS/K_S}{1 + TS/K_S + TF/K_F} \right)$$

Equation 39

$$H_{\text{sws}} = \{H\}$$

Equation 40

$$H_{\text{free}} = \frac{\{H\}}{1 + TS/K_S + TF/K_F}$$

Equation 41

$$H_{\text{actual}} = \{H\} \times f_H$$

Finally, output pH on the user-selected scale is given by:

Equation 42

$$\text{pH} = -\log_{10}(H_x)$$

where H_x is H_{total} , H_{sws} , H_{free} , or H_{actual} depending on which pH scale is selected. The default option is 2, seawater scale.

3.2 Total Inorganic Carbon Kinetics

Within each segment, total inorganic carbon increases or decreases in response to several kinetic processes. The kinetic derivative, S_{TIC} [$\text{gC}/\text{m}^3\text{-day}$], increases with CBOD oxidation and plant respiration and decreases with plant photosynthesis. CO_2 can be gained or lost via reaeration:

Equation 43

$$S_{TIC} = S_{CO_2,r} + S_{CO_2,dam} + \frac{12}{32} S_{CBOD} - S_{P-Phyt} + S_{R-Phyt} - S_{P-Peri} + S_{R-Peri}$$

where $S_{CO_2,r}$ is reaeration source [$\text{gC}/\text{m}^3\text{-day}$], $S_{CO_2,dam}$ is dam overflow source [$\text{gC}/\text{m}^3\text{-day}$], S_{CBOD} is total CBOD oxidation [$\text{gO}_2/\text{m}^3\text{-day}$], $12/32$ is [gC/gO_2], S_{P-Phyt} is phytoplankton photosynthesis [$\text{gC}/\text{m}^3\text{-day}$], S_{R-Phyt} is phytoplankton respiration [$\text{gC}/\text{m}^3\text{-day}$], S_{P-Peri} is bottom algae (periphyton) photosynthesis [$\text{gC}/\text{m}^3\text{-day}$], and S_{R-Peri} is bottom algae respiration [$\text{gC}/\text{m}^3\text{-day}$]. Values for the CBOD, phytoplankton, and benthic algae source and sink terms are

calculated in their respective subroutines and passed into the inorganic carbon subroutine. The reaeration and dam overflow net source terms are treated in the following sections.

3.2.1 Carbon Dioxide Reaeration

Reaeration is a source or a sink of TIC depending on whether the water is undersaturated or oversaturated with CO₂:

Equation 44

$$S_{CO_2,r} = k_{ac} D_{CO_2} \times 12011$$

where k_{ac} is the temperature-dependent carbon dioxide reaeration coefficient [day⁻¹], D_{CO_2} is the carbon dioxide deficit [mol C/L], 12.011 is molecular weight [gC/mol C], and 1000 is [L/m³].

The CO₂ reaeration coefficient can be computed from the temperature-corrected oxygen reaeration rate constant:

Equation 45

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

Values for k_a are calculated in the DO subroutine and passed to the inorganic carbon subroutine for use in this equation.

The CO₂ deficit is given by:

Equation 46

$$D_{CO_2} = [CO_2]_{sat} - [H_2CO_3^*]$$

where $[CO_2]_{sat}$ is the saturation concentration of carbon dioxide [mol C/L], which is computed with Henry's law:

Equation 47

$$[CO_2]_{sat} = K_H p_{CO_2} f_{CO_2}$$

where K_H is Henry's constant [(mol C/L) / atm], p_{CO_2} is the partial pressure of carbon dioxide in the atmosphere [atm], and f_{CO_2} is the fugacity of carbon dioxide in the atmosphere. Note that the partial pressure can be input as a constant or as an environmental time function. The value of K_H is computed as a function of temperature (Edmond and Gieskes 1970):

Equation 48

$$\ln K_H = -\frac{2385.73}{T_a} - 0.0152642 T_a + 14.0184$$

The partial pressure of CO₂ in the atmosphere has been increasing, largely due to the combustion of fossil fuels (Figure 2). Values in 2007 were approximately 10^{-3.416} atm (= 383.7 ppm).

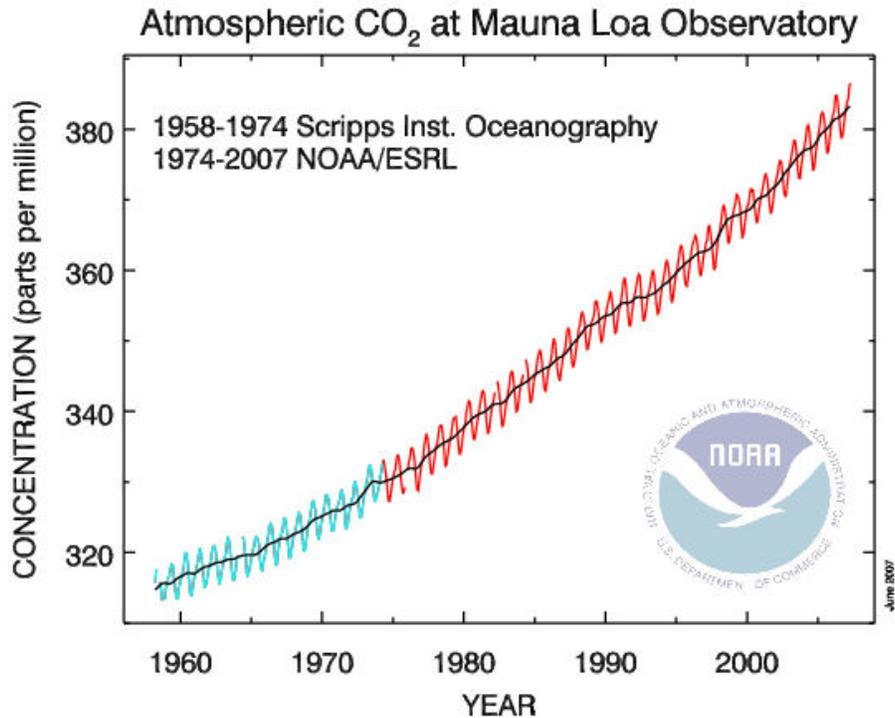


Figure 2 Concentration of carbon dioxide in the atmosphere as recorded at Mauna Loa Observatory, Hawaii.

3.2.2 Effect of Low-Head Dams

As was the case for dissolved oxygen, carbon dioxide gas transfer in streams can be influenced by the presence of control structures, such as low-head dams or weirs. Following the approach used in QUAL2K, WASP assumes that carbon dioxide behaves similarly to dissolved oxygen. From Butts and Evans (1983), the ratio of the DO deficit above and below the dam, r_d , is given by:

Equation 49

$$r_d = D_j / D_i = 1 + 0.38 a_d b_d H_d (1 - 0.11 H_d) (1 + 0.046 T_w)$$

where D_j and D_i are the DO deficits above and below the dam [mg/L], H_d is the difference in water elevation above and below the dam [m], T_w is water temperature [°C] and a_d and b_d are coefficients that correct for water-quality and dam-type. Typical values are given in Table 1.

Table 1 Coefficient values used to predict the effect of dams on stream reaeration.

(a) Water-quality coefficient		(b) Dam-type coefficient	
Polluted state	a_d	Dam type	b_d
Gross	0.65	Flat broad-crested regular step	0.70

Moderate	1.0
Slight	1.6
Clean	1.8

Flat broad-crested irregular step	0.80
Flat broad-crested vertical face	0.60
Flat broad-crested straight-slope face	0.75
Flat broad-crested curved face	0.45
Round broad-crested curved face	0.75
Sharp-crested straight-slope face	1.00
Sharp-crested vertical face	0.80
Sluice gates	0.05

The CO₂ loading introduced by the control structure is:

Equation 50

$$L_{CO_2,d} = Q_j (D_{CO_2,j} - D_{CO_2,i}) \times 86400 \times 1000$$

where $L_{CO_2,d}$ is the loading [mol C/day], $D_{CO_2,i}$ and $D_{CO_2,j}$ are the CO₂ deficits above and below the dam [mol C/L], Q_j is the flow over the structure [m³/sec], 86400 is [sec/day], and 1000 is [L/m³]. Substituting Equation 49 into Equation 50 and grouping terms, the CO₂ source term for dam reaeration is:

Equation 51

$$S_{CO_2,dam} = D_{CO_2,j} \left(\frac{Q_j \times 86400}{V_i} \right) \left(\frac{r_d - 1}{r_d} \right) \times 12.011 \times 1000$$

where $S_{CO_2,dam}$ is the dam reaeration source term for downstream segment i [gC/m³-day], V_i is the volume for for downstream segment i [m³], and 12.011 is molecular weight [gC/mol C], and 1000 is [L/m³].

3.2.3 Initial and Boundary Concentrations

In WASP, the user does not directly specify initial concentrations and boundary concentrations for TIC. WASP calculates initial and boundary concentrations for TIC based on specified initial and boundary values for pH and alkalinity. First, WASP calculates [H⁺] from pH using Equation 37 through Equation 42 along with segment temperature, salinity (or TDS) and pressure (depth). Next, WASP uses [H⁺] along with alkalinity, substituting Equation 21, Equation 28, and Equation 29 into Equation 32 (ignoring the phosphate terms), and solving for TIC_{mol} :

Equation 52

$$TIC_{mol} = \frac{Alk_{eq} + H^+ - \frac{K_w}{H^+}}{\alpha_1 + 2\alpha_2}$$

Finally initial and boundary concentrations of TIC are expressed in [mgC/L]:

Equation 53

$$TIC = TIC_{mol} \times 12.011 \times 1000$$

where 12.011 is molecular weight of carbon [gC/mol] and 1000 is [mg/g].

3.3 Alkalinity Kinetics

Within each segment, alkalinity increases or decreases in response to several kinetic processes. The kinetic derivative, S_{ALK} [gCaCO₃/m³-day], increases with the addition of positive ions such as NH₄⁺, which causes a decline in H⁺ and an increase in OH⁻ to maintain electro-neutrality. The subtraction of positive ions causes a decrease in S_{ALK} by forcing an increase in H⁺ and a decrease in OH⁻ to maintain electro-neutrality. Conversely the subtraction of negative ions such as HPO₄⁻ causes a decline in H⁺ and an increase in OH⁻, and thus an increase in S_{ALK} . The addition of negative ions causes an increase in H⁺ and a decrease in OH⁻, leading to a decrease in S_{ALK} . The alkalinity kinetic equation in WASP is:

Equation 54

$$S_{ALK} = \left(\begin{array}{l} -\frac{2}{14.007} S_{NH_4, nitr} + \frac{2}{14.007} S_{NO_3, denit} + \frac{f_{NH_4}}{14.007} S_{ON, h} - \frac{\alpha_p}{30.974} S_{OR, h} \\ + \frac{f_{NH_4}}{14.007} S_{NH_4, atm} - \frac{1}{14.007} S_{NO_3, atm} - \frac{\alpha_p}{30.974} S_{PO_4, atm} \\ + \frac{f_{NH_4}}{14.007} S_{NH_4, sed} - \frac{\alpha_p}{30.974} S_{PO_4, atm} \\ - \frac{1}{14.007} S_{NH_4, phytP} + \frac{1}{14.007} S_{NO_3, phytP} + \frac{\alpha_p}{30.974} S_{PO_4, phytP} \\ + \frac{f_{NH_4}}{14.007} S_{NH_4, phytR} - \frac{\alpha_p}{30.974} S_{PO_4, phytR} \\ - \frac{1}{14.007} S_{NH_4, ba1gP} + \frac{1}{14.007} S_{NO_3, ba1gP} + \frac{\alpha_p}{30.974} S_{PO_4, ba1gP} \\ + \frac{f_{NH_4}}{14.007} S_{NH_4, ba1gR} - \frac{\alpha_p}{30.974} S_{PO_4, ba1gR} \end{array} \right) \times 50.450$$

where 50.450 is [moles CaCO₃/eq]. The first line includes biogeochemical reactions. The second and third lines are atmospheric deposition and sediment flux. The fourth and fifth lines are phytoplankton growth and respiration. The sixth and seventh lines are bottom algae uptake and excretion. Specific terms in Equation 54 are explained in the paragraphs below. Values for the source and sink terms are calculated in their respective subroutines and passed into the inorganic carbon subroutine. The term f_{NH_4} , the fraction of total ammonia as ammonium (Equation 30), is equal to the average charge associated with a mole of total ammonia [eq/mole NH₃+NH₄]. The

term α_P is the average charge associated with a mole of total phosphate [eq/mole PO₄], and is given by:

Equation 55

$$\alpha_P = \alpha_{H_2PO_4} + 2\alpha_{HPO_4} + 3\alpha_{PO_4}$$

where $\alpha_{H_2PO_4}$, α_{HPO_4} , and α_{PO_4} are the fractions of total phosphate by species as calculated in Equation 27, Equation 28, and Equation 29.

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

3.3.1 Biochemical Reactions

Four biochemical reactions are represented in the first line of Equation 54 – nitrification, denitrification, hydrolysis of organic nitrogen, and hydrolysis of organic phosphorus.

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. $S_{NH_4,nitr}$ is NH₄ nitrification [gNH₄-N/m³-day], calculated in Subroutine N-Cycle and passed to the alkalinity routines.

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. $S_{NO_3,denit}$ is NO₃ denitrification [gNO₃-N/m³-day], calculated in Subroutine N-Cycle and passed to the alkalinity routines..

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. $S_{ON,h}$ is ON hydrolysis [gN/m³-day], calculated in Subroutine N-Cycle and passed to the alkalinity routines.

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. $S_{OP,h}$ is OP hydrolysis [gP/m³-day], calculated in Subroutine P-Cycle and passed to the alkalinity routines.

3.3.2 Intermedia Loading

Five intermedia transfer reactions are represented in lines 2 and 3 of Equation 54 – atmospheric deposition of total ammonia, nitrate, and phosphate, and sediment flux of total ammonia and phosphate.

Atmospheric deposition and sediment flux of total ammonia add NH_4^+ to the water. The positive ions increase the alkalinity by one equivalent per mole. Constant atmospheric deposition and variable sediment fluxes of total ammonia specified in the model input are converted to source terms $S_{\text{NH}_4,\text{atm}}$ and $S_{\text{NH}_4,\text{sed}}$ [$\text{gN}/\text{m}^3\text{-day}$] in Subroutine N-Cycle and passed to the alkalinity routines.

Atmospheric deposition of nitrate adds negative ions to the water, decreasing the alkalinity by one equivalent per mole. Constant atmospheric deposition of nitrate specified in the model input is converted to source term $S_{\text{NO}_3,\text{atm}}$ [$\text{gN}/\text{m}^3\text{-day}$] in Subroutine N-Cycle and passed to the alkalinity routines.

Atmospheric deposition and sediment flux of total phosphate add negative ions to the water, decreasing the alkalinity by 1 or 2 equivalents per mole. Constant atmospheric deposition and variable sediment fluxes of total phosphate specified in the model input are converted to source terms $S_{\text{PO}_4,\text{atm}}$ and $S_{\text{PO}_4,\text{sed}}$ [$\text{gP}/\text{m}^3\text{-day}$] in Subroutine P-Cycle and passed to the alkalinity routines.

3.3.3 Algal Reactions

Phytoplankton photosynthesis and respiration reactions are represented in lines 4 and 5 of Equation 54. Bottom algal uptake and excretion reactions are represented in lines 6 and 7.

Phytoplankton photosynthesis takes up nitrogen as either ammonia or nitrate and phosphorus as inorganic phosphate. The uptake of ammonium-N removes positive ions from solution, causing a decrease of alkalinity by 1 eq/mole. The uptake of nitrate-N removes negative ions from solution, causing an increase of alkalinity by 1 eq/mole. Similarly, the uptake of phosphate-P removes negative ions from solution, causing an increase of alkalinity by 1 to 2 eq/mole, depending on the pH. If ammonia is the primary nitrogen source, photosynthesis 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, photosynthesis leads to an increase in alkalinity because both nitrate and phosphate are negatively charged. The source terms $S_{\text{NH}_4,\text{phytP}}$ [$\text{gNH}_4\text{-N}/\text{m}^3\text{-day}$] and $S_{\text{NO}_3,\text{phytP}}$ [$\text{gNO}_3\text{-N}/\text{m}^3\text{-day}$] are accumulated in Subroutine N-Cycle for all three species of phytoplankton and passed to the alkalinity routines. Similarly, the source term $S_{\text{PO}_4,\text{phytP}}$ [$\text{gPO}_4\text{-P}/\text{m}^3\text{-day}$] is calculated in Subroutine P-Cycle for all three species of phytoplankton and passed to the alkalinity routines.

Phytoplankton respiration and death release ammonia and inorganic phosphate. The excretion of ammonium-N adds positive ions to the water, causing an increase of alkalinity by 1 eq/mole. The excretion of phosphate-P adds negative ions to the water, causing a decrease of alkalinity by 1 to 2 eq/mole depending on pH. The source terms $S_{NH_4,phytR}$ [gNH₄-N/m³-day] and $S_{PO_4,phytR}$ [gPO₄-P/m³-day] are calculated in Subroutines N-Cycle and P-Cycle for all three species of phytoplankton and passed to the alkalinity routines.

To support photosynthesis, bottom algae take up nitrogen as either ammonia or nitrate and phosphorus as inorganic phosphate. The uptake of ammonium-N removes positive ions from solution, causing a decrease of alkalinity by 1 eq/mole. The uptake of nitrate-N removes negative ions from solution, causing an increase of alkalinity by 1 eq/mole. Similarly, the uptake of phosphate-P removes negative ions from solution, causing an increase of alkalinity by 1 to 2 eq/mole depending on the pH. The source terms $S_{NH_4,balgP}$ [gNH₄-N/m³-day] and $S_{NO_3,balgP}$ [gNO₃-N/m³-day] is calculated in Subroutine N-Cycle and passed to the alkalinity routines. Similarly, the source term $S_{PO_4,balgP}$ [gPO₄-P/m³-day] is calculated in Subroutine P-Cycle and passed to the alkalinity routines.

With respiration and death, bottom algae excrete ammonia and inorganic phosphate. The excretion of ammonium-N adds positive ions to the water, causing an increase of alkalinity by 1 eq/mole. The excretion of phosphate-P adds negative ions to the water, causing a decrease of alkalinity by 1 to 2 eq/mole depending on pH. The source terms $S_{NH_4,balgR}$ [gNH₄-N/m³-day] and $S_{PO_4,balgR}$ [gPO₄-P/m³-day] are calculated in Subroutines N-Cycle and P-Cycle and passed to the alkalinity routines.

4 Model Inputs and Outputs

The data inputs required to support the application of the advanced eutrophication model to predict pH are described in this section.

4.1 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 should set their simulation option to Bypass if pH calculations are not needed (Figure 3).

	System	Option	Particulate	Mass	Dispersion	Flow
			Transport Field	Balance	Bypass	Bypass
17	Salinity (PSU) or TDS (mg/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
18	Benthic Algae (g-DW/m2)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
19	Periphyton Cell Quota Nitrogen	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
20	Periphyton Cell Quota Phosphoc	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
21	Inorganic Solids 1 (mg-DW/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
22	Inorganic Solids 2 (mg-DW/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
23	Inorganic Solids 3 (mg-DW/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
24	Phytoplankton 1 (ug-Chla/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
25	Phytoplankton 2 (ug-Chla/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
26	Phytoplankton 3 (ug-Chla/L)	Bypassed	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
27	pH (su)	Simulated	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
28	Alkalinity (CaCO3 mg/l)	Simulated	Solids 1	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Figure 3 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.

4.2 Time Functions

Figure 4 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 4.3, 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.

	Time Function	Used	Interpolation
	Zooplankton Population (count)	<input type="checkbox"/>	Linear
	Reaeration Function (per day)	<input type="checkbox"/>	Linear
	Settling rate for algal group 1 (m/day)	<input type="checkbox"/>	Linear
	Settling rate for algal group 2 (m/day)	<input type="checkbox"/>	Linear
	Settling rate for algal group 3 (m/day)	<input type="checkbox"/>	Linear
▶	CO2 Atmospheric Partial Pressure (Atmospheres)	<input checked="" type="checkbox"/>	Linear

Time/value pairs for CO2 Atmospheric Partial Pressure (Atmospheres)			
	Date	Time	Value
1	1/ 1/1960	0:00	3.1597E-4
2	1/ 1/1960	6:00	3.1597E-4
3	1/ 1/1960	12:00	3.16E-4
4	1/ 1/2010	0:00	3.85E-4
5	2/ 1/2010	0:00	3.85E-4

Figure 4 Time Function for CO2 Atmospheric Partial Pressure

4.3 Constants

Four new constants were created in the “Globals” constants group for the pH calculations (Figure 5). To access this menu, the user must select “Constants” from the main menu and then “Globals” from the Constant Group drop-down pick list. In addition to specifying values for the constants, the user must check the “Used” radio button for the interface to send this information to the model. If a time function as described in Section 4.2 provides data for CO₂ atmospheric partial pressure it supersedes the value specified here.

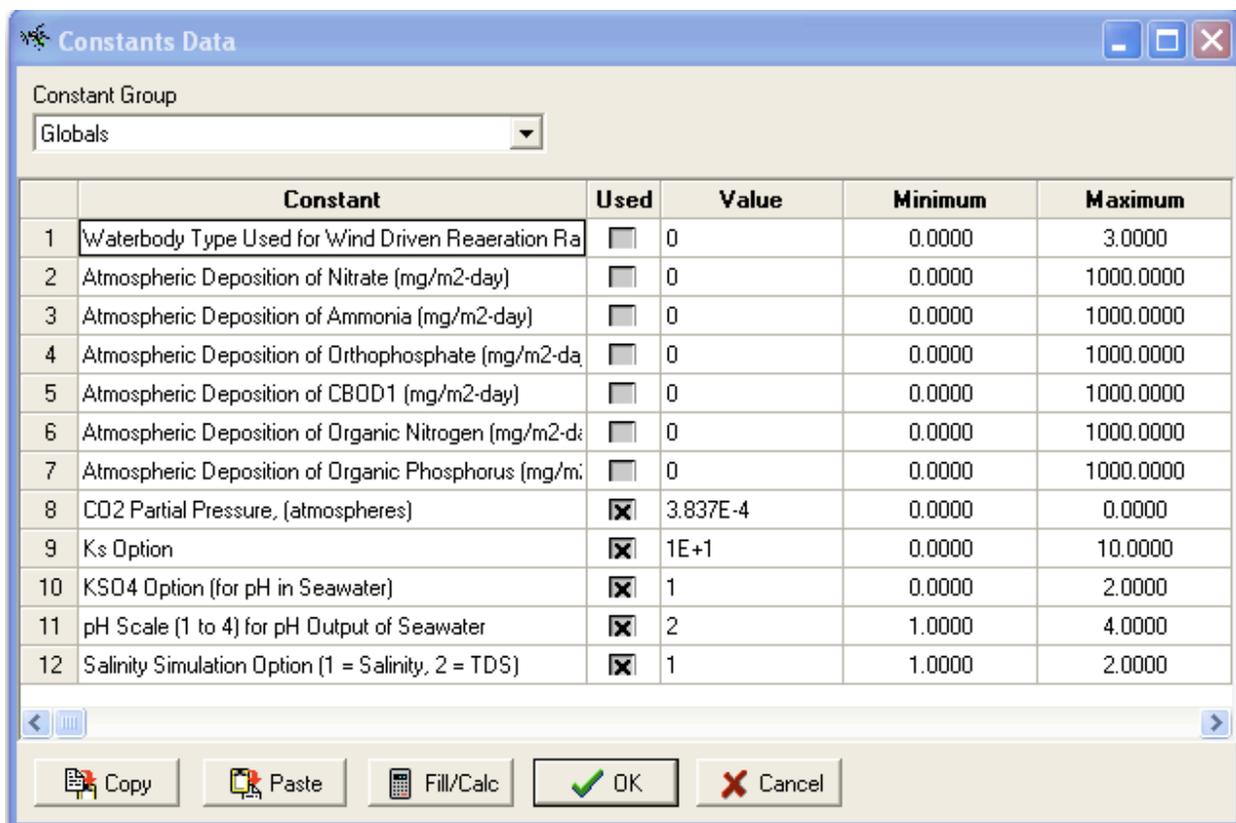


Figure 5 Constants for pH calculations

CO₂ Partial Pressure – a constant value for CO₂ atmospheric partial pressure can be specified. This value will be used if the time function for CO₂ atmospheric partial pressure is not specified. A default value of 0.003715 [atm], characteristic of average 2003 conditions, is assumed if the time function and this constant are not specified.

Ks Option – this constant determines which of ten approaches will be used to calculate pH constants in marine or estuarine systems where salinity exceeds 0.5 ppt. These options are equivalent to CO2SYS. The default is option 10, which is used if this constant is not set.

1. K1, K2 from Roy et al. (1993)
2. K1, K2 from Goyet and Poisson (1989)
3. K1, K2 from Hansson (1973a, 1973b), refit by Dickson and Millero (1987)
4. K1, K2 from Mehrbach et al. (1973), refit by Dickson and Millero (1987)
5. K1, K2 from Hansson/Mehrbach data, refit by Dickson and Millero (1987)
6. GEOSECS Constants from Takahashi et al. (1982) (NBS scale); K1, K2 from Mehrbach et al. (1973)
7. Constants from Peng et al. (1987) (NBS Scale); K1, K2 from Mehrbach et al., (1973)

8. K1, K2 from Millero (1979) for freshwater systems
9. K1, K2 from Cal and Wang (1998) for estuarine systems
10. K1, K2 from Milero et al. (2006) for most estuarine and marine waters

Option 1 is recommended. The values are valid in most estuarine and marine waters for salinities from 0 to 50 psu, and for temperatures from 0 to 50 C.

KSO4 Option – this constant determines which of two approaches will be used to calculate the constant controlling SO₄ speciation in marine or estuarine systems where salinity exceeds 0.5 ppt. The default is option 1, which is used if this constant is not set.

1. KSO4 from Dickson (1990)
2. KSO4 from Khoo et al. (1977)

Option 1 is recommended in CO2SYS. The values of KSO₄ from Khoo et al. are 15% - 45% lower than those from Dickson, depending mostly on temperature.

pH Option – this constant selects the pH scale for output (log mol/kg units. The default is option 2 (seawater scale), which is used if this constant is not set.

1. Total scale (mol/kg-SW)
2. Seawater scale (mol/kg-SW)
3. Free scale (mol/kg-SW)
4. NBS scale (mol/kg-water)

Salinity-TDS Option – this constant determines whether salinity or TDS is simulated. The default is option 1 (simulate salinity), which is used if this constant is not set. If salinity is simulated, TDS is derived from salinity concentration. Initial concentrations and boundary concentrations should be specified as salinity in units of psu. If TDS is simulated, salinity is derived from TDS concentration. Initial concentrations and boundary concentrations should be specified as TDS in units of mg/L.

1. Simulate salinity (psu)
2. Simulate TDS (mg/L)

4.4 Model Outputs

When WASP is run, a binary model output data file (*.bmd) is generated containing the values of output variables for all segments and output times. Output variables from the pH/alkalinity and total inorganic carbon calculation in the advanced eutrophication module are listed in Figure 6. In addition to the two new state variables – total inorganic carbon [mg C/L] and alkalinity [mg CaCO₃/L] – new calculated variables are included: water density [kg/L], pH (molar), and pH (selected scale). Two previous state variables – total ammonia [mg N/L] and salinity [kg/L] –

are supplemented with new output variables: un-ionized ammonia [mg N/L], and salinity expressed in practical salinity units [PSU]. Variables checked in the “Output” box will be included in the bmd file 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.

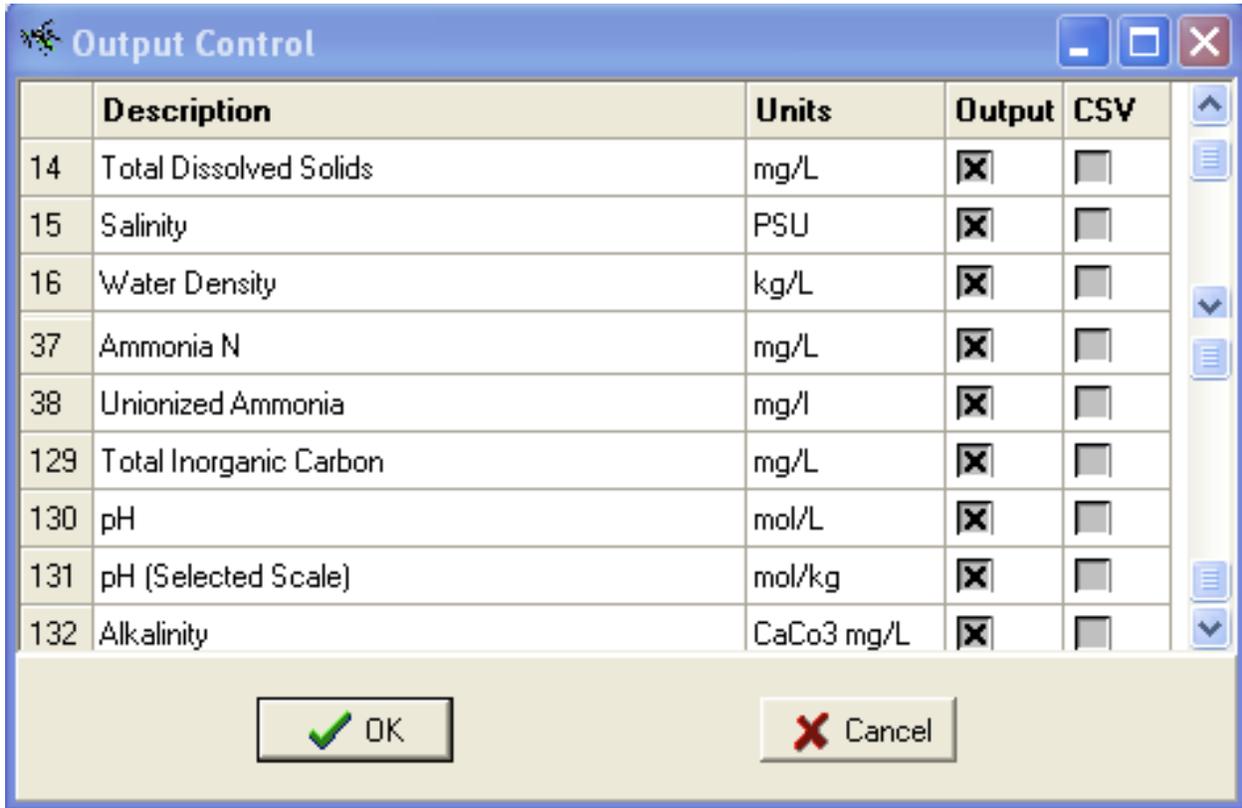


Figure 6 WASP Output Variables for pH Calculation

When WASP is run, an ASCII output file is generated (*.out) with tables of input data, intermediate calculations, warning and error messages, and limited output. New output tables added to the Advanced Eutrophication module include Adjusted Initial Conditions, Initial K Array for Calculating pH, and Final Output Variables. The Adjusted Initial Conditions table gives initial variable values by segment, adjusted for changes in units. These include total inorganic carbon in mgC/L (calculated from initial pH and alkalinity), pH adjusted to selected pH units, salinity in psu, water density in kg/L, and average segment pressure depth, in m. The Initial K Array table gives initial equilibrium constant values by segment, adjusted for initial temperature, salinity, and pressure. The Final Output Variables table gives output variable values (to 7 significant figures) by segment for the final simulation time step. This table will be generated only if the user selects File-Preferences-Diagnostics-Moderate from the WASP user interface (Figure 7).

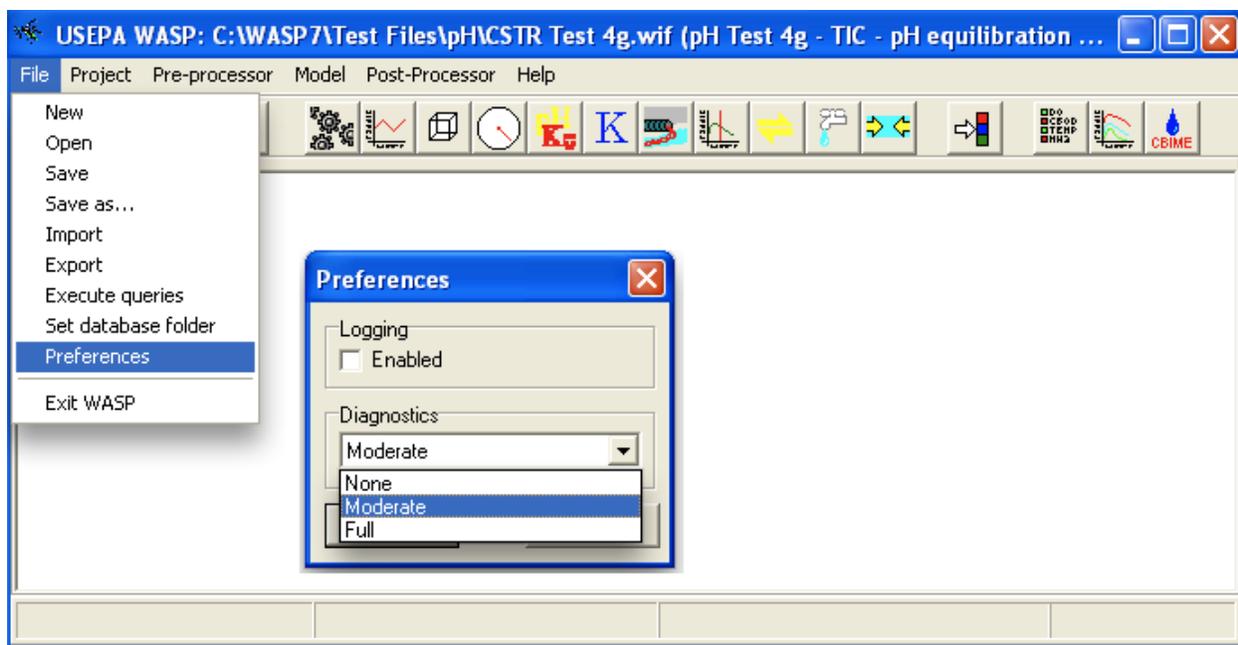


Figure 7 Selecting WASP diagnostic preference

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APPENDIX MATERIAL