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Approach for Simulating Acidification and the Carbon Cycle in the Salish Sea to Distinguish Regional Source Impacts

by

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Abstract

Several monitoring programs indicate declining pH in the marine waters of the Pacific Northwest. Global atmospheric carbon dioxide levels have been identified as the dominant contributor. However, a question that cannot be answered with available information is the degree to which regional human contributions exacerbate low levels of pH and aragonite saturation state. Aragonite is the form of calcium carbonate used in many shell-building organisms. If aragonite saturation state is low or undersaturated, organisms may not be able to build shells, which would have a cascade of impacts to the food web. Recent model development has quantified the relative impacts of regional human nutrient sources on dissolved oxygen in the Salish Sea.

The purpose of this document is to describe the approach that could be used to (1) expand the existing Salish Sea model to evaluate pH and aragonite saturation state and (2) quantify the relative influences of regional and global sources. This would include simulating total dissolved inorganic carbon and alkalinity as state variables including source/sink terms related to air-sea exchange, respiration, photosynthesis, nutrient gains and losses, sediment fluxes, and boundary conditions. Boundary conditions would account for both Pacific Ocean upwelled water and regional contributions.

This approach document also identifies critical information gaps that should be considered in acidification modeling programs. We recommend an iterative approach that evaluates relative impacts using available information. A critical component will be to identify what processes are most influential and the level of uncertainty in the results.

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[1] National Oceanic and Atmospheric Administration

1.0 Introduction

Several monitoring programs indicate declining pH in the marine waters of the Pacific Northwest. Global atmospheric carbon dioxide levels have been identified as the dominant contributor. The decline in pH also reduces the saturation state of aragonite and calcite forms of calcium carbonate. Aragonite is the form of calcium carbonate used in many shell-building organisms. If aragonite saturation state is low or undersaturated, organisms may not be able to build shells, which would have a cascade of impacts to the food web.

Pacific Northwest National Laboratory (PNNL) in collaboration with Washington State Department of Ecology (Ecology) and U.S. Environmental Protection Agency (EPA) have developed a circulation and water quality model of the Salish Sea ecosystem. The goal is to understand circulation and annual biogeochemical cycles in the system to distinguish the relative impacts from local human sources (Khangaonkar et al., 2012; Khangaonkar et al., 2011). This work was primarily driven by the regulatory question as to whether nutrient pollution from rivers, nonpoint source runoff, and nearly 100 wastewater discharges are potential threats to the ecological health of Puget Sound and the Salish Sea. Roberts et al. (2014) evaluates the relative influence of local nutrient sources, climate change, and Pacific Ocean trends on dissolved oxygen (DO) in the Salish Sea now and through 2070.

While low DO levels have been a water quality concern, a new concern was identified recently through its impacts to the shellfish industry. Between 2005 and 2009 there were significant production failures at the Pacific Northwest oyster hatcheries, and exposure to waters with low pH and low aragonite saturation was identified as the cause. Aragonite is a form of calcium carbonate used by shell-forming organisms. Acidifying waters with a low aragonite saturation state ($\Omega_{arag} < 1$) can prevent shell-formation and can dissolve shell materials in marine organisms such as oysters (Washington State Blue Ribbon Panel on Ocean Acidification, 2012).

The Blue Ribbon Panel of scientists, tribes, and shellfish managers appointed by Governor Christine Gregoire made several recommendations for future research, monitoring, and actions to understand, prevent or mitigate, and adapt to acidification of Washington State marine waters. The panel recommended efforts to quantify how much regional human sources (water nutrients and air emissions) exacerbate the effects of the Pacific Ocean and global atmospheric carbon dioxide. Task 7.2.1 directs Ecology to lead this work (www.ecy.wa.gov/water/marine/oceanacidification.html). A related modeling effort currently underway at the University of Washington will provide a forecasting tool that can be used by the shellfish industry and others affected by acidic conditions (Task 7.4.1). The two model approaches are complementary; the forecasting tool does not distinguish the relative impacts of local sources.

This document summarizes the initial approach recommended to simulate the relative impacts of regional human sources on acidification. No funds have been identified to date to implement this modeling. However, EPA's National Estuary Program funded Ecology through the Toxics and Nutrients Lead Organization grant process to develop this initial approach document for adding acidification processes to the DO model.

The processes that influence DO also affect pH and aragonite saturation. The existing model of the Salish Sea, including both Puget Sound and the Georgia Basin, conducts carbon-based biogeochemical simulations and is well suited for incorporating acidification kinetics. Additional software development, testing, and calibration using Salish Sea monitoring data will ensure proper simulation and mass balance of a carbonate cycle. Because modeling acidification in estuarine waters such as Puget Sound and the Georgia Basin is relatively new, PNNL, Ecology, and EPA have initiated a collaborative process with scientists specializing in ocean acidification to develop an approach and framework that is scientifically valid and useful. This report is a part of that effort and presents an approach for simulating acidification and the carbon cycle in the Salish Sea. This first step is a precursor to a Quality Assurance (QA) Project Plan that would be developed prior to the initiating model development.

1.1 Why model pH and aragonite saturation?

The primary cause of ocean acidification has been identified as the uptake of atmospheric carbon dioxide by the ocean. Increase in atmospheric carbon dioxide concentrations over the last 250 years has resulted in a reduction in pH approximately from 8.2 to 8.1 (about 30% increase in acidity) with a projected further reduction by 0.2-0.3 units by the end of this century (Caldeira and Wickett, 2005). While this is a global problem, Washington coastal resources are particularly vulnerable as oceanographic and meteorological conditions along the coast often create upwelling events bringing deep water rich in carbon dioxide and low in pH to the surface (Feely et al., 2008). The seawater with low pH and low aragonite saturation has been observed off the Oregon coast during upwelling events and has been identified as the primary cause impacting oyster fisheries in Washington State.

Regional factors have the potential to exacerbate the acidification problem. These include runoff of nutrients and organic carbon (such as plants and freshwater algae) from land as well as local emissions of carbon dioxide, nitrogen oxides, and sulfur oxides.

Biogeochemical processes such as algal growth and die-off affect total inorganic carbon in the water column and therefore impact pH and aragonite saturation. Surface waters in some areas of Puget Sound are almost completely depleted of surface nutrients during the spring and summer algae blooms. Discharge of regional human nutrient sources into the Salish Sea could increase algal productivity. High levels of algae during the day lead to super-saturated DO levels. The same algae during the night produce carbon dioxide through respiration resulting in reduction in pH (Feely et al., 2010, King County 2012). At the conclusions of the spring and summer blooms, algae die, decay and settle to sediments leading to conditions favorable for developing hypoxia. The decaying algae also release large amounts of inorganic carbon back to the water column.

The air-sea exchange of carbon dioxide is affected by the partial pressure of atmospheric carbon dioxide over marine waters. Local carbon dioxide emissions can influence these partial pressures and reduce the off gassing of marine water carbon dioxide. Nitrogen and sulfur oxides are acids that can be deposited from air pollution. Air pollution also represents a potential source of human nitrogen to the marine environment.

While low pH may inhibit some marine organisms, shell-forming organisms are most sensitive to aragonite saturation. If the saturation state is greater than 1, aragonite can be used for shells. However, if the saturation state is below 1, then seawater would dissolve shells containing aragonite or would prevent shells from forming. Aragonite saturation state is highly influenced by pH.

The purpose of this investigation is to simulate acidification parameters under current conditions and to distinguish how much of that signal results from regional human sources. Results could be used to prioritize management actions to control nutrient releases and air emissions. The Pacific Ocean and global atmospheric carbon dioxide are expected to have the greatest influence, as they appear to form DO (Roberts et al., 2014). However, identifying where and how much regional sources add to acidification is a first step in effective regional source management.

1.2 pH scales in seawater

"pH" is an abbreviation for *pondus hydrogenii* in Danish, and it means the weight of hydrogen (Sørensen, 1909). In modern aquatic chemistry, pH is used to describe the activity of the proton ion H^+. H^+ is one of the most important species in a surface water system, as it reacts with almost all other ions in the water. Hence H^+ is sometimes also called the master variable in an aquatic system. Rigorous definition of pH is

$$pH = -log_{10} a_{H^+} \tag{1}$$

where a_{H^+} is the activity (effective concentration) of proton (hydrogen ion) H^+. For a dilute aqueous solution, a_{H^+} is approximately the same as concentration of H^+, or $[H^+]$, with [ ] symbolizing concentration (unit: mole/liter) of a species. For natural waters, the pH is generally calculated as

$$pH \cong p[H^+] \equiv -log_{10}[H^+] \tag{2}$$

This definition of pH is also called the *free scale pH*. In seawater chemistry, pH plays an important role in the carbon cycle. Measuring the proton ion concentration $[H^+]$ in seawater is difficult due to presence of many other species such as sulfate ions SO_4^{2-}, which can be protonated (made to accept a proton) to generate hydrogen sulfate ions, HSO_4^-:

$$\mathrm{H}^+ + SO_4^{2-} \rightleftharpoons HSO_4^- . \tag{3}$$

In order to bypass the difficulty of separating HSO_4^- and H^+, the *total scale pH* was defined by Dickson (1981) as

$$pH_T = -log_{10}[H_T^+] \tag{4}$$

where $[H_T^+] = [\mathrm{H}^+](1 + C_{TS}/K_S) \cong [\mathrm{H}^+] + [HSO_4^-]$ is approximately the total concentration (mole/L) of H^+ and HSO_4^- ions when $pH \geq 4$. C_{TS} is the total concentration of sulfate and hydrogen sulfate (non-protonated and protonated together)

$$C_{TS} = [SO_4^{2-}] + [HSO_4^-], \tag{5}$$

and K_S is the equilibrium constant of the reaction $[HSO_4^-] \rightleftharpoons [H^+] + [SO_4^{2-}]$

$$K_S = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \tag{6}$$

The above approach can be expanded to include other species such as fluoride ions F^-, which are abundant in seawater and can also be protonated through the reaction

$$\mathrm{H}^+ + F^- \rightleftharpoons \mathrm{HF}, \tag{7}$$

A corresponding pH scale that includes the effect of fluoride as well as sulfate was created and is called *seawater scale pH* defined as

$$pH_{SWS} = -log_{10}[H^+_{SWS}], \tag{8}$$

where

$$[H^+_{SWS}] = [\mathrm{H}^+](1 + \frac{C_{TS}}{K_S} + \frac{C_{TF}}{K_F}) \cong [\mathrm{H}^+] + [HSO_4^-] + [HF], \tag{9}$$

with K_F the HF dissociation reaction equilibrium constant (see (56) in next subsection) and $C_{TF} = [F^-] + [\mathrm{HF}]$ is the total fluoride concentration.

In seawater, in addition to hydrogen fluoride, hydrogen sulfate, discussed above, dissociation of ammonium, phosphoric acid, boric acid, and silicic acids also play a role in determining pH. The ability of most biogeochemical and water quality models to simulate multiple species depends on the availability of data for calibration and validation. Sulfate, fluoride, and borate are not typically included in routine water column monitoring efforts. Hence in the present work, a simplifying approach is to use the free scale pH for the model development work. Total scale may be incorporated when information about $[HSO_4^-]$ and other constituents of total pH becomes available.

1.3 Overview of carbon cycle in the water column and its relationship with pH

The chemistry of carbonic acid in water involves the following carbon species: gaseous carbon dioxide $CO_2(g)$, dissolved carbon dioxide $CO_2(aq)$, dissolved carbonic acid $\mathrm{H_2CO_3}$, bicarbonate ion HCO_3^-, and carbonate ion CO_3^{2-} . The chemical reactions are expressed as

a) dissolution of carbon dioxide gas $CO_2(\mathrm{g}) + H_2\mathrm{O} \rightleftharpoons CO_2(\mathrm{aq}) + H_2\mathrm{O}$ (10)
b) formation of carbonic acid $CO_2(\mathrm{aq}) + H_2\mathrm{O} \rightleftharpoons H_2CO_3$ (11)
c) dissociation of carbonic acid $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (12)
d) dissociation of bicarbonate ion $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (13)
e) dissociation of water $H_2O \rightleftharpoons H^+ + OH^-$ (14)

Due to the fact that reaction b) is quite unstable, there is a difficulty in distinguishing between $CO_2(aq)$ and H_2CO_3. An imaginary species $CO_2^*(aq)$ is introduced to represent both of them for convenience. Reactions a) and b) may then be combined and written as one reaction

f) $CO_2(\mathrm{g}) \rightleftharpoons CO_2^*(aq)$ (15)

In an open system at steady state, the water column is in equilibrium with the atmosphere. Assuming that reaction f) is at equilibrium, with the partial pressure of $CO_2\ (g)$ in water being the same as partial pressure of CO_2 in the atmosphere (p_{CO_2}), then $CO_2^*(aq)$ is saturated in water and can be calculated from Henry's law as follows,

$$[CO^*_{2,sat}(aq)] = K_0 f(CO_2) \tag{16}$$

where K_0 (mole/L/atm) is the equilibrium constant of reaction f), also called Henry's constant or Weiss (1974) solubility constant for CO_2. $f(CO_2)$ is the fugacity (atm) of CO_2(g) in the atmosphere which is related to partial pressure of CO_2 in the atmosphere by

$$f(CO_2) = p_{CO_2}\exp\left(\frac{1}{RT}\int_0^p [V(CO_2) - RT/p']dp'\right) \tag{17}$$

where p is total pressure (atm) in atmosphere, $V(CO_2)$ is volume (L) of one mole of CO_2 gas in the atmosphere at pressure p' (atm) at given temperature T ($^\circ K$), and R is the universal gas constant. The use of fugacity $f(CO_2)$ is to account for the non-idealized gas state of CO_2 (g) in the atmosphere. In reality, the system is not at perfect steady state. The concentration of $CO_2^*(aq)$ in the water column is not in full equilibrium with the atmosphere due to variations in both the atmosphere and in the water, except in a thin layer at the surface. There will be a flux of CO_2 (g) through the air-water interface resulting in loss or gain of CO_2 (g) in the air and a gain or loss of $CO_2^*(aq)$ in the water. From the water column point of view, the source of $CO_2^*(aq)$ flux from the air can be modeled with a first order equation

$$F_{s,CO_2^*(aq)} = K_{a,CO_2^*(aq)}(CO_{2,sat}^*(aq) - CO_2^*(aq)) \tag{18}$$

where $K_{a,CO_2^*(aq)}$is the re-aeration coefficient (meter/day) for $CO_2^*(aq)$ in the water column.

Most water quality models which simulate DO kinetics include a re-aeration coefficient to properly simulate the natural recovery of oxygen in surface waters as a function of internal mixing and turbulence due to velocity gradients, wind-induced mixing, and temperature. Oxygen transfer from the atmosphere to surface waters as a function of mixing and turbulence has been the subject of much study and investigation. In practice it is common to utilize a theoretical formulation such as O'Connor and Dobbins (1958) or an empirically derived formulation such as Churchill et al. (1962). The re-aeration coefficient for oxygen may be correlated to the re-aeration coefficient for carbon dioxide (CO_2) as a ratio of their molecular weights. Using the molecular weight of oxygen O_2 as 32 g/mole, and CO_2 as 44 g/mole, the re-aeration coefficient of $CO_2^*(aq)$ can be related to re-aeration rate of oxygen through the following relationship provided by Chapra (1997)

$$K_{a,CO_2^*(aq)} = (32/44)^{1/4}K_{a,O_2} \tag{19}$$

Another important aspect of inorganic carbon chemistry in the water column is the dissolution and precipitation of aragonite and calcite forms of calcium carbonate. Both aragonite and calcite have the same molecular formula $CaCO_3$ and are different only in their crystalline structure. However, aragonite is generally more soluble and more important for biota. For simplicity we will use $CaCO_3(s)$ to denote the solid state and $CaCO_3(aq)$ for dissolved state with the assumption that we are referring to aragonite form of $CaCO_3$. $CaCO_3(s)$ is dissolved into $CaCO_3(aq)$ and undergoes a dissociation reaction to form carbonate ions CO_3^{2-} (Dreybrodt, 1980):

$$CaCO_3(s) \rightleftharpoons CaCO_3(\text{aq}) \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{20}$$

This process also affects other species of carbon and pH. Solid-state calcium carbonate $CaCO_3(s)$ exists in the form of inorganic suspended solids and shells of calcifying algae (coccolithophores) and zooplanktons (pteropods, heteropods, foraminifera) in the water column

(Findlay et al., 2009). It is also present in the form of deposits at the seabed, coral reefs and banks along coast lines. In the water column and in steady state, the dissolution equilibrium constant of reaction (19) is designated by $K_{sp\,CaCO_3}$ (Millero, 1995) which is greater for aragonite than calcite (see equation (A63) and (A64) in Appendix A), and is also a function of temperature.

$$K_{spCaCO_3} = [Ca^{2+}][CO_3^{2-}] \tag{21}$$

In addition to inorganic chemical reactions of carbon species discussed above, photosynthesis of algae, remineralization of detritus and dissolved organic matter also play important roles in carbon cycling and pH kinetics in the water column (Suzuki, 1998). Figure 1 provides an overview of the processes and pathways to consider while Figure 2 provides a schematic representation of the integrated inorganic and organic carbon cycle with pathways to biogeochemical processes.

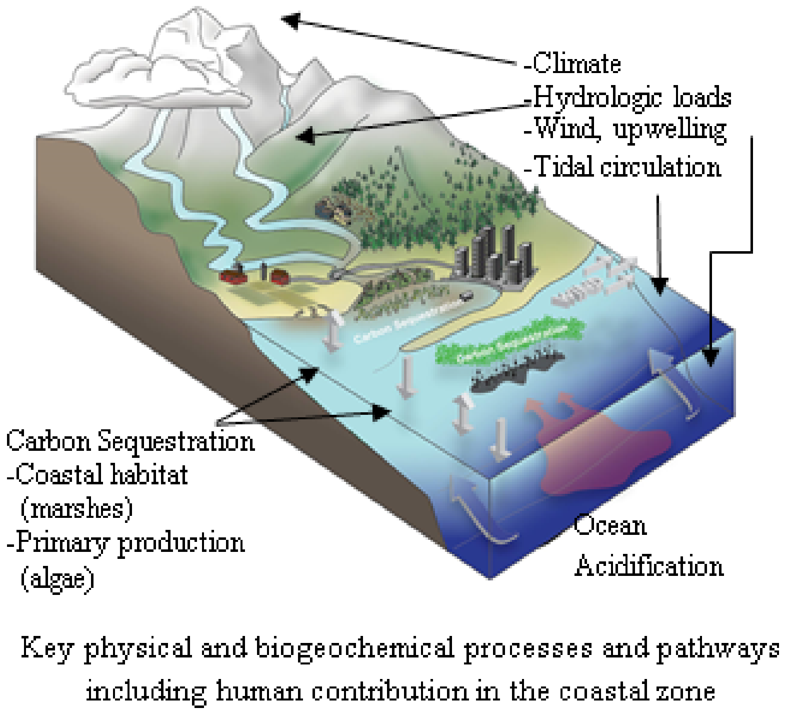

Figure 1. Key physical and biogeochemical processes and pathways including human contributions in the coastal zone.

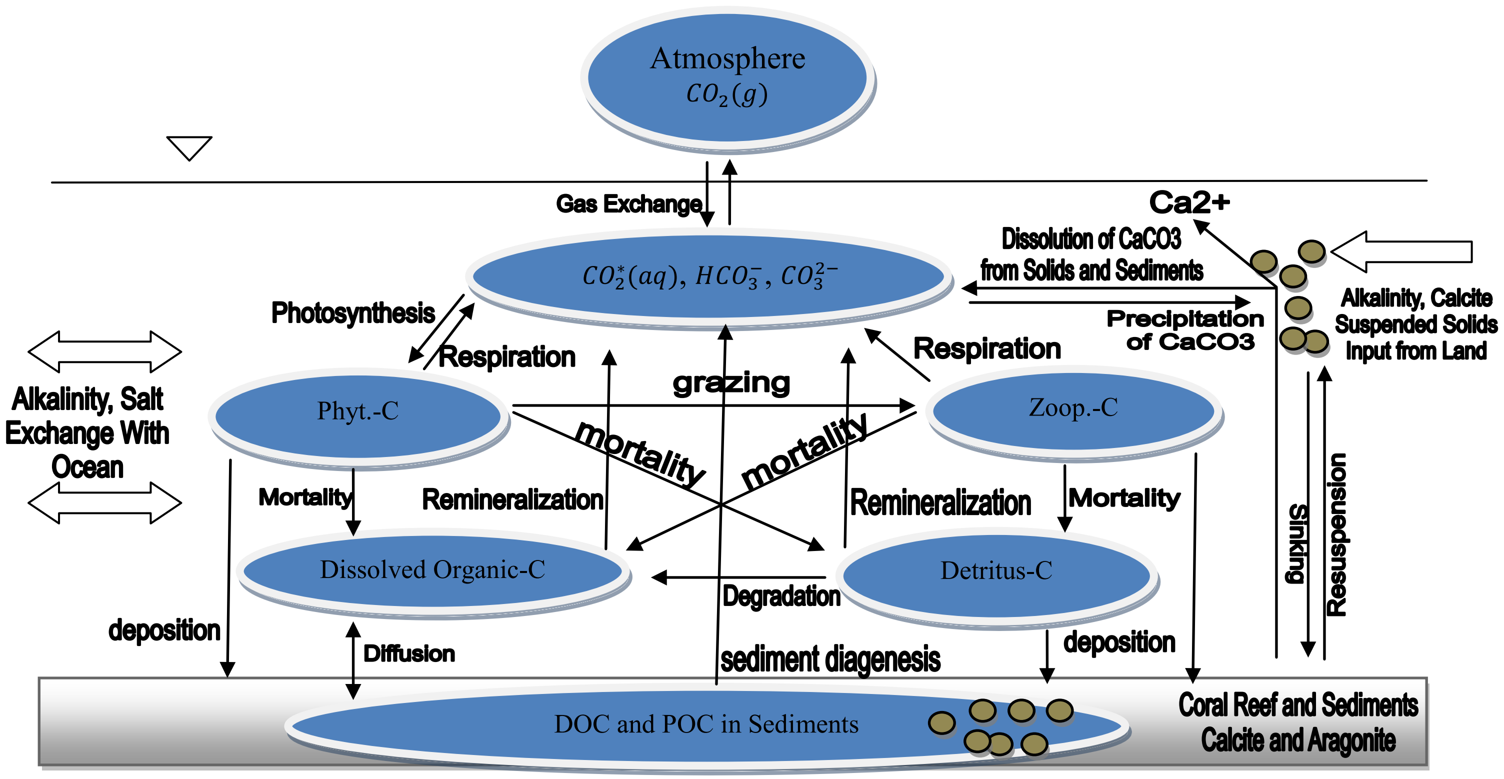

Figure 2. Schematic diagram of carbon cycle in coastal and estuarine system. Similar processes involve nitrogen and phosphorus.

DOC: dissolved organic carbon
POC: particulate organic carbon

1.4 Aragonite and calcite saturation

Aragonite and calcite are two forms of calcium carbonate used by shell-forming organisms. Of these, aragonite is generally more soluble than calcite. The saturation state of seawater for calcium carbonate is defined as

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp,CaCO_3}}. \tag{22}$$

$[Ca^{2+}]$ can be estimated from salinity relationships or modeled as a state variable. When the saturation state is <1, calcium carbonate tends to dissolve. Dissolution of calcium carbonate occurs when the product of the concentrations of Ca^{2+} and CO_3^{2-} are below the solubility product:

$$[Ca^{2+}][CO_3^{2-}] < K_{sp,CaCO_3} \ . \tag{23}$$

Conversely, if the saturation state is greater than 1, then shell formation can occur. However, even aragonite saturation levels just over 1 can have negative effects on biota.

For the Salish Sea, abiotic precipitation is not a factor. In seawater, Ca^{2+} is abundant, and it is CO_3^{2-} concentration that influences formation of $CaCO_3\ (s)$.

1.5 Role of alkalinity and inorganic carbon in pH kinetics

To determine the speciation of various forms of carbon and to solve for pH, the approach includes the key chemical reactions discussed above as well as mass and charge balances. The mass balance principle states that in a closed system, mass of a given element (e.g., number of moles of carbon C) is conserved. The charge balance is based on the assumption that the system is electrically neutral. Due to the fact that proton H^+ is the master variable in an aquatic system, accounting of charge in the system can be done in terms of number of excessive protons instead of total charges of all ions. This leads to proton balance equation (PBE; see Pankow, 1991) as an alternative form of charge balance equation (CBE). Chemists find that PBE is more convenient than CBE as it is a direct equation of H^+ hence suitable for finding the concentration of free proton $[H^+]$ in the solution.

This approach leads to the concept of alkalinity. In order to count charges in terms of protons, all dissolved species in the solution are labeled as being either proton rich or proton poor relative to some standard species (proton neutral) in the solution. The aggregate of all components (counted positively for proton-rich species and negatively for proton-poor species) gives the net proton charge in the system. For a carbonate system, the natural choice of the standard species is water H_2O and dissolved carbon dioxide $CO_2(aq)$. Expressing all ions in the system in terms of H_2O, $CO_2(aq)$, and H^+, we can write the following equations (White, 2013)

$$H^+ = H^+ \tag{24}$$

$$OH^- = H_2O - H^+ \tag{25}$$

$$HCO_3^- = H_2O + CO_2 - H^+ \tag{26}$$
$$CO_3^{2-} = H_2O + CO_2 - 2H^+ \tag{27}$$

These are imaginary half chemical reactions that may or may not take place explicitly but are used for the convenience of accounting for protons. We can label H^+ as being proton rich, OH^- as being proton poor for it can be viewed as H_2O with deficit of one proton. Similarly, HCO_3^- is also proton poor, and CO_3^{2-} is also proton poor in the magnitude of 2 per CO_3^{2-} ion. The net amount (in mole/L) of electrical charge due to proton excess in the solution is then

$$TOTH = [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] \tag{28}$$

equivalent to

$$TOTH = [H^+] - ([OH^-] + [HCO_3^-] + 2[CO_3^{2-}]). \tag{29}$$

Proton poor species are counted negatively and the coefficient in front of $[CO_3^{2-}]$ is 2 for its magnitude is 2 (i.e., each mole of CO_3^{2-} ions are deficient by 2 moles of H^+ relative to $H_2O + CO_2$). Without other ions in a closed system, the charge balance equation (CBE) requires that

$$[H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] = 0 \tag{30}$$

or

$$TOTH = 0 \tag{31}$$

which gives the following proton balance equation (PBE)

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]. \tag{32}$$

However, a natural system in seawater also consists of many other cations (positively charged ions) and anions (negatively charged ions). The CBE requires that $TOTH$ be equal to the sum of charges (mole-electrons/L) including all other species that are not accounted for in the PBE above. In that case, the PBE above may not be balanced, and the imbalance can be expressed as $[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$. This is called *alkalinity* (mole/L):

$$Alk = -TOTH = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \tag{33}$$

Here we used $H_2O + CO_2$ as a reference point and Alk above is also called *carbonate alkalinity*. In seawater, a large suite of additional ions are not accounted for in $TOTH$ above. They include (non-exhaustively), for example $Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HSO_4^-, NO_3^-, NH_4^+, B(OH)_4^-, H_3\ SiO_4^-, HS^-, PO_4^{3-}$ $HPO_4^{2-}, H_2\ PO_4^-, H_4\ SiO_4$, and un-dissociated or un-protonated dissolved molecules such as NH_3, HF, H_3PO_4 etc. Among these ions and dissolved molecules, some are *chemically conservative* ions, which means their concentrations are not affected by changes in pH, temperature, or pressure (assuming no precipitation, no dissolution and that the system is closed and well mixed). The other ions are *chemically non-conservative*, meaning that their concentrations change due to chemical reactions with different rates under different temperature and pressure, pH, etc. In this complex case, the accounting of charge in terms of protons $TOTH$ (i.e. $-Alk$) becomes more involved. A convenient way is to only include chemically non-conservative quantities, in which case Alk is expressed as:

$$Alk = -TOTH = \sum[charges\ of\ nonconservative\ \ anions] - \sum[charges\ of\ nonconservative\ cations] \quad (34)$$

Overall the charge balance equation (CBE) requires that the net charge be zero, hence

$$0 = \sum[charges\ of\ cations] - \sum[charges\ of\ anions] \quad (35)$$

i.e.

$$0 = \sum[charges\ of\ conservative\ cations - conservative\ anions] + \sum\ (\ [charges\ of\ nonconservative\ \ \ cations] - [nonconservative\ \ \ anions]\ )$$

which gives

$$Alk = \sum[charges\ of\ nonconservative\ \ anions] - \sum[charges\ of\ nonconservative\ cations]$$

$$= \sum[charges\ of\ conservative\ cations]\ - \sum[charges\ of\ conservative\ anions]. \quad (36)$$

With this definition of alkalinity, we find that Alk is the concentration of the sum of the charges of *chemically conservative* species (counted negatively for anions and positively for cations). Hence alkalinity itself is conservative**.** The convenience of having chemically conservative alkalinity in a system makes it easier for chemists to solve for pH using a proton balance equation. That is, we only need to account for non-conservative anions and non-conservative cations, and can express them in terms of being proton-rich or proton-poor to obtain a PBE. Because free proton (free hydrogen ion H^+) is proton-rich and non-conservative, it enters PBE eqn. (34).

Assuming Alk is known, then one can solve for $[H^+]$ from this equation along with chemical equilibrium equations of the non-conservative species and mass balance equations of the elements in the non-conservative species. In essence, the introduction of Alk permits lumping of conservative species in a quantity called alkalinity. This simplifies mathematical and analytical methods of solving the system significantly. This approach allows us to focus on species that undergo concentration changes with different pH, temperature, and pressure in the system.

The caveat of treating alkalinity in this form is the assumption that the conservative property of alkalinity is not affected by physical transport or mixing and that associated changes in alkalinity are only due to mixing and dilution and not due to solution-chemistry related processes. Changes to alkalinity can also occur due to dissolution and precipitation, formation of gases, biological uptake, and remineralization which need to be accounted in the form of source and sink terms with a biogeochemical model.

In order to solve for the carbon cycle and also pH in an estuarine system, the major biological processes shown in Figure 2 have to be considered using a mathematical model capable of nutrient-phytoplankton-zooplankton-detritus (NPZD) type of food web interactions. In this approach the alkalinity in the system may be solved as a tracer with no chemical sources or sinks except dissolution and precipitation of calcium carbonate $CaCO_3$, dissolution of silicate, photosynthesis, nitrification and denitrification. Other sources and sinks of alkalinity are purely physical transport of alkalinity from river runoffs and exchange with the open ocean including upwelling and downwelling processes. As shown in Figure 2, carbon, as well as nutrient, loads enter the system through water surface and sediments and indirectly affect alkalinity.

2.0 Potential Modeling Approaches

In this section, some of the candidate approaches for modeling pH and aragonite saturation in an estuarine environment are reviewed. Some of the methods are purely inorganic chemistry models. Others involve coupling to biological processes at different levels of complexity.

2.1 CO2SYS

CO2SYS is a framework for calculating the parameters of the CO_2 system, pH, and calcium solubility given input of any two of the four measurable parameters (alkalinity, total inorganic carbon, pH, and fCO_2 or pCO_2). CO2SYS is not a fate and transport model. It calculates the parameters of the CO_2 system corresponding to input conditions that assume the system is at equilibrium. The CO2SYS algorithms can be used at each time step of any fate and transport model to solve for the CO_2 system and pH. CO2SYS is widely used in ocean acidification research (e.g., Feely et al., 2011) to calculate the parameters of the CO_2 system or calcium solubility in seawater from observations of measurable parameters.

CO2SYS was originally developed by Lewis and Wallace (1998) at Oak Ridge National Laboratory under a DOS platform using the FORTRAN programming language. Since then, several other versions have been made available, including a MATLAB version by van Heuven et al. (2011), an Excel version by Pelletier et al. (2012), and Mac OS and iOS (iPhone) versions by Robbins et al. (2010). The technical details of the CO2SYS model follow the handbook by Dickson and Goyet (1994). Formulations presented below are based on a recent update by Dickson et al. (2007). CO2SYS can be used to predict carbon system parameters (pH, pCO_2, alkalinity, total dissolved inorganic carbon -TDIC) from any two values.

The equilibrium constants for chemical reactions given in (12) to (14) are

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2^*]} \tag{37}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{38}$$

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} \cong [H^+][OH^-] \tag{39}$$

with $[H_2O] \cong 55.6$ mole H_2O/L for dilute solution or 1 if we absorb the 55.6 in K_w. At room temperature (25 $^\circ C$) $K_w = 10^{-14}\ (\frac{\text{mole}}{\text{L}})^2$.

In seawater, other inorganic chemical reactions that are important to pH include

$$B(OH)_3 + H_2O \rightleftharpoons H^+ + B(OH)_4^- \tag{40}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{41}$$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \tag{42}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \tag{43}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \tag{44}$$

$$Si(OH)_4 \rightleftharpoons H^+ + SiO(OH)_3^- \tag{45}$$
$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{46}$$
$$H_2\,S \rightleftharpoons H^+ + HS^- \tag{47}$$

with the corresponding equilibrium constants being

$$K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3\,]} \tag{48}$$
$$K_S = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \tag{49}$$
$$K_{1P} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4\,]} \tag{50}$$
$$K_{2P} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \tag{51}$$
$$K_{3P} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^-]} \tag{52}$$
$$K_{Si} = \frac{[H^+][SiO(OH)_3^-]}{[Si(OH)_4\,]} \tag{53}$$
$$K_{NH_3} = \frac{[H^+][NH_3\,]}{[NH_4^+]} \tag{54}$$
$$K_{H_2\,S} = \frac{[H^+][HS^-]}{[H_2\,S]} \tag{55}$$

The hydrogen fluoride dissociation reaction is also important with the equilibrium constant defined by

$$K_F = \frac{[H^+][F^-]}{[HF]} \tag{56}$$

The total concentration of dissolved inorganic carbon, borate, sulfate-S, fluoride, phosphate-P, silicate, ammonia-N, and sulfide-S (mass balance equations) are

$$C_{TDIC} = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{57}$$
$$C_{TB} = [B(OH)_3\,] + [B(OH)_4^-] \tag{58}$$
$$C_{TS} = [SO_4^{2-}] + [HSO_4^-] \tag{59}$$
$$C_{TF} = [F^-] + [HF] \tag{60}$$
$$C_{TDIP} = [PO_4^{3-}] + [H_2PO_4^-] + \left[H_3PO_4\,\right] + [HPO_4^{2-}] \tag{61}$$
$$C_{TDSi} = \left[Si(OH)_4\,\right] + [\,SiO(OH)_3^-] \tag{62}$$
$$C_{TNH_3} = \left[NH_3\,\right] + [NH_4^+] \tag{63}$$
$$C_{TH_2S} = [H_2S] + [HS^-] \tag{64}$$

The proton balance equation (PBE) gives the following equation for total alkalinity.

$$\begin{aligned} A_T &= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + 2[PO_4^{3-}] \\ &\quad + [HPO_4^{2-}] + [SiO(OH)_3^-] + \left[NH_3\,\right] + [HS^-] + \ldots \\ &\quad - [H^+] - [HSO_4^-] - [HF] - \left[H_3PO_4\,\right] - \cdots \\ &= A_c + [B(OH)_4^-] + 2[PO_4^{3-}] \end{aligned} \tag{65}$$

$$+HPO_4^{2-} + [SiO(OH)_3^-] + [NH_3\ ] + [HS^-] + \ldots$$
$$-[HSO_4^-] - [HF] - [H_3PO_4\ ] - \cdots. \tag{66}$$

where A_c is carbonate alkalinity defined in (33).

The equations of equilibrium constants (37) to (39) and (48) to (56) combined with mass balance equations (57) to (64) give the following kinetic solution of ionic species in terms of $[H^+]$

$$[HCO_3^-] = \frac{C_{TDIC}K_1[H^+]}{[H^+]^2+K_1[H^+]+K_1K_2} \tag{67}$$
$$[CO_3^{2-}] = \frac{C_{TDIC}K_1K_2}{[H^+]^2+K_1[H^+]+K_1K_2} \tag{68}$$
$$[CO_2^*] = \frac{C_{TDIC}[H^+]^2}{[H^+]^2+K_1[H^+]+K_1K_2} \tag{69}$$
$$[B(OH)_4^-] = \frac{C_{TB}}{1+[H^+]/K_B} \tag{70}$$
$$[OH^-] = \frac{K_w}{[H^+]} \tag{71}$$
$$[H_3PO_4\ ] = \frac{C_{TDIP}[H^+]^3}{[H^+]^3+K_{1P}[H^+]^2+K_{1P}K_{2P}[H^+]\ \ +K_{1P}K_{2P}K_{3P}} \tag{72}$$
$$[H_2PO_4^-] = \frac{C_{TDIP}K_{1P}[H^+]^2}{[H^+]^3+K_{1P}[H^+]^2+K_{1P}K_{2P}[H^+]\ \ +K_{1P}K_{2P}K_{3P}} \tag{73}$$
$$[HPO_4^{2-}] = \frac{C_{TDIP}K_{1P}K_{2P}[H^+]}{[H^+]^3+K_{1P}[H^+]^2+K_{1P}K_{2P}[H^+]\ \ +K_{1P}K_{2P}K_{3P}} \tag{74}$$
$$[PO_4^{3-}] = \frac{C_{TDIP}K_{1P}K_{2P}K_{3P}}{[H^+]^3+K_{1P}[H^+]^2+K_{1P}K_{2P}[H^+]\ \ +K_{1P}K_{2P}K_{3P}} \tag{75}$$
$$[SiO(OH)_3^-] = \frac{C_{TDSi}}{1+[H^+]/K_{Si}} \tag{76}$$
$$[NH_3\ ] = \frac{C_{TNH_3}}{1+[H^+]/K_{NH_3}} \tag{77}$$
$$[HS^-] = \frac{C_{TH_2S}}{1+[H^+]/K_{H_2S}} \tag{78}$$
$$[\mathrm{HF}] = \frac{C_{TF}}{1+K_F/[H^+]} \tag{79}$$
$$[HSO_4^-] = \frac{C_{TS}}{1+K_S/[H^+]} \tag{80}$$

For a closed system, given total alkalinity A_T and the total amounts of dissolved constituents such as inorganic carbon C_{TDIC}, borate C_{TB}, sulfate-S C_{TS}, fluoride, phosphate-P C_{TDIP}, silicate C_{TDSi}, ammonia-N C_{TNH_3}, sulfide-S C_{TH_2S}, it is possible to calculate the free proton concentration $[H^+]$ (mole/L) by substituting the above terms into the PBE assuming we know the reaction rate constants. We can then calculate the total proton concentration $[H_T^+]$ providing both pH and pH_T.

2.2 Water Quality Analysis Simulation Program (WASP)

WASP is a generalized framework for modeling contaminant fate and transport in surface waters supported by EPA (www.epa.gov/athens/research/wasp.html). Its flexible, compartmental approach allows it to address problems in one, two, or three dimensions. It is designed to allow easy substitution of user-written routines into the program structure. WASP has been used to answer questions regarding biochemical oxygen demand, DO dynamics, nutrients and eutrophication, bacterial contamination, and organic chemical and heavy metal contamination. The current WASP software package includes the scientific modules TOXI, EUTRO, and DYNHYD. EUTRO simulates inorganic carbon, alkalinity and pH, as well as DO and other eutrophication processes.

The pH, alkalinity, and inorganic carbon algorithms that are incorporated into WASP were adapted from QUAL2K (Chapra et al., 2008) and extended to saline systems with routines adapted from CO2SYS. A detailed description of the WASP model theory and equations for the CO_2 system and pH are provided in Ambrose et al. (2010).

2.3 CE-QUAL-W2 model

The CE-QUAL-W2 model by Cole and Buchak (1995) is an example of a coupled circulation and biogeochemical model that includes transport and mixing processes, biological processes such as primary production and remineralization, air-sea exchanges, and calcium carbonate dissolution and precipitation processes. These are needed to develop mass balance equations for total dissolved inorganic carbon (TDIC). CE-QUAL-W2 operates on a two-dimensional (longitudinal and vertical), laterally averaged grid and conducts hydrodynamic and water quality simulations. CE-QUAL-W2 has been used to simulate pH in rivers and lakes/reservoirs (e.g., Martin and Martin, 1988; Sullivan et al., 2013). The model assumes that non-carbonate alkalinity is zero:

$$Alk = A_T \cong A_C = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (81)$$

pH and carbonate species CO_2^*, HCO_3^-, CO_3^{2-} are calculated using a combination of the C_{TDIC} eqn. (57), carbonate alkalinity equation (PBE) eqn.(80), and equilibrium constants of carbonate-bicarbonate reactions. Assuming carbonate alkalinity A_C and C_{TDIC} are known, by substituting[HCO_3^-],[CO_3^{2-}], and $[OH^-]$ concentrations into the above PBE, we obtain the following equation in terms of $[H^+]$

$$A_C = \frac{C_{TDIC}[H^+]K_1}{[H^+]^2+[H^+]K_1+K_1K_2} \times \frac{[H^+]+2K_2}{[H^+]} + \frac{K_W}{[H^+]} - [H^+] \qquad (82)$$

This nonlinear equation is solved using an iterative method for $[H^+]$. Subsequently, $[HCO_3^-]$, $[CO_3^{2-}]$ and $[CO_2^*]$ are calculated from equations (67), (68), and (69).

The C_{TDIC} is simulated as a state variable in the model. Air-sea exchange of CO_2 and algae growth and mortality contributes to the carbon pool through transport and mixing processes. The equation describing C_{TDIC} (without advection and diffusion terms) in a fixed box of volume V is given by

$$\frac{\partial C_{TDIC}\times V}{\partial t} = \{\alpha_C Alg\left(K_{ar} - K_{ag}\right) + \alpha_C K_{dt} Det + \alpha_C K_{dom} DOM + \alpha_C K_S SOM\} \times V + \alpha_{C,O_2} A_{sed} SOD + A_s K_{a,CO_2^*}([CO_2^*]_{sat} - [CO_2^*]) \quad (83)$$

where K_{ar} is algae respiration rate (1/day), K_{ag} is algae growth rate (1/day), α_C is carbon to algae mass stoichiometric ratio (g-C/g-Algae), Alg is algae concentration (g/m^3), K_{dt} is detritus decay rate, and Det is particulate detritus concentration (g/m^3). DOM is dissolved organic matter concentration (g/m^3) and K_{dom} is DOM decay rate (1/day). SOM is suspended sediment organic mass (gC/m^3), K_S is sediment organic matter decay rate (1/day) due to oxidation, SOD is sediment oxygen demand ($\frac{gO_2}{m^2}/day$), A_{sed} is surface area of bottom sediment, $\alpha_{C,O_2}$is carbon to oxygen equivalent stoichiometric ratio, $[CO_2^*]_{sat}$ (gC/m^3) is saturation concentration of CO_2^*, A_s is surface area of air sea exchange (m^2), K_{a,CO_2^*} (m/day) is air sea exchange rate of CO_2^*. V (m^3) is the volume of the cell. The C_{TDIC} simulated in (gC/m^3) is converted to mole-C/L units before being used in equation (57) and (67) to (69). K_{a,CO_2^*} is given by Mackay (1980) and Chapra and Reckhow (1983) as

$$K_{a,CO_2^*} = 6.4185 \times 10^{-6} \times 86400 \times \frac{Wind^{1.5}}{\sqrt{M_{CO_2}}} \qquad (m/day) \qquad (84)$$

$$[CO_2^*]_{sat} = 0.286 e^{(-0.0314 T_s) f_a} \qquad (g - C/m^3) \qquad (85)$$

where $Wind$ is wind speed (m/s), M_{CO_2} is molecular weight of carbon dioxide (≈ 44 g/mole), T_s is surface temperature ($^\circ C$), $f_a$is altitude correction factor from Mortimer (1981)

$$f_a = (1 - \frac{H_s}{44.3})^{5.25} \qquad (86)$$

with H_s being elevation above sea level (km) for reservoir simulations, which is not applicable for estuaries. Complex processes such as bubble entrainment and re-aeration due to ship wake are not explicitly included in the above approach but are accounted for by reaeration rates.

2.4 Potomac Eutrophication Model (PEM)

The Potomac Eutrophication Model (PEM) by HydroQual Inc. (1991) is a eutrophication model of two functional algal groups that was developed for the Potomac River estuary, one of the major tributaries of Chesapeake Bay, USA. It includes calcium carbonate chemical equilibrium kinetics and pH-mediated sediment phosphorus flux. The model was calibrated to successfully reproduce algal bloom of *Microcystis aeruginosa* during summer of 1983 and reproduced trends of observed water quality in 1984 and 1985. The model takes the same approach in solving for pH and carbonate species in water column as in CE-QUAL-W2, with the following notable difference

- TDIC simulation includes additional processes such as denitrification, calcium carbonate precipitation, calcium carbonate dissolution and settling.
- Changes in alkalinity (carbonate and non-carbonate) due to algae growth, denitrification, nitrification and calcium carbonate ($CaCO_3$ (s)) settling are also considered.

The model simulates depth-averaged quantities. The depth-averaged TDIC concentration ($moleC/m^3$) equation is given as

$$\frac{\partial C_{TDIC}}{\partial t} = Alg1\left(K_{ar1} - K_{ag1}\right) + Alg2\left(K_{ar2} - K_{ag2}\right) + \alpha_{C,O_2M} K_{rc} CBOD$$
$$+K_{a,CO_2^*}([CO_2^*]_{sat} - [CO_2^*])/H + K_{DN}[NO_3^-] \times (5/4) - [CaCO_3\ (s)]w_{set}/H \tag{87}$$

where $Alg1$ and $Alg2$ are concentrations of algal group 1 and 2 respectively ($moleC/m^3$), K_{ar1} and K_{ar2} are algae respiration rates (1/day) for group 1 and group 2, and K_{ag1} and K_{ag2} are growth rates (1/day) for group 1 and group 2. $CBOD$ is carbonaceous biochemical oxygen demand (gO_2/m^3), and K_{rc} is CBOD decay rate (1/day). α_{C,O_2M} is molar ratio of carbon to oxygen in CBOD respiration (mole-C/mole-O_2). K_{a,CO_2^*} is the carbon dioxide CO_2^* re-aeration coefficient (m/day), K_{DN} is denitrification rate (1/day), $[NO_3^-]$ is nitrate concentration ($mole\ N/m^3$), $\left[CaCO_3\ (s)\right]$ is calcium carbonate (solid state) concentration ($mole/m^3$), w_{set} is vertical sinking speed (m/day) of calcium carbonate particles, and H is water depth. $[CO_2^*]_{sat}$ and $[CO_2^*]$ here are also in $mole/m^3$units. Calculation of $[CO_2^*]_{sat}$ is based on equation (16).
Note that settling of $CaCO_3\ (s)$ in C_{TDIC} equation is a simplified approach to account for $CaCO_3$ precipitation.

The ratio 5/4 in the denitrification term is due to the following simplified reaction that occurs in relatively low DO regimes:

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \tag{88}$$

The algae growth affects alkalinity following the simplified photosynthetic and respiratory processes in natural waters presented by Stumm and Morgan (1970)

$$106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \leftrightarrow C_{106}N_{16}P_1 + 106O_2 + 15H^+ \tag{89}$$
$$106CO_2 + 16NO_{23}^- + H_2PO_4^- + 122H_2O \leftrightarrow C_{106}N_{16}P_1 + 138O_2 - 17H^+ \tag{90}$$

Hence with each mole of algae biomass increase ($C_{106}N_{16}P_1$), there is a reduction in alkalinity by 15 moles (increase of H^+) with NH_4^+ assimilation. The increase in alkalinity is 17 moles (decrease of H^+) with NO_3^{2-} assimilation. Similarly nitrification decreases alkalinity through the following reaction

$$2NH_4^+ + 3O_2 \leftrightarrow 2\,NO_2^- + 4H^+ + 2H_2O \tag{91}$$
$$2\,NO_2^- + O_2 \leftrightarrow 2\,NO_3^- \tag{92}$$

Each 2 moles of NH_4^+ nitrified will decrease 4 moles of alkalinity. Similarly, denitrification which only occurs in anoxic conditions, will also affect alkalinity in the following reaction:

$$4NO_3^- + 5\mathrm{CH_2O} + 4H^+ \leftrightarrow 2N_2 + 5CO_2 + 7H_2O \tag{93}$$

Each 4 moles of nitrate NO_3^- denitrified would increase alkalinity by 4 moles (consuming 4 moles of H^+) and generate 5 moles of CO_2. Alkalinity is also lost due to settling of solid phase calcium carbonate. Two moles of alkalinity are removed for each moles of $CaCO_3\ (s)$] removal. Net change rate of alkalinity (depth averaged) is then expressed as ($\frac{mole}{m^3}/day$)

$$\begin{aligned}\frac{dAlk}{dt} = {} & \alpha_{NCM}\left(K_{ag1}Alg1 + K_{ag2}Alg2\right)\left(1-\alpha_{NH_3}\right)[NO_3] \times (\tfrac{15}{16}) \\ & +K_{DN}[NO_3]\left(\frac{k_{NO_3}}{k_{NO_3}+DO}\right) - \alpha_{NCM}\left(K_{ag1}Alg1 + K_{ag2}Alg2\right)\alpha_{NH_3}[NH_3] \times (\tfrac{17}{16}) \\ & -2K_{NT}[NH_3] - 2[CaCO_3\ (s)]w_{set}/H \end{aligned} \tag{94}$$

where α_{NCM} is molar ratio of nitrogen to carbon in algae ($\cong 16/106$), α_{NH_3} is preference parameter (dimensionless, ranges from 0 to 1) for ammonia NH_3 uptake. k_{NO_3} is Michaelis constant for oxygen of denitrification (mg O_2/L), K_{NT} is nitrification rate (1/day), K_{DN} is denitrification rate (1/day), $[NO_3]$, $[NH_3]$ are nitrate and ammonia concentration (mole-N/m^3). w_{set} is settling velocity (m/day).

Suspended calcium carbonate (depth averaged) change rate can be modeled with a simple dissolution and sinking equation:

$$\frac{d[CaCO_3\ (s)]}{dt} = \frac{[CaCO_3\ (s)]w_{set}}{H} + K_{s,CaCO_3}\left(1 - -[CaCO_3\ (s)]/[CaCO_3\ (s)]_{eq}\right)^{\eta} \tag{95}$$

where $[CaCO_3\ (s)]_{eq}$ is equilibrium calcium carbonate concentration, $K_{s,CaCO_3}$ (unit: 1/day) is rate of calcium carbonate dissolution, and η is the order of reaction with approximate value of 2 (Stumm and Morgan, 1970) or 1.87 ± 0.15 (Equation 6 of Feely et al., 1988) . The formed solid state $CaCO_3\ (s)$ is then removed due to sinking or added to the system due to river loading.

3.0 Recommended Acidification Modeling Framework for the Salish Sea Model

This document begins developing an approach for acidification modeling of the Salish Sea based on best available existing information. This general approach will be revisited in a QA Project Plan when funding for acidification model development is secured. These recommendations are intended to be iterative. This initial step will enable collaboration with other modeling efforts underway through Task 7.4.1 and with those developing monitoring networks for acidification.

3.1 Overview of linked FVCOM-ICM application for the Salish Sea

As described in the introduction, PNNL has already developed a three-dimensional model of the Salish Sea, including Puget Sound and Georgia Basin. The model uses an unstructured grid Finite Volume Coastal Ocean Model (FVCOM, Chen et al., 2003) framework and the Integrated Compartment Model (CE-QUAL-ICM, Cerco and Cole, 1995) for conducting water quality kinetics. The FVCOM-based hydrodynamic model has successfully simulated the tidal wave propagation, freshwater inputs, and fjordal estuarine exchange flows (Khangaonkar et al., 2011). The model has also reproduced the annual biogeochemical cycles of nutrient consumption and algae growth in Puget Sound for the years 2006 and 2007 (Khangaonkar et al., 2012). The model domain includes all of Puget Sound and Georgia Basin divided into an unstructured mesh using triangular cells. The grid resolution is, on average, 250 meters in the inlets and bays and approximately 800 meters in the main basin of Puget Sound.

The biogeochemistry model was developed, tested, and implemented on the same FVCOM unstructured grid as that used for hydrodynamic calculations for the Salish Sea (Kim et al., 2012; Khangaonkar et al., 2012). The transport and mixing of chemical and biological constituents were conducted using the same finite volume numerical scheme as that used in FVCOM. This model has significant advantages over structured grid-based models for a system such as the Salish Sea, with its complex shoreline and presence of many islands. In its present configuration, the model simulates a total of 19 state variables, including two species of algae, dissolved and particulate carbon, and nutrients, as part of the carbon cycle to calculate algal production, decay and the impact on DO.

The Salish Sea model includes loads (nutrient, phytoplankton, and DO) from the open ocean boundaries, 64 river inflows, and 99 wastewater treatment plants. To properly incorporate the effects of anthropogenic loads, all known sources of nutrients such as natural and human sources within watershed inflows and wastewater outfalls were included (Mohamedali et al., 2011). Meteorological forcing includes wind stress and solar irradiance based on Weather Research & Forecasting (WRF) model predictions for the domain from the University of Washington. Phytoplankton primary production, inorganic and organic carbon fluxes, and nutrient (nitrogen and phosphorus) sources and sinks were specified as the key biogeochemical parameters.

The linked FV-COM-ICM model uses the carbon cycle as the basis for DO simulations. The Salish Sea model was applied to a variety of current and future scenarios that include increasing population, land cover changes, hydrologic changes resulting from climate change, Pacific Ocean trends in DO, and air temperature increases from climate change (Roberts et al., 2014). The goal was to understand the relative contributions of local human sources and Pacific Ocean conditions now through 2070. Further model development, underway now, will add the ability to simulate sediment diagenesis, and important process that influences oxygen as well as carbon. The existing model, together with the planned addition of sediment diagenesis, is suitable for simulating acidification parameters tied to the carbon cycle and distinguishing the relative contribution from regional human sources of nutrients and carbon.

3.2 Recommended approach for simulating acidification within the FVCOM-ICM framework

The approach presented below describes incorporation of acidification kinetics into the FVCOM-ICM framework and draws heavily from the processes and methods in CO2SYS, WASP, CE-QUAL-W2 and PEM described in previous sections. Key processes are shown schematically in Figure 2 and described in Section 1.3.

This approach requires modifications of the existing FVCOM-ICM model to include two new quantities in the computational domain. $TDIC$ and Alk will be included as state variables in advection, transport, and turbulent mixing computations. CO_2^*, CO_3^{2-}, HCO_3^-, pH, aragonite saturation, and calcite saturation will be secondary quantities computed based on predicted values of TDIC and alkalinity. The user may select the appropriate pH scale for output values.

$TDIC$ is a new state variable that will be added to the present FVCOM-ICM model. Sources and sinks of TDIC will include loads from the open ocean and watershed inflow boundaries, air-sea exchange of CO_2 (expressed as CO_2^* concentration in water), uptake of $TDIC$ by photosynthesis, generation of CO_2 by oxidation of dissolved organic carbon, respiration, and remineralization from sediment-water exchanges.

Alk is also a new state variable that will be added to the FVCOM-ICM model. In addition to transport and mixing, sources and sinks of alkalinity include loads from the river and open ocean boundaries. Alkalinity will be affected due to biological uptake of nitrate and ammonia, nitrification, and denitrification.

Other processes affect alkalinity as well, including phosphate protonation and silicate protonation. These will not be considered in the acidification model development because they are not expected to be dominant processes.

The aragonite and calcite saturation states will be calculated as secondary variables in terms of the solubility ratio, Ω, which are defined as follows:

$$\Omega_{arag} = [CO_3^{2-}] * [Ca^{2+}] / K_{sp}^{*}{}_{,arag} \qquad (96)$$

$$\Omega_{calc} = [CO_3^{2-}] * [Ca^{2+}] / K_{sp}^{*}{}_{,calc} \qquad (97)$$

Thus values of $\Omega < 1$ represent conditions of undersaturation, and values of $\Omega > 1$ represent supersaturation. For the initial acidification model development, the concentration of $[Ca^{2+}]$ will be calculated as a secondary variable assuming proportionality with salinity (Riley and Tongudai, 1967), $[CO_3^{2-}]$ will be calculated from the adapted CO2SYS algorithms, and K_{sp} will be calculated from published empirical equations (Mucci, 1983) as a function of temperature and salinity.

Additional processes that change alkalinity include shell formation of algae and zooplankton groups that appear to have calcifying and de-calcifying functions. General research data and documents related to biogenic calcification are available (e.g., Gattuso et al., 1999; Leclercq et al., 2002; Anderson et al., 2003). Rupp and Adams (1981) conducted lab experiments on the influence of primary production on calcium carbonate precipitation in stream waters. Equation (98) assumes the system is at steady state for aragonite and calcite saturation process and that the dissolution process is controlled by abiotic factors. Accounting for biogenic factors or time-varying responses would require additional information and model development. Only limited available information on these processes exists for the Salish Sea and will not be considered in the initial acidification model development.

Similarly, although the FVCOM-ICM model includes two species of phytoplankton (diatoms and dinoflagellates) and uptake of nutrients and carbon cycling as part growth and metabolism, the interaction including competition with submerged aquatic vegetation (SAV) is not presently included. SAV is not included in the current model application and will not be activated in the initial acidification model development. The FVCOM-ICM framework includes an SAV module which may be activated and calibrated for selected sites such as Padilla Bay and other nearshore regions if required in the future.

3.3 Analytical steps within the FVCOM-ICM framework

The overall procedure of the proposed method can be summarized in the following steps:

- Apply FVCOM to solve for hydrodynamics (temperature, salinity, velocity, turbulent mixing and sea surface elevation) for the selected baseline year if different than 2006 and 2007 used in the existing application:
    - Continue with the existing model grid that covers the domain of interest
    - Specify tidal elevation, temperature T and salinity S data at the open boundary
    - Specify river and wastewater treatment plant discharges that flow into the domain, including TDIC and alkalinity
    - Specify surface wind speed, wind direction, precipitation rates, solar radiation (short wave, long wave and latent heat fluxes)
    - Run the FVCOM model with desired output intervals to generate the hydrodynamic solution for use by the FVCOM-ICM water quality model

- In FVCOM-ICM, establish initial conditions for $TDIC$ and Alk in the ICM model domain, where initial conditions for Alk will be empirically estimated from salinity (or from measured data) using methods such as the regression developed by Alin (personal communication, 2013), as described in Section 3.4. Domain-wide $TDIC$ will be set up using measured data interpolated to the model grid points.

Simulate algae, zooplankton, detritus, and pools of nitrate, ammonia, dissolved organic nitrogen, particulate organic nitrogen, dissolved organic carbon, particulate organic carbon, and DO.

- At each model time step, compute the sources and sinks of $TDIC$:
  - Reaeration (air-sea exchange rate of CO_2^*) estimated from oxygen
  - Gain of CO_2^* due to oxidation of dissolved organic carbon (DOC) and heterotrophic respiration
  - Gain or loss of CO_2^* due to phytoplankton respiration/production
  - Sediment processes (oxygen demand)
  - Pacific Ocean supply of TDIC
  - Freshwater inputs (rivers and wastewater treatment plants)

- At each model time step, compute the sources and sinks of Alk:
  - Loss of NH4 and gain of NO3 due to nitrification
  - Loss of NO3 due to denitrification
  - Gain of NH4 due to organic nitrogen hydrolysis
  - Gain of NH4, NO3 due to atmospheric deposition
  - Gain of NH due to sediment flux
  - Loss or gain of NO3 due to sediment flux
  - Settling of sorbed NH4
  - Uptake and excretion of NH4, NO3 by phytoplankton
  - Boundary conditions of alkalinity include open boundary exchange
  - Boundary conditions of alkalinity from rivers and wastewater treatment plants

- Solve for pH, CO_2^*, CO_3^{2-}, HCO_3^- concentrations with $TDIC$ and Alk known using the adapted algorithms of CO2SYS.
  - In freshwater, we will estimate alkalinity as [HCO3] + 2[CO3] + [OH] – [H] (Lewis and Wallace, 1998).
  - In freshwater, K_1, K_2, and K_w based on freshwater equations included in the CO2SYS implementation of Millero (1979)
  - In brackish water, K_1, K_2, and K_w will use Millero et al. (2006), which is appropriate for salinities even below 16 psu.

- Estimate aragonite and calcite saturation using simulated CO_3^{2-} estimated from CO_2 system calculations and Ca^{2+} estimated from salinity relationships

Numerical methods involved in executing the above steps include

- Discretization of domain with finite volume elements in the horizontal plane and sigma coordinate in the vertical direction
- Upwind scheme for advection
- Implicit scheme for solving vertical mixing (turbulent mixing)
- Nonlinear equation solver for finding pH through the nonlinear PBE (64) in terms of $[H^+]$.

There are a few caveats in the aforementioned framework that may require further attention. Because the model specifies incoming ocean water as a boundary condition, it does not capture processes that affect carbon in the deep ocean. We also assumed that carbonate chemical reactions such as hydrolysis, protonation and dissociation are at equilibrium state so that chemical equilibrium equations can be solved independent of flow equations. This is valid for well-mixed systems with fast reaction rates. This may not be appropriate in locations with large chemical loading with strong gradients in concentrations due to advection/diffusion. This assumption is appropriate when simulating natural waters where physical processes are generally slow compared to chemical processes. The slower biological processes, such as algae growth and mortality, are solved explicitly along with the flow through the transport and mixing equation, and no equilibrium is assumed. Turbulent mixing can change reaction rates significantly. Reaction rates derived from lab experiments without turbulence may be different from in-situ rates.

3.4 Estimation of alkalinity from salinity

Ecology's ambient monitoring program does not include alkalinity measurements in the marine waters of the Salish Sea, although limited monitoring is now planned for 2014. Salinity data are widely available, however. To provide initial conditions for alkalinity and marine values for model comparison, we will estimate alkalinity from salinity. Salinity can reach 20 psu in the surface layers of Whidbey Basin in winter high-flow conditions. These relationships will also be used to estimate alkalinity at the Pacific Ocean open boundary and also as a check of *Alk* as state variability.

NOAA's Pacific Marine Environmental Laboratory (PMEL) has a large database of alkalinity measurements from the Salish Sea. A linear regression between observed alkalinity and salinity can be developed for the purpose of estimating alkalinity from salinity (Simone Alin, personal communication). The relationship between alkalinity and salinity is expected to be fairly linear between the saltwater and freshwater endpoints (Andrew Dickson, personal communication).

Figure 3 shows a linear regression of alkalinity and salinity from a subset of the PMEL-PRISM data from the Salish Sea. The complete PMEL-PRISM database of alkalinity and salinity observations from the Salish Sea will be used to develop a regression equation to estimate alkalinity from salinity if alkalinity data are absent. The RMSE of the regression residuals is 4.1 umol/kg-sw, which suggests that regression estimates of alkalinity would be reasonably accurate considering that measurement uncertainty for alkalinity is approximately ±3 umol/kg-sw.

The regression equation in Figure 3 is intended only to demonstrate the feasibility of the concept and should not be used because only a subset of the database was used. Instead, a regression from the complete database will be used for this project when the analysis is completed. The regression equation from the complete database is expected to be reasonably accurate within the typical range of salinity in Puget Sound including when extrapolating below the range of salinity observations in the regression database. For example, the y-intercept of the regression of 645 umol/kg-sw from the subset of data is within the expected range of observed alkalinity from major rivers discharging into Puget Sound (mean ± std dev of 522 ± 209 umol/kg-sw from unpublished data in Ecology's EIM[2] database). Therefore, the regression is likely to provide reasonably accurate estimates for alkalinity for the typical range of salinity throughout Puget Sound. Besides the freshwater monitoring data, very few alkalinity data are available at salinities below 29 psu, and we recommend additional data collection.

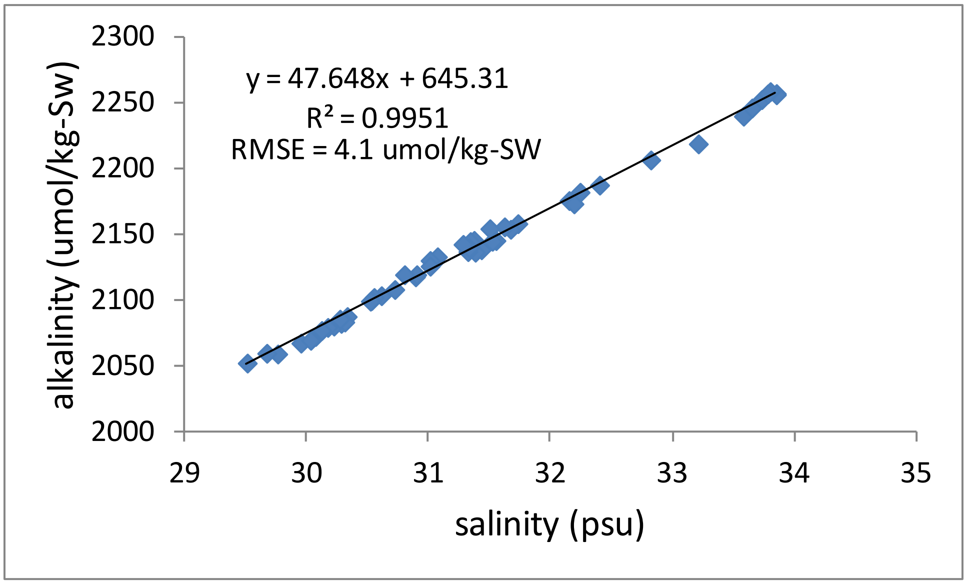

Figure 3. Linear regression of alkalinity and salinity from a subset of the PMEL-PRISM data from the Salish Sea.

This regression is preliminary and subject to revision and is intended only to demonstrate the feasibility of the approach. The regression equation shown in this figure should not be used, and instead a regression from the complete data set will be used for this project.

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[2] Environmental Information Management

4.0 Existing Information and Anticipated Data Gaps

The investigation of ocean acidification in Washington is relatively new. No comprehensive monitoring program has been designed to describe critical parameters or patterns. Several recent studies and ongoing efforts provide some existing information, although extensive data gaps remain.

Data needed for acidification modeling can be described in three general categories: (1) boundary conditions for inputs, (2) marine monitoring for initial conditions and model comparisons, and (3) process-based parameters to understand specific components of the system.

First, acidification modeling will require boundary condition time series to characterize the Pacific Ocean incoming water; meteorological parameters such as precipitation quantity and quality, wind speed and direction, and cloud cover; sediment fluxes; and freshwater inputs such as river and marine wastewater outfall quantity and quality. Boundary conditions used for the current DO model of the Salish Sea are described in Mohamedali et al. (2011) for the period 1999 to 2008. However, additional parameters will be needed for acidification modeling:

- **Pacific Ocean water entering the model domain:** The model will need at least two of the four carbon system parameters (pH, alkalinity, pCO_2, TDIC) for the Strait of Juan de Fuca and also the Johnstone Strait boundary, especially for near-bottom water with a net inflow to the model domain. In addition, if the model is expanded to include phosphorus and silica, the ocean boundary also will need time series for dissolved and particulate phosphorus and particulate and dissolved silica.
- **Air-sea exchanges of carbon:** While CO_2 fluxes may be scaled from oxygen reaeration, the model will need atmospheric pCO_2 across the model domain to determine flux direction and magnitude. In addition, because the project purpose is to distinguish the effect of human activities, the proportion from regional human sources relative to global atmospheric and regional natural pCO_2 must be estimated. Atmospheric deposition is a source of alkalinity and phosphorus directly to the marine surface.
- **Sediment fluxes:** The approach used in the current DO model prescribes sediment fluxes to the water column, and values for the carbon system parameters (alkalinity, TDIC) would be needed. Ongoing work will develop sediment diagenesis functions in the DO model. Additional information would be needed to calibrate the sediment diagenesis process on acidification.
- **Freshwater inputs:** Time series must be developed for carbon system parameters for all watershed inflows and wastewater treatment plants discharging to marine waters. In addition, because the project purpose is to distinguish the effect of regional human activities, the proportion of carbon from regional human activities in rivers must be estimated. Also, if the baseline year selected is after 2008, then the time series described in Mohamedali et al. (2011) for parameters related to DO modeling would need to be extended.

Second, model comparisons require ambient data to check for model errors, to calibrate, and to estimate uncertainty in the predictions. Marine data used to check the DO model are described in Yang et al. (2010) and Khangaonkar et al. (2012). These include both circulation parameters such as salinity and temperature profiles but also water quality data. While the circulation data are common to both DO and acidification modeling, additional water quality parameters are needed to test the model predictions of the carbon system and related parameters:

- At least two of the four carbon system parameter concentrations are needed at key locations within the model domain covering the water column in shallow- and deep-water regions over time, since the others can be computed from the first two. Selection should consider what combination provides the lowest uncertainty in describing the other two parameters, based on an initial analysis of available information. Sea surface pCO_2 is particularly needed to verify the direction and magnitude of the air-sea flux of CO_2. We recommend marine alkalinity measurements where salinity is below 29 psu, and as low as 20 psu.
- Saturation state of aragonite, Ω_{arag}, as well as Ca^{2+} concentration will be needed throughout the Salish Sea, from the surface through the water column, and over time.
- Phosphorus data are needed if the acidification model is expanded to include phosphorus. The current DO model has not been calibrated to phosphorus, which will have a secondary effect on alkalinity.
- Particulate and dissolved silica are needed throughout the water column if the acidification model is expanded to include dissolved silica. The current DO model has not been calibrated to dissolved silica, and we assume that silica is not limiting. If these are included in the future, then TSS should be considered as well.

Finally, acidification modeling requires physical, chemical, and biological rate parameters to describe the processes that govern the carbon system. Because many of the processes also influence DO, several parameters have been studied or calibrated during the development of DO modeling in the region. Khangaonkar et al. (2012) describes DO modeling rate processes for parameters common to acidification simulation, such as algal respiration and growth rate. Additional process information is needed for acidification modeling:

- Dissociation constants, K_1 (Equation 36) and K_2 (Equation 37) for salinities that typically range from 25 to 35 psu but can be <20 psu at the surface during high river flows.
- Carbon dioxide air-sea exchange rate $K_{a,CO_2^*(aq)}$
- Silica parameters, if the model is expanded to simulate it as a state variable.
- Aragonite and calcite apparent solubility products, $K_{sp}*_{arag}$ and $K_{sp}*_{calc}$, which vary with temperature, salinity, and pressure. A relationship between salinity and Ca^{2+} will be needed to estimate Ca^{2+} from salinity as well, unless Ca^{2+} is simulated as a state variable.

Several monitoring programs address some of these data needs. However, significant information gaps remain, as described below.

4.1 Ecology's monthly ambient monitoring program and South Puget Sound Dissolved Oxygen Study

Ecology has monitored water quality monthly from dozens of core (annual) and rotating (approximately every 5 years) stations throughout Puget Sound and the Straits. Data are available from www.ecy.wa.gov/programs/eap/mar_wat/index.html, and www.ecy.wa.gov/programs/eap/mar_wat/index.html provides an overview of the marine ambient monitoring program. Results have been used in the Salish Sea DO model comparisons.

In addition to parameters used in the DO modeling application (including DO, chlorophyll, nitrate, and ammonia) the marine ambient monitoring program includes pH. Since 1989, pH data have been recorded using a Seabird Electronics instrument (SBE18). However, these data have not been checked for quality assurance and their accuracy assessed for use in model comparisons. The program does not include alkalinity, pCO_2, or TDIC, although alkalinity monitoring is proposed for 2014 in limited locations.

Ecology's freshwater ambient monitoring program covers large and intermediate rivers discharging to Puget Sound and the Straits (www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html). The program includes monthly monitoring of nitrogen species (total nitrogen, nitrate, ammonium), phosphorus species (total phosphorus, orthophosphate), temperature, DO, and pH. A few stations have continuous monitoring data for temperature, DO, pH, and nitrate, including the Deschutes River (June to November 2011). Carbon data are not typically collected. Limited alkalinity data are available for larger rivers but mostly from the 1970s and 1980s.

Ecology conducted targeted monitoring in the South and Central Puget Sound marine waters and watershed in 2006 and 2007 (Roberts et al., 2008). In addition to parameters monitored in the ambient monitoring program, the South and Central Sound marine data set includes total nitrogen and total dissolved nitrogen, which can be used to estimate dissolved organic nitrogen and particulate organic nitrogen; total organic carbon, and particulate carbon. The river and wastewater treatment plant data include alkalinity, pH, total organic carbon, and dissolved organic carbon. No subsequent studies of these parameters have occurred.

4.2 Wastewater treatment plant monitoring data

Wastewater treatment plants that discharge to the marine waters of Washington must comply with requirements established in the individual National Pollutant Discharge Elimination System (NPDES) permits. The Department of Ecology issues these permits under the federal Clean Water Act. EPA has delegated authority to the State of Washington to enforce this part of the Clean Water Act. Permits are issued for 5-year periods.

Permits include effluent limits, effluent monitoring requirements, and may also include receiving water monitoring requirements, in addition to other plant-specific information. Permits for the discharge from a municipal wastewater treatment plant require that effluent must discharge at pH above 6.0 SU and below 9.0 SU. Each plant also has a limit for carbonaceous (5-day) biochemical oxygen demand as a concentration in mg/L averaged over a week and a month, as well as a load expressed as lbs/d. One plant has a limit for total inorganic nitrogen, but no other plant has this limit. Several plants monitor nitrogen concentrations in the effluent as a reporting requirement. Some, but not all plants, monitor effluent alkalinity, but at a lower frequency than other discharge monitoring parameters. Receiving water monitoring includes DO and pH, but generally not alkalinity or other carbon system parameters.

Most wastewater treatment plant technologies typically do not modify the alkalinity during the treatment process unless the plant is designed and operated to nitrify ammonia to nitrate. Therefore, alkalinity in treated municipal wastewater generally reflects the drinking water supply alkalinity. Alkalinity tends to be higher in groundwater sources than in surface water.

4.3 Department of Fisheries and Oceans ambient monitoring programs

Scientists from Canada's Department of Fisheries and Oceans (DFO) are monitoring ocean acidification along the Pacific Coast. The Southern Coastal Waters monitoring includes profiles and buoys of salinity and temperature. DFO has monitored dissolved inorganic carbon, alkalinity, pH, nutrients, salinity, and DO at deep rosette casts on the Pacific Ocean Line P.

4.4 Cruises

Several organizations conduct intensive monitoring during periodic scientific cruises within the Puget Sound / Georgia Basin, either within a particular organization or in partnership across several organizations. Many were described in Feely et al. (2012).

Since 1998, the PRISM (Puget Sound Regional Synthesis Model) program at University of Washington has conducted semiannual cruises to ~40 stations within the greater Puget Sound basin. The cruises are designed to collect a synoptic snapshot of the oceanographic conditions in Puget Sound in summer and winter. These cruises routinely collected basic water column measurements: temperature, salinity, oxygen, nutrients, chlorophyll, and often other samples, depending on interest. In February 2008, NOAA-PMEL participated in the UW-PRISM cruise and measured TDIC and TA within Puget Sound aboard the R/V Thompson (Simone Alin, personal communication, 2/26/13 email; http://www.pmel.noaa.gov/co2/story/PRISM+cruise+February+2008).

In August 2008, EPA's Ocean Survey Vessel Bold hosted the UW-PRISM cruise in collaboration with Ecology and NOAA-PMEL. Measured data include discrete samples from multiple depths analyzed for pH, alkalinity, TDIC, and pCO_2 measurements in water plus atmospheric pCO_2. Discrete spectrophotometric pH data have not been finalized, but the other parameters have been reviewed and assessed (Simone Alin, personal communication, 2/26/13 email) and published in Feely et al. (2010).

In October 2011, a PRISM/NANOOS cruise focused on Puget Sound was held by UW, again with NOAA staff invited to measure OA variables. The measurements included TDIC, alkalinity, and discrete spectrophotometric pH. The pH data are still being assessed for quality assurance, but the other parameters have been reviewed and assessed (Simone Alin, personal communication, 2/26/13 email).

Additional cruises by NOAA-PMEL in 2007, 2011, and 2012 focused on the Pacific coast and did not include data within Puget Sound and the Straits. However, results may help describe carbon system parameters and may be applicable to Puget Sound or Pacific Ocean characteristics to consider for boundary conditions. For further information on the 2007 cruise, see http://cdiac.ornl.gov/oceans/Coastal/NACP_West.html.

UW's Friday Harbor Laboratories conducts monthly or semi-monthly cruises in winter, spring, and summer but increases frequency to weekly in the fall (Jan Newton, personal communication, 3/1/13 email). Parameters include TDIC, alkalinity, temperature, salinity, oxygen, chlorophyll, and nutrients (pH is calculated from TDIC and alkalinity). Many variables are available from NANOOS, although the TDIC and alkalinity data must be requested from UW. The survey visits two stations:

- North: 48º 35.00' N, 123º 02.50' W
- South: 48º 25.20' N, 122º 56.60' W

Canada's DFO conducts annual cruises along Line P to Ocean Station Papa (www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/line-p/2010-14/Documents/2010-14_post_cruise_report.pdf).

4.5 Moorings and other continuous data

Several organizations, independently or collaborating with others, monitor continuous data in time or space that may be relevant to acidification modeling. Many were described in Feely et al. (2012).

UW operates ORCA buoys instrumented for acidification-related parameters at Dabob Bay and Twanoh, in collaboration with NOAA and funded in part by EPA (Newton and Devol, 2012). The Twanoh and Dabob profiling buoys include DO, temperature, salinity, chlorophyll, current velocity, and nitrate. The stations also include surface water and atmospheric pCO_2, but do not monitor pH. The pCO_2 data are viewable through NANOOS but the data must be requested and must be checked for quality control. Feely et al. (2012) summarizes the buoy data, which are available through www.nanoos.org.

NOAA's Ocean Acidification program and the U.S. Integrated Ocean Observing System fund a buoy at La Push as part of NANOOS. Measurements include continuous pCO_2 and pH at several depths and profiles of temperature, salinity, DO, nitrate, and chlorophyll (Feely et al., 2012). NOAA's National Buoy Data Center also operates a buoy at Cape Elizabeth, but the NOAA-PMEL CO_2 system measurements may not continue.

Researchers at the University of Chicago have monitored acidification-related parameters at Tatoosh Island, where the Pacific Ocean and the Strait of Juan de Fuca meet. Wootton and Pfister (2012) describe late spring through late summer monitoring at 30-minute intervals using a

Hydrolab DataSonde for pH, temperature, DO, and salinity. Discrete samples were collected monthly from April to September from 10 stations around Tatoosh Island and 4 stations on a transect extending offshore. Samples were analyzed for dissolved silica, nitrate, nitrite, and ammonium. Measurements were from a tide pool, but the site was representative of local ocean conditions. Eighty-nine discrete samples collected in 2009 and 2010 were also analyzed using spectrophotometric pH to compare with the Hydrolab values. Wootton and Pfister (2012) also assessed water quality in offshore transects to determine that the monitoring locations were broadly representative of the region and not an artifact of an unusual local condition.

NOAA, in collaboration with the Seattle Aquarium, monitors the seawater intake for the Seattle Aquarium and has been testing various instruments for oxygen, pCO_2, and TDIC. The data would need to be assessed by NOAA prior to using quantitatively to check for representativeness of Puget Sound conditions and to rule out respiration in the intake (Simone Alin, personal communication, 2/26/13 email).

NOAA collected and analyzed discrete water samples from Totten Inlet in South Puget Sound and Dabob Bay in Hood Canal in 2009-2010. The samples were analyzed weekly for TDIC and TA in late 2009 and throughout the 2010 growing season. Continuous pH data were collected in 2011 using an in situ probe and would need to be assessed by NOAA for data quality prior to using (Simone Alin, personal communication, 2/26/13 email).

Taylor Shellfish Farms operates the Dabob Bay hatchery in Hood Canal. Sensors monitor pCO_2 and pH as well as temperature and salinity at two depths.

The Pacific Shellfish Institute collaborates with the Lummi Tribe to conduct continuous monitoring at the Lummi Hatchery (Andy Suhrbier, personal communication, 2/28/13 email). Discrete samples are analyzed for nutrients and TDIC, total CO_2, alkalinity, pCO_2, pH; calcite saturation and aragonite saturation are calculated from other variables. A YSI 6600 has recorded pH, DO, temperature, salinity and chlorophyll for the past two years. The Pacific Shellfish Institute also monitors carbon chemistry twice a month at a station on Harstine Island in South Puget Sound and has a YSI installed at two locations.

Western Washington University monitors water quality in a seawater intake at Shannon Point in Bellingham Bay. Parameters include pH but not carbonate system parameters (Brooke Love, personal communication, 4/9/13 email). The data have not yet been assessed for usability.

4.6 Rate parameters

Very little information exists to characterize key rate parameters related to acidification for Puget Sound /Georgia Basin conditions. Recent and ongoing analyses by NOAA-PMEL may be mined to assess dissociation constants based on preliminary analyses by Simone Alin and Greg Pelletier, but results have not been finalized or published. Newton et al. (2013) summarizes literature related to productivity and acidification, including how various efforts characterize the carbonate system and rate processes. However, the evaluation did not locate regional rate parameters. Appendix A of that document includes additional information on rate parameters but not necessarily specific to Puget Sound conditions.

4.7 Primary information gaps

Recent and ongoing studies of DO in Puget Sound, the Straits, and various inlets have identified a few parameters that lead to the greatest uncertainty in DO predictions, and these would also affect acidification modeling. These include physical, chemical, and biological processes.

Studies of DO in Hood Canal found that the greatest source and also the greatest uncertainty in nitrogen driving algal growth is the amount of nitrogen mixing into the euphotic zone from deeper marine waters (summarized in Cope and Roberts, 2013). The highest estimates based on data are 30 times the lowest estimates based on aggregated modeling. This produces an uncertainty range of an order of magnitude for predicted DO for regions of Hood Canal. Gaps in understanding of physical mixing processes, particularly at sills, will affect acidification and other modeling of the Salish Sea.

In late summer, sediment fluxes of nitrogen can be the largest local source of nitrogen (Roberts et al., 2008; DeGasperi, 2010; DeGasperi, 2012) but also have the greatest uncertainty in the local nitrogen source estimates. Sediment fluxes represent recycled nutrients from autochthonous production (productivity within the model domain) and allochthonous inputs (fluxes from ocean, atmosphere, and watershed boundary conditions). Khangaonkar et al. (2012) prescribe these fluxes based on best available information, but very little data exist to quantify such an influential process. This is an information gap that will also affect acidification modeling. Sheibley and Paulson (2014) recently summarized available information on Puget Sound benthic fluxes.

Biological processes strongly influence DO and acidification. No comprehensive monitoring program surveys phytoplankton abundance and communities throughout the system, and chlorophyll is the primary proxy used to describe spatial and temporal patterns. This information gap also will influence acidification modeling.

Very little information exists on alkalinity, pCO_2, or TDIC in the marine waters of Puget Sound and the Straits, including the water masses entering from the Pacific Ocean. Newer pH instruments that improve precision and reliability have been used in only limited monitoring. While other pH data exist, quality assurance protocols must be applied to assess usability for acidification modeling. Aragonite saturation requires the concentration of Ca^{2+}. Either marine data are needed or a relationship that describes Ca^{2+} as a function of salinity.

Finally, very few process studies have characterized rate parameters under the range of conditions present in the Salish Sea. These include dissociation constants under low salinity.

Given these information gaps, however, we recommend an iterative approach to modeling acidification in the Salish Sea. The initial model development would be based on available information and must assess the uncertainty in resulting predictions. Sensitivity analyses with the initial modeling tools will provide a solid foundation for identifying what rate constants or parameter values have the strongest influence on predicted acidification or result in a large uncertainty in predictions. This information could be used to refine monitoring programs in the future.

5.0 Model Performance and Calibration Approach

Simulating acidification will require software code development, testing, and calibration to Salish Sea conditions prior to exploring the relative influence of regional and global human activities. This will occur in two phases, introduced below.

5.1 FVCOM-ICM acidification model performance tests

First, the revised model will be tested against exact analytical solutions under idealized conditions and controlled experiments. The goal is to test for model errors in coding and model concepts to verify that the model provides the expected performance. Three potential sequential tests could be conducted as part of model QA/QC prior to initiating calibration to Salish Sea data.

- Simple exact solution test (comparison to CO2SYS) with a batch reactor

  Exact solutions exist for simple cases (e.g., well mixed solution with closed lateral boundaries at equilibrium with atmosphere) where we know total alkalinity and total dissolved inorganic carbon (TDIC). The FVCOM-ICM model results of pH and pCO_2 may be compared with the analytical results and results of CO2SYS model as a QA/QC test of pH kinetics newly incorporated into the code.

  Tests: TDIC-pH equilibration with the atmosphere; biogeochemical effects on alkalinity with constant TDIC; algal effects on TDIC and alkalinity and TDIC.

- Simple one-dimensional, steady-state channel case

  A more comprehensive test case is through an idealized channel with a steady freshwater input with or without tides under different pCO_2 cases. Exact solutions may or may not exist depending on the components being tested. However, in a fully mixed condition beyond the mixing zone, the model result may be compared with spreadsheet based models such as CO2SYS/pHmix3. The channel test case may also be used to test responses of pH to wind, mass balance of TDIC, total alkalinity, effects of temperature control, effects of biological loops, benthic fluxes, etc.

- Simple one-dimensional, dynamic channel case

  Similar to steady-state conditions, but with time-varying freshwater inputs to test responses to dynamic input.

5.2 Calibration for the Salish Sea

Following completion of the above model tests, the model will be applied to simulate a selected year over the Salish Sea domain. Selection of the baseline year for setup and calibration of the acidification model for Salish Sea model will depend on available data. We recommend that this be conducted in two steps. First, we will apply the model to a selected baseline year by specifying the boundary conditions and river loads based on available data. There are three options for selecting the baseline year, and we recommend option 1 for the initial calibration, with a subsequent recalibration as under option 3:

1. Use 2006 or 2007 since the existing DO application has been calibrated and applied for those years. While more acidification data are available for other years, this will test whether predictions are within reasonable ranges; however, this may result in a rough calibration with high uncertainty, depending on data limitations.

2. Apply the model to 2008, 2011, or 2012 by updating the initial and boundary conditions. More acidification data are available for these time periods, although less boundary condition data are available. This may result in a rough calibration with high uncertainty, depending on data limitations.

3. Defer model application until more complete monitoring programs occur. Several organizations are currently discussing options for monitoring programs. These would not be expected to begin until 2014 and would likely require 2015 to complete data quality assurance and compilation. Therefore, calibration to a new, more complete dataset would not likely begin until 2016. This could be considered a follow-up calibration should the uncertainty in predictions based on calibrating to existing data be too large for management action.

The model calibration effort will consist of running the model and comparing the results to observed data (TDIC, alkalinity and pH) for different locations and time periods. In the first step the model will be set up using literature-based values for model rate constants.

A series of sensitivity tests will then be carried out by perturbing the baseline case for key parameters and modules in the model, including the effects of ocean boundary conditions, surface winds, ammonia preference in nutrient uptake, precipitation, and sinking of aragonite. Additional sensitivity tests will explore remineralization of particulate organic carbon (POC) and dissolved organic carbon (DOC) under different oxygen regimes, denitrification, as well as sediment fluxes of TDIC.

Additional details on calibration approach will be developed in the subsequent QA Project Plan, pending funding.

6.0 Next Steps and Recommendations

Ecology's task is to quantify the degree to which regional human sources (water nutrients and air emissions) exacerbate acidification, which is expected to be dominated by the effects of the Pacific Ocean and global atmospheric carbon dioxide. However, as a regulatory agency, Ecology must determine if and how much regional sources must be controlled.

Modeling acidification will be challenging given that knowledge of the processes governing acidification and the datasets that describe the system are incomplete. Plans are underway to improve monitoring, but results will not be available until 2015 or later. However, we anticipate that regional leaders will want to know soon whether or not and where regional sources should be controlled to mitigate any impact. This modeling effort will help inform decision makers where investments will have the greatest benefit and also the degree of uncertainty in the answer. We also anticipate that this initial application to acidification will result in considerable uncertainty in the results that will likely require subsequent model development once better monitoring information becomes available.

No funding is currently available to pursue acidification model development that evaluates the relative impacts from regional human sources. In advance of model development, EPA funded this initial compilation of the modeling approach. When funded, the next phase will begin with the development of a more detailed modeling QA Project Plan, building from this approach document. The QA Project Plan must be drafted, reviewed, and published before model development and application begin. This approach document will be shared with groups currently discussing monitoring needs for acidification. The subsequent modeling QA Project Plan will reflect specific plans for monitoring to fill information gaps in collaboration with other organizations.

As part of any future QA Project Plan development, we recommend several analyses:

- Perform sensitivity tests of how errors in measured parameters propagate to remaining carbon system parameters. For example, evaluate the sensitivity of carbon system parameters to variations in freshwater inputs from rivers and wastewater treatment plants.
- Evaluate sources of calcium data for freshwater inputs and ocean boundary conditions.
- Evaluate seasonal silica patterns to test the assumption that silica has a negligible effect on alkalinity variability and is not a limiting factor for phytoplankton growth.
- Evaluate the assumption that phosphorus has a negligible effect on alkalinity variations.
- Collaborate with Pacific Ocean models to establish boundary conditions.
- Collaborate with NOAA on atmospheric and surface water pCO_2 to explore seasonal flux patterns.
- Collaborate with NOAA to propose methods or derive relationships between alkalinity and salinity using NOAA data from the Salish Sea for the purpose of estimating alkalinity at the model open boundary.

Ocean acidification modeling and data collection will both require multiple iterations to succeed in understanding the relative contributions of different regional and global human contributions to acidification in the Salish Sea. Modeling will inform monitoring, and monitoring will inform modeling as well.

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Appendices

Appendix A. Equilibrium Constants of Key Chemical Reactions – pH Model

A key to the success of the method in solving ocean pH kinetics described in Section 3.2 is to have reasonably accurate values for the chemical equilibrium constants of the reactions. Here we summarize the rates and estimates based on literature. (Note that little is known on the impact of turbulent kinetic energy (TKE) on these reaction rates)

- K_0 (mole/L/atm)

Weiss solubility constant for K_0 (mole/L/atm.) (equation (16)) in seawater is calculated as (Robbins et al., 2010; Weiss, 1974)

$$K_0 = A_1 + A_2\left(\frac{100}{T}\right) + A_3 \ln\left(\frac{T}{100}\right) + S[B_1 + B_2\left(\frac{T}{100}\right) + B_3(\frac{T}{100})^2] \quad \text{(A1)}$$

where T is temperature (Kelvin), S is salinity (psu), $A_1, A_2, A_3, B_1, B_2, B_3$ are given in Weiss (1974) :

$$A_1 = -58.0931, \qquad A_2 = 90.5069, \qquad A_3 = 22.2940 \quad \text{(A2)}$$

$$B_1 = 0.027766, \qquad B_2 = -0.025888, \qquad B_3 = 0.0050578 \quad \text{(A3)}$$

- $K_{a,CO_2^*(aq)}$ (meter/day)

CO_2 gas transfer coefficient $K_{a,CO_2^*(aq)}$ is given by Wanninkhof (1992), Nightingale et al. (2000), and Ho et al. (2006)

$$K_{a,CO_2^*(aq)} = k \times K_0 \times 24/1000000 \quad \text{(A4)}$$

where k is empirically related to wind speed:

$$k = \begin{cases} 0.31U^2\sqrt{\frac{660}{S_c}} & \text{Wanninkhof (1992)} \\ (0.33U + 0.222U^2)\sqrt{\frac{600}{S_c}} & \text{Nightingale (2000)} \\ 0.266U^2\sqrt{\frac{600}{S_c}} & Ho\ \text{(2006)} \end{cases} \quad \text{(A5)}$$

and S_c is Schmidt number empirically related to temperature T (Kelvin) as (Robbins et al., 2010)

$$S_c = A - B(T - 273.15) + C(T - 273.15)^2 - D(T - 273.15)^3 \quad \text{(A6)}$$

and

$A = 2073.1,$ $C = 3.6276,$ (A7)
B$= 125.62,$ $D = 0.043219$

Raymond and Cole (2001) provided some measurements of k at $S_c = 600$ with varying wind speed.

- $K_1,\ K_2$ (mole/L)

The equilibrium constants of $K_1,\ K_2$ for dissociation of carbon dioxide and bicarbonate are dependent on the pH scale selected. Essentially, $K_1,\ K_2$ can be defined differently using different pH scales. Equations

$$K_{1,F} \equiv K_1 = \frac{[H^+][HCO_3^-]}{[CO_2^*]} \tag{A8}$$
$$K_{2,F} \equiv K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{A9}$$

are used to define equilibrium constants based on free proton concentration $[H^+]$. In practice, due to difficulties in measuring $[H^+]$, total scale $[H_T^+]$ and seawater scale $[H_{SWS}^+]$ are used instead, which means that the measured rates would be defined as follows.

$$K_{1,T} = \frac{[H_T^+][HCO_3^-]}{[CO_2^*]} \tag{A10}$$
$$K_{2,T} = \frac{[H_T^+][CO_3^{2-}]}{[HCO_3^-]} \tag{A11}$$

for total scale and

$$K_{1,SWS} = \frac{[H_{SWS}^+][HCO_3^-]}{[CO_2^*]} \tag{A12}$$
$$K_{2,SWS} = \frac{[H_{SWS}^+][CO_3^{2-}]}{[HCO_3^-]}$$

(A13)

for seawater scale. The relationships of these constants are described by (see Millero 2010)

$$K_{1,F} \equiv K_1 = K_{1,SWS}/(1 + C_{TS}/K_S + C_{TF}/K_F) \tag{A14}$$
$$K_{2,F} \equiv K_2 = K_{2,SWS}/(1 + C_{TS}/K_S + C_{TF}/K_F) \tag{A15}$$
$$K_{1,T} = K_{1,SWS}(1 + C_{TS}/K_S)/(1 + C_{TS}/K_S + C_{TF}/K_F) \tag{A16}$$
$$K_{2,T} = K_{2,SWS}(1 + C_{TS}/K_S)/(1 + C_{TS}/K_S + C_{TF}/K_F) \tag{A17}$$

For saline waters (Salinity > 19 psu), Dickson et al. (2007) and Lueker et al. (2000) presented regression of $K_{1,T}$ and $K_{2,T}$ against temperature T (Kelvin) and salinity S (psu) using measured data from Mehrbach et al. (1973)

$$log_{10}(K_{1,T}[mole/kg]) = \frac{-3633.86}{T} + 61.2172 - 9.67770\ln(\mathrm{T})$$

$$+0.011555S - 0.0001152S^2 \tag{A18}$$

$$log_{10}(K_{2,T}[mole/kg]) = \frac{-471.78}{T} - 25.9290 + 3.16967\ln(T) + 0.01781S - 0.0001122S^2 \tag{A19}$$

We then can convert K_1, K_2 from mole/kg unit to mole/L unit (if necessary).

For estuarine waters, Cai and Wang (1998) provided the following calculation

$$pK_1 = \frac{3404.7}{T} + 0.032786 \times T - 14.843 - 0.071692 \times F(T) \times \sqrt{S} + 0.0021487 \times S \times F(T) \tag{A20}$$

$$pK_2 = \frac{2902.39}{T} + 0.02379 \times T - 6.4980 - 0.3191 \times (1.4381 - \frac{129.24}{T}) \times \sqrt{S} + 0.0198 \times S \tag{A21}$$

where $F(T)$ is not given in the publication, T is in Kelvin and S is in psu. More recently, Millero (2010) gives the following formula

$$pK_{i,*} = pK_i^0 + A_i + \frac{B_i}{T} + C_i \ln(T) \qquad (i = 1,2) \tag{A22}$$

where $pK_{i,*}$ represents free scale, total scale or seawater scale values of K_i, and $pK_{i,*} = -log_{10}K_{i,*}$ and pK_i^0 (i=1,2) are pure water values obtained by fitting (Millero et al. 2006) data from Harned and Scholes (1941) and Harned and Bonner (1945)

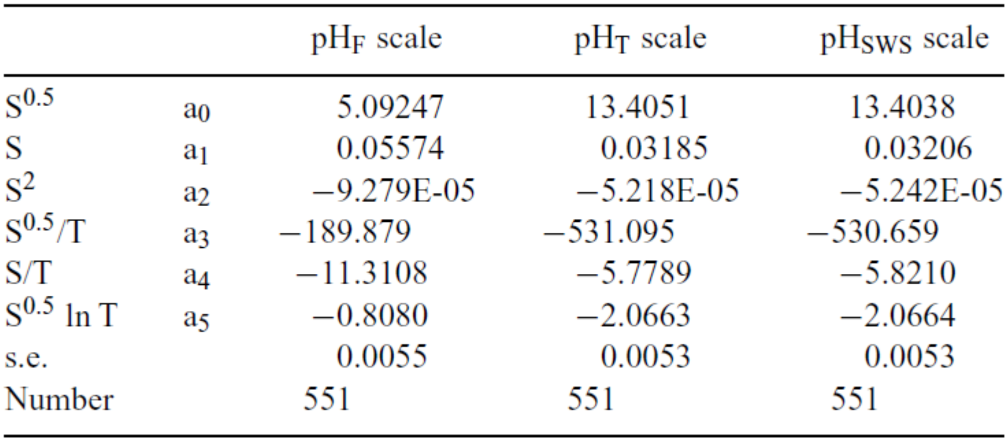
$$pK_1^0 = -126.34048 + 6320.813/\text{T} + 19.568224 \ln \text{T} \tag{A23}$$
$$pK_2^0 = -90.18333 + 5143.692/\text{T} + 14.613358 \ln \text{T} \tag{A24}$$

Coefficients in (A22) are

$$A_i = a_0\sqrt{S} + a_1S + a_2S^2 \tag{A25}$$
$$B_i = a_3\sqrt{S} + a_4S \tag{A26}$$
$$C_i = a_5\sqrt{S} \tag{A27}$$

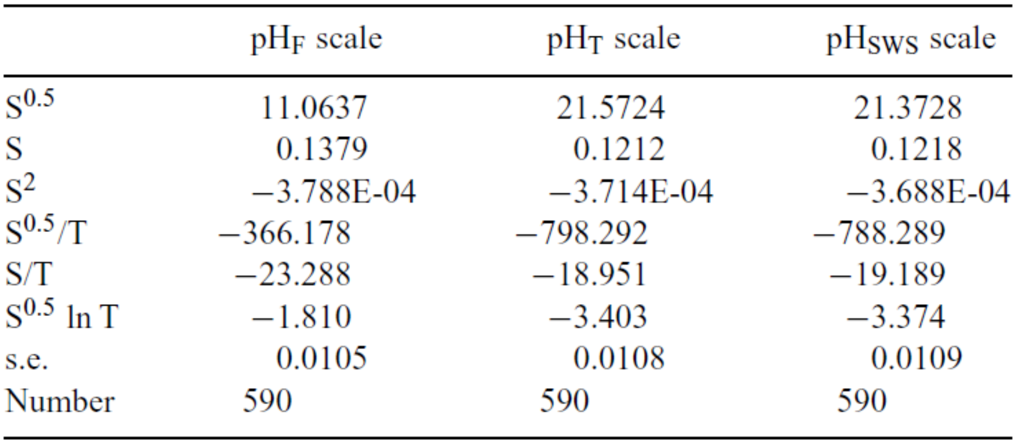
with $a_0 \sim a_5$ tabulated (Millero 2010) in tables A-1 and A-2 below for $pK_{i,*}$ (i=1,2)

Table A-1. Coefficients for $pK_{1,*}$ fitting (from Millero 2010).



		pH_F scale	pH_T scale	pH_{SWS} scale
$S^{0.5}$	a_0	5.09247	13.4051	13.4038
S	a_1	0.05574	0.03185	0.03206
S^2	a_2	−9.279E-05	−5.218E-05	−5.242E-05
$S^{0.5}/T$	a_3	−189.879	−531.095	−530.659
S/T	a_4	−11.3108	−5.7789	−5.8210
$S^{0.5}$ ln T	a_5	−0.8080	−2.0663	−2.0664
s.e.		0.0055	0.0053	0.0053
Number		551	551	551

Table A-2. Coefficients for $pK_{2,*}$fitting (from Millero 2010).



	pH_F scale	pH_T scale	pH_{SWS} scale
$S^{0.5}$	11.0637	21.5724	21.3728
S	0.1379	0.1212	0.1218
S^2	−3.788E-04	−3.714E-04	−3.688E-04
$S^{0.5}/T$	−366.178	−798.292	−788.289
S/T	−23.288	−18.951	−19.189
$S^{0.5}$ ln T	−1.810	−3.403	−3.374
s.e.	0.0105	0.0108	0.0109
Number	590	590	590

- K_w ((mole/L)(mole/L))

Based on seawater scale definition of K_w

$$K_{w,SWS} = [H^+_{SWS}][\, OH^-_{SWS}], \tag{A28}$$

where $[\, OH^-_{SWS}]$ is seawater scale concentration of hydroxide, Dickson and Riley (1979) measured K_w under different temperature T (Kelvin) and ionic strength I with artificial seawater. The regressed results in terms of temperature T (Kelvin) and ionic strength I or salinity S (psu) are given as (Dickson and Riley 1979 equation (6) and equation (7))

$$pK_{w,SWS}\left(\left(\frac{mole}{kg-water}\right)^2\right) = \frac{3441.0}{\mathrm{T}} + 2.256 - 0.709\sqrt{I} \tag{A29}$$

$$pK_{w,SWS}\left(\left(\frac{mole}{kg-water}\right)^2\right) = \frac{3441.0}{\mathrm{T}} + 2.241 - 0.9415\sqrt{S} \tag{A30}$$

Millero (1995) provided free pH scale value of K_w

$$\ln(K_w(\frac{mole}{kg})) = 148.9802 - \frac{13847.26}{\mathrm{T}} - 23.6521 \ln \mathrm{T} \\ + \left(-5.977 + \frac{118.67}{T} + 1.0495 \ln T\right) \sqrt{\boldsymbol{S}} - 0.01615S \qquad \text{(A31)}$$

Hence we can also convert from mole/kg-solution unit to mole/L units using above values.

- K_B (mole/L)

Dickson (1990b) conducted study on thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K (also see Millero, 1995)

$$\ln\left(K_{B,T}\left(\frac{mole}{kg}\right)\right) = (-8966.90 - 2890.51\sqrt{S} - 77.942S + 1.726\mathrm{S}^{\frac{3}{2}} - 0.0993\mathrm{S}^2)/\mathrm{T} \\ +(148.0248 + 137.194\sqrt{S} + 1.62247S) + (-24.4344 - 25.085\sqrt{S} - 0.2474S)\ln T \\ +0.053105\sqrt{S}T \qquad \text{(A32)}$$

Roy et al. (1993) measured dissociation of boric acid in seawater at S = 35 psu and temperature from 0 to 55 °C using total scale and the fitted dissociation constant as a function of T (Kelvin) is (see equation (15) in Roy et al. 1993)

$$\ln\left(K_{B,T}\left(\frac{mole}{kg}\right)\right) = -\frac{31364.3974}{T} + 1124.3838 \\ -200.46578 \ln T + 0.346237T \qquad \text{(A33)}$$

where $K_{B,T}$

$$K_{B,T} = \frac{[H_T^+][B(OH)_4^-]}{[B(OH)_3\ ]} \qquad \text{(A34)}$$

Conversion to free scale and mole/L unit can be done with the knowledge of C_{TS}, K_S and density of the seawater.

- K_S (mole/L)

Khoo et al. (1977a, equation (20)) gives the following regression equation of K_S (free scale) based on measurements from 0 to 40 °C and salinity from 20 to 45 psu.

$$log_{10}K_S\left(\frac{mole}{kg-solution}\right) = -\frac{647.59}{T} + 6.3451 - 0.019085T + 0.5208\sqrt{I} \qquad \text{(A35)}$$

where T is temperature (Kelvin) and I is ionic strength (mole/kg) related to salinity by (Khoo et al. 1977, equation (8))

$$I = 0.0029 + 0.018575S + 1.639 \times 10^{-5}S^2 \qquad \text{(A36)}$$

Dickson (1990a) measured K_S in synthetic seawater with temperature from 273.15 to 318.15 K, and the free scale K_S is regressed with temperature and ionic strength I as (equation (23) in Dickson (1990a))

$$\begin{aligned}\ln\left(\mathrm{K_S}(\tfrac{\mathrm{mole}}{\mathrm{kg-solution}})\right) &= \ln\left(\mathrm{K_S}^0\right)\\ &+\left(\tfrac{\mathrm{e_1}}{\mathrm{T}}+\mathrm{e_2}+\mathrm{e_3}\ln\mathrm{T}\right)\sqrt{\mathrm{I}}\\ &+\left(\tfrac{\mathrm{e_4}}{\mathrm{T}}+\mathrm{e_5}+\mathrm{e_6}\ln\mathrm{T}\right)\mathrm{I}\\ &+\mathrm{e_7}(\sqrt{\mathrm{I}})^3+\mathrm{e_8}\mathrm{I}^2\end{aligned} \tag{A37}$$

with

$$\ln\left(K_S{}^0(\tfrac{mole}{kg-solution})\right)=\tfrac{d_1}{T}+d_2+d_3lnT \tag{A38}$$

where T is temperature (Kelvin), I is ionic strength (mole/kg). Coefficients d_1, d_2, d_3, e_1~ e_8 are given as

$$d_1=-4276.1 \quad d_2=141.328 \quad d_3=-23.093 \tag{A39}$$

$$\begin{aligned}&e_1=-13856 \quad e_2=324.57 \quad e_3=-47.986\\ &e_4=35474 \quad e_5=-771.54 \quad e_6=114.723\\ &e_7=-2698 \quad e_8=1776\end{aligned} \tag{A40}$$

The conversion from free scale to total scale is

$$K_{S,T}\equiv\frac{[H_T^+][SO_4^{2-}]}{[HSO_4^-]}=\left(1+\frac{C_{TS}}{K_S}\right)\frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}=\left(1+\frac{C_{TS}}{K_S}\right)K_S \tag{A41}$$

and we also may want to convert the unit from mole/kg-solution to mole/L .

- K_{1P},K_{2P}, K_{3P} (mole/L)

For aqueous speciation of phosphate (TDIP), the equilibrium constants (based on free scale pH) are (Millero, 1995; Yao and Millero, 1995) regressed against temperature T (Kelvin) and salinity S (psu)

$$\begin{aligned}lnK_{1p}&=115.54-\frac{4576.752}{T}-18.453lnT\\ &+(0.69171-\tfrac{106.736}{T})\sqrt{S}\\ &+\left(-0.01844-\tfrac{0.65643}{T}\right)S\end{aligned} \tag{A42}$$

$$\begin{aligned}lnK_{2p}&=172.1033-\frac{8814.715}{T}-27.927ln\mathrm{T}\\ &+(1.3566-\tfrac{160.340}{T})\sqrt{S}\\ &+(-0.05778+\tfrac{0.37335}{T})S\end{aligned} \tag{A43}$$

$$lnK_{3p} = -18.126 - \frac{3070.75}{T}$$
$$+(2.81197 + \tfrac{17.27039}{T})\sqrt{S}$$
$$+(-0.09984 - \tfrac{44.99486}{T})S \quad \text{(A44)}$$

- K_{Si} (mole/L)

Dissolution of quartz is through reaction

$$SiO_2(s) + 2H_2O \rightleftharpoons H_4SiO_4(aq) \quad \text{(A45)}$$

with saturation concentration $[H_4SiO_4(aq)]_{Sat}$ of 10^{-4} (moke/kg) of $H_4SiO_4(aq)$ at 25 °C, i.e. 7.8 mg-quartz/kg-solution (7.8 ppm) by $SiO_2(s)$ weight (White, 2013) Dissociation of aqueous $H_4SiO_4(aq)$ is

$$H_4SiO_4(aq) \rightleftharpoons [H^+] + [SiO(OH)_3^-] \quad \text{(A46)}$$

with equilibrium constant K_{Si} (equation (53)) equal to $10^{-9.9}$ (mole/kg) at 25 °C (White, 2013). Yao and Millero (1995) and Millero (2007) provided estimate of K_{Si} as

$$lnK_{Si}\left(\frac{mole}{kg}\right) = 117.40 - \frac{8904.2}{\mathrm{T}} - 19.334\mathrm{lnT}$$
$$+\left(3.5913 - \frac{458.79}{T}\right)\sqrt{I} + \left(-1.5998 + \frac{188.74}{T}\right)I + \left(0.07871 - \frac{12.1652}{T}\right)I^2 \quad \text{(A47)}$$

where T is in Kelvin units. This formula is not intended for seawater. Instead it is based on ionization equilibria of silicic acid in sodium chloride solutions with ionic strength *I*=0 to 5 mole/kg and temperature 60 to 300 °C (data from Busey and Mesmer, 1977). Nevertheless, one may roughly apply this formula in modeling and estimate *I* from total dissolved solids for seawater using salinity or total dissolved solids (Sawyer and McCarty 1967)

$$I = 0.00147 + 0.019885S + 0.000038S^2 \quad \text{(A48)}$$

or the regression provided by Khoo et al. (1977) (see equation (A36)).

- K_{NH_3} (mole/L)

Ammonium NH_4^+ dissociation constant is studied in Khoo et al. (1977b) and revisited in Bell et al. (2008a) and a correction in Bell et al. (2008b). Bell et al. (2008b) gives

$$pK_{NH_3} = -log_{10}K_{NH_3} = 10.0423 - 0.0315536 \times (\mathrm{T} - 273.15) + 0.003071\mathrm{S}, \quad \text{(A49)}$$

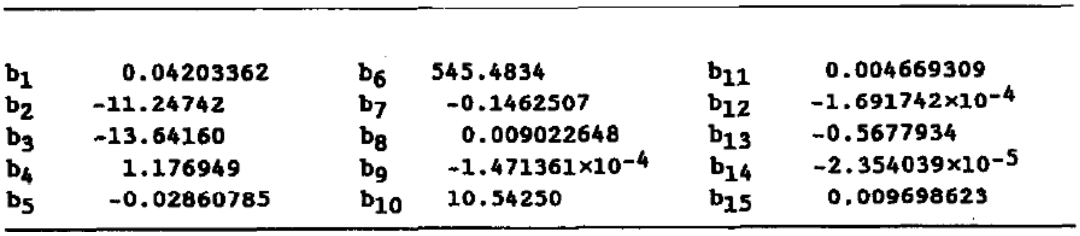
for seawater with T being temperature (Kelvin) and S being salinity (psu). Clegg and Whitfield (1995) provided an equally accurate regression equation based on total scale (equation 18 of Clegg and Whitfield 1995) for temperature from -2 to 40 °C and Salinity from 0 to 40 (psu)

$$\begin{aligned} pK_{NH_3,T}(mole/kg) \equiv -log_{10}K_{NH_3,T} = pK_{NH_3}{}^{0} + (b_1 + b_2/T)S^{0.25} \\ + \left(b_3 + b_4\sqrt{T} + b_5 T + \tfrac{b_6}{T}\right)S^{0.5} \\ + \left(b_7 + b_8 T + b_9 T + \tfrac{b_{10}}{T}\right)S^{1.5} \\ + \left(b_{11} + b_{12}\sqrt{T} + \tfrac{b_{13}}{T}\right)S^{2} \\ + \left(b_{14} + \tfrac{b_{15}}{T}\right)S^{2.5} \end{aligned} \tag{A50}$$

where

$$pK_{NH_3}{}^{0} = 9.244605 - 2729.33\left(\tfrac{1}{298.15} - \tfrac{1}{T}\right) \tag{A51}$$

with T and S being temperature (Kelvin) and salinity (psu). Coefficients are listed as



b_1	0.04203362	b_6	545.4834	b_{11}	0.004669309
b_2	-11.24742	b_7	-0.1462507	b_{12}	-1.691742×10^{-4}
b_3	-13.64160	b_8	0.009022648	b_{13}	-0.5677934
b_4	1.176949	b_9	-1.471361×10^{-4}	b_{14}	-2.354039×10^{-5}
b_5	-0.02860785	b_{10}	10.54250	b_{15}	0.009698623

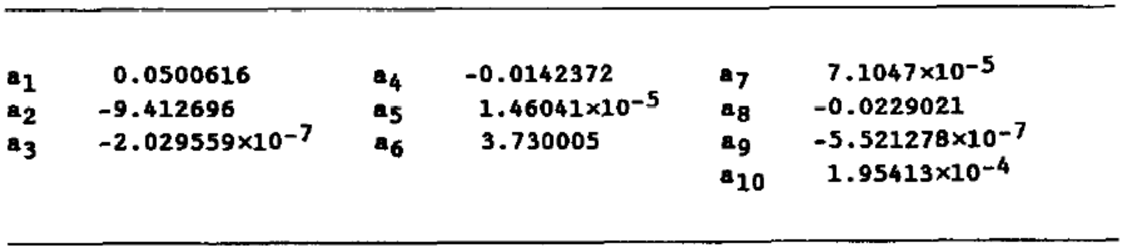
One can convert to free scale K_{NH_3} using

$$K_{NH_3,T} \equiv \frac{[H_T^+][NH_3]}{[NH_4^+]} = \left(1 + \frac{C_{TS}}{K_S}\right)\frac{[H^+][NH_3]}{[NH_4^+]} = \left(1 + \frac{C_{TS}}{K_S}\right)K_{NH_3} \tag{A52}$$

if C_{TS} and K_S are known. Alternatively, free scale value is also provided by Clegg and Whitfield (1995, equation (12))

$$\begin{aligned} pK_{NH_3} \equiv -log_{10}K_{NH_3}\left(\frac{mole}{kg}\right) \\ = pK_{NH_3,T}{}^{0} + \left(a_1 + \frac{a_2}{T} + a_3 T^2\right)\sqrt{S} \\ + \left(a_4 + a_5 T + \frac{a_6}{T}\right)S \\ + \left(a_7 + \tfrac{a_8}{T}\right)S^2 + \left(a_9 + \tfrac{a_{10}}{T}\right)S^3 \end{aligned} \tag{A53}$$

with coefficients a_1~ a_{10} tabulated below.



a_1	0.0500616	a_4	-0.0142372	a_7	7.1047×10^{-5}
a_2	-9.412696	a_5	1.46041×10^{-5}	a_8	-0.0229021
a_3	-2.029559×10^{-7}	a_6	3.730005	a_9	-5.521278×10^{-7}
				a_{10}	1.95413×10^{-4}

Conversion to mole/L unit is necessary for model to use volume-based concentration instead of mass-based concentration.

- $K_{H_2\ S}$ (mole/L)

Millero et al. (1988) measured dissociation of $H_2\ S$ dissociation equilibrium constant with artificial seawater of salinity range 5 to 40 psu and temperature 5 to 25 °C using total scale definition

$$K_{H_2\ S,T} = \frac{[H_T^+][HS^-]}{[H_2\ S]} = (1+\frac{C_{TS}}{K_S})\frac{[H^+][HS^-]}{[H_2\ S]} = (1+\frac{C_{TS}}{K_S})K_{H_2\ S} \qquad \text{(A54)}$$

where $K_{H_2\ S}$ is defined in (54) using free scale. The fitted equation as function of temperature and salinity is

$$pK_{H_2\ S,T} \equiv -log_{10}K_{H_2\ S,T}(\frac{mole}{kg}) = pK^0_{H_2\ S} + A\sqrt{S} + BS \qquad \text{(A55)}$$

where $pK^0_{H_2\ S,T}$ is the value at infinite dilution given by

$$pK^0_{H_2\ S,T} = -98.080 + \frac{5765.4}{T} + 15.0455\ln\ T \qquad \text{(A56)}$$

with temperature T in Kelvin units and $A = -0.1570$, $B = 0.0135$. Conversion from total scale to free scale is though

$$K_{H_2\ S,T} = (1+\frac{C_{TS}}{K_S})K_{H_2\ S} \qquad \text{(A57)}$$

which gives free scale value to be

$$K_{H_2\ S} = K_{H_2\ S,T}/(1+\frac{C_{TS}}{K_S}) \qquad \text{(A58)}$$

Conversion of unit from mole/kg-solution to mole/L is necessary and can be done through density of seawater.

- K_F (mole/L)

  Perez and Fraga (1987) provided fluoride and hydrogen association constant measurement of seawater with salinity range 10 to 40 psu and temperature 9 to 33 °C. The results are fitted with the following equation (based on sea water scale and in mole/kg-solution unit) (notice that in equation (1) of Perez and Fraga 1987, the total concentration of hydrogen ion there is really sea water scale here in equation (9)

  $$\ln K_{F,SWS}(\frac{mole}{kg}) = -\frac{874}{T} - 0.111\sqrt{S} + 9.68 \qquad \text{(A59)}$$

  where $K_{F,SWS}$ is hydrogen fluoride dissociation constant (inverse of association constant) based on total scale

  $$K_{F,SWS} = \frac{[H^+_{SWS}][F^-]}{[HF]} = \left(1 + \frac{C_{TS}}{K_S} + \frac{C_{TF}}{K_F}\right)\frac{[H^+][F^-]}{[HF]} = (1 + \frac{C_{TS}}{K_S} + \frac{C_{TF}}{K_F})K_F \qquad \text{(A60)}$$

  and we have

  $$K_F{=}K_{F,SWS}/(1 + \frac{C_{TS}}{K_S} + \frac{C_{TF}}{K_F}). \qquad \text{(A61)}$$

  This equation can be solved to obtain K_F directly or iteratively with K_S, $K_{F,SWS}$, C_{TS} and C_{TF} given. Alternatively, Perez and Fraga (1987, equation (15)) also provided regression of K_F directly (inverse of association constant in Perez and Fraga (1987))

  $$\ln K_F(\frac{mole}{kg}) = -\frac{1594}{T} - 0.342\sqrt{I} + 12.26 \qquad \text{(A62)}$$

  where temperature T is in Kelvin units and $I = 0.5$.

- $K_{sp,CaCO_3}$ ((mole/L) (mole/L))

  Mucci (1983) provided the following equation for estimating calcium carbonate (calcite and aragonite) solubility constant (Millero, 1995; Millero, 2007)

  $$\begin{aligned} lnK_{CaCO_3,Calcite}(mole/kg)^2 = &-171.9065 - 0.077993T \\ &\mp \frac{2839.319}{T} \mp 71.595 log_{10}T \\ &+(-0.77712 + 0.0028426T + 178.34/T)S^{1/2} \\ &-0.07711S + 0.00412S^{3/2} \end{aligned} \qquad \text{(A63)}$$

  $$\begin{aligned} lnK_{CaCO_3,Aragonite}(mole/kg)^2 = &-171.945 - 0.077993T \\ &+\frac{2903.293}{T} + 71.595 log_{10}T \\ &+(-0.068393 + 0.0017276T + 88.135/T)S^{1/2} \\ &-0.10018S + 0.0059415S^{3/2} \end{aligned} \qquad \text{(A64)}$$

where *T* is in Kelvin and *S* is in psu units.

- $K_{s,CaCO_3}$ (1/day)

Precipitation and dissolution rates of calcium carbonate (calcite and aragonite) were studied by Acker et al. (1987), Feely et al. (1988), Zhong and Mucci (1989), Walter and Morse (1985), Cai et al. (1995), and Andersson et al. (2003). According to Cai et al. (1995, equation A1, parameter *k*), the dissolution rate of $K_{s,CaCO_3}$ is approximately 0.01/day. The Acker et al. (1987) approach gives rate in

$$K_{s,CaCO_3} = k(1 - \Omega)^n \tag{A65}$$

and

$$K_{s,CaCO_3} = k'([CO_3^{2-}]_s - [CO_3^{2-}]) \tag{A66}$$

with $[CO_3^{2-}]_s$ being the saturation carbonate ion concentration

$$[CO_3^{2-}]_s = \frac{K_{sp,CaCO_3}}{[Ca^{2+}]} \tag{A66}$$

and k' (1/day) of range $(3.32 \pm 1.77) \times 10^{-3}$, and *n* of range 1.87 ± 0.15 .

Appendix B. Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

Alk	Alkalinity
Ca^{2+}	Calcium ion
$CaCO_3$	Calcium carbonate
CBE	Charge balance equation
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
DFO	Department of Fisheries and Oceans (Canada)
DO	Dissolved oxygen
DOM	Dissolved organic matter
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency

f	Fugacity
H^+	Hydrogen ion
K_1	Dissociation constant (HCO^{3-})
K_2	Dissociation constant (CO_3^{2-})
K_a	Reaeration coefficient
K_{sp}	Saturation coefficient
K_w	Dissociation constant (water)
NH4	Ammonium, also NH^{4+}
NO3	Nitrate
NOAA	National Oceanic and Atmospheric Administration
NPZD	Nutrient, phytoplankton, zooplankton, and detritus food webs
OA	Ocean acidification
PBE	Proton balance equation
pCO_2	Partial pressure of carbon dioxide
PEM	Potomac Estuary Model
PMEL	Pacific Marine Environmental Laboratory
PRISM	Puget Sound Regional Synthesis Model
QA	Quality assurance
QC	Quality control
S	Salinity
SAV	Submerged Aquatic Vegetation
sw	Seawater
T	Temperature
TDIC	Total dissolved inorganic carbon
TMDL	(See Glossary above)
TOTH	Total hydrogen ion charge
UW	University of Washington
V	Volume
WASP	Water Analysis Simulation Program
WRF	Weather Research & Forecasting Model

Units of Measurement

°C	degrees centigrade
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
mg/L	milligrams per liter (parts per million)
mole	an International System of Units (IS) unit of matter
psu	practical salinity units
s.u.	standard units, units of pH
umol	micromoles, a chemistry unit
uM	micromolar, a chemistry unit
Ω_{arag}	aragonite saturation state