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Washington Shellfish Initiative
Blue Ribbon Panel on Ocean Acidification

Scientific Summary of Ocean Acidification in Washington State Marine Waters

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Washington State Blue Ribbon Panel on Ocean Acidification

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November 2012

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Map of the Salish Sea & Surrounding Basin
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Contents

Preamble

This Scientific Summary was developed through the combined efforts of a group of natural scientists from Washington State with assistance from colleagues in Oregon. The purpose of this white paper is specifically to inform members of the Washington Shellfish Initiative Blue Ribbon Panel on Ocean Acidification regarding the conditions and likely biological and ecological responses to ocean acidification in the estuarine and coastal waters of Washington. We draw from examples within Washington wherever possible; where that is not possible, we use relevant examples from other coastal ecosystems. We identify areas where the knowledge base is thin, and note areas where more research could improve our understanding of ocean acidification in Washington marine waters.

Throughout, we present information in detail sufficient to support our conclusions, and we encourage interested readers to inspect those details. However, we caution all readers to avoid getting lost in the details, and instead to focus on the conclusions we draw from the information available and their relevance to Washington State. We specifically DO NOT include discussion of strategies for mitigation, adaptation, or remediation of declining pH in this Scientific Summary. This topic is treated separately as part of the full panel report, *Ocean Acidification: From Knowledge to Action, Washington State's Strategic Response*.

Executive Summary

The estuarine and coastal waters of Washington State provide important resources and services for supporting and sustaining the lives and culture of its population, including food, recreation, nutrient cycling, and moderating climate, all of which contribute substantially to Washington's economy. However, in recent years, scientists have demonstrated that the chemistry of the oceans is changing in ways that will have significant impacts on the services and resources it provides. For more than two and a half centuries, humans have injected vast quantities of carbon dioxide (CO_2) into earth's atmosphere through the burning of fossil fuels and land use changes. Approximately one quarter of this anthropogenic, or human generated, CO_2 has been absorbed by the ocean, causing the ocean's upper-ocean pH to decrease by about 0.1, in a process known as "ocean acidification" (OA). By the end of this century, surface ocean pH is expected to decline by another 0.3–0.4 pH units, with aragonite saturation state decreasing below the current range of annual variability within 12–40 years.

Washington State is particularly vulnerable because of its location and regional oceanography. Atmospheric CO_2 is indisputably the most important driver of ocean acidification in the open-ocean waters of the North Pacific, and unless carbon emissions are rapidly brought under control, it will dominate at the local level as well within the coming decades. For now, however, acidification in Washington State coastal waters is driven by a combination of factors, particularly in the deep waters of Puget Sound and the nearshore regions that are so important to Washington's shellfish industry. Our waters are exhibiting the effects of not only the global atmospheric CO_2 increase, but also other processes that can contribute to regional acidification:

- **Upwelling of high-CO_2 ocean waters** — When northerly winds blow across Washington's offshore waters, cold, CO_2-rich seawater wells up from the ocean depths to flow onto the continental shelf and eventually into Puget Sound and coastal estuaries. These waters have naturally low pH from respiration processes and, combined with the added contribution of the anthropogenic CO_2, become corrosive to shell-forming organisms such as oyster larvae, clams, mussels, crabs, abalone, and pteropods.

- **Nutrients**—Many different processes deliver nutrients such as nitrogen, silicate, and phosphorus to Washington waters. Upwelling, for example, may bring nutrients from deeper offshore regions, while erosion or fertilizer runoff may bring nutrients from the land to the sea. These nutrients can stimulate the growth of marine algae, thus serving to temporarily decrease seawater CO_2 and increase pH of the surface waters. These algal blooms, however, are eventually followed by death and decomposition at depth, which returns CO_2 to these waters and drives pH values down in the deeper waters. Episodes of coastal hypoxia (very low oxygen levels) are an indicator of this process.
- **Organic carbon**—Similarly, rivers and streams may deliver living or once-living organic matter to the coastal ocean. The eventual decay of this biogenic material releases acidifying CO_2 back into the water via bacterial respiration.
- **Freshwater**—Rivers and stormwater runoff also deliver freshwater, which often has pH values and calcium carbonate saturation states lower than seawater.
- **Other acidifying gases**—Gases such as nitrogen oxides (NO_X) and sulfur oxides (SO_X) from the burning of fossil fuels form acids when dissolved in seawater.
- **Other acidifying wastes**—Wastes from industrial or other human activities are sometimes delivered directly to marine waters. Some of these wastes can be acidic.

Experiments performed under laboratory conditions indicate that many marine species are sensitive to CO_2 enrichment of seawater. Some of the most compelling evidence to date comes from marine invertebrates. While substantial variation in response occurs among species and life stages, shelled invertebrates generally exhibit negative responses to conditions of elevated CO_2 and reduced pH. Invertebrates that have exhibited negative responses to OA conditions include several of economic and cultural importance in Washington State; for example, oysters, clams, and mussels. In many of these, larval stages have been demonstrated to be more sensitive to OA conditions than adult stages. Elevated seawater temperature has been shown to exacerbate the negative effects of OA in many species.

Negative effects of OA are not restricted to invertebrate species. In systems outside Washington, marine fish species have exhibited negative responses to OA conditions that include changes in growth, survivorship, and behavior. Marine phytoplankton have shown varied responses to OA that include changes in growth rate and calcification. Some toxic species of phytoplankton have shown elevated production of biotoxins under OA conditions. Given the large number of species for which negative responses to OA have been demonstrated, changes in food web structure and function are likely.

Not all species respond negatively to OA conditions. For example, some seagrass species appear to benefit from CO_2 enrichment, and some macroalgae (for example, kelps) also could respond positively to elevated CO_2. These findings offer potential mitigation benefits that, under appropriate conditions, could help to ameliorate the negative effects of CO_2 enrichment in Washington waters.

The scientists on the Panel reviewed the current literature and research and monitoring capabilities with respect to OA in Washington State coastal waters and have identified critical gaps in our understanding and capacity. We have made recommendations for four Research and Monitoring Strategies of equal importance. Under each of these strategies we have provided a prioritized list of specific actions. These are presented in Chapter 7.

1

Introduction to Ocean Acidification in Washington State Waters

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1.0 Key Points

1.0.1 What we know about ocean acidification

- Due to the release of carbon dioxide (CO_2) into the atmosphere resulting from human activities such as fossil fuel combustion and land use changes, average ocean pH has decreased by 0.1 (~30% increase in acidity) since the industrial revolution.
- Increased acidity reduces the aragonite and calcite saturation states of seawater, making it more difficult for calcifying organisms to build their shells and skeletons.
- Intermediate depth waters (150–400 m) in the offshore regions of the northeastern Pacific are naturally corrosive to shell-forming organisms such as clams, oysters, mussels, and pteropods.
- Upwelling of these corrosive waters onto the continental shelf brings the corrosive waters closer to the surface in the spring, summer, and early fall months.
- The input of human-generated (*anthropogenic*) CO_2 has caused a further shoaling of this corrosive layer on the Washington coast; it is now within 20–100 m of the surface.
- The current rate of ocean acidification is 10 times faster than anything the earth has experienced during the past 50 million years.
- Washington State is particularly vulnerable to pH decline because regional drivers can combine with the global atmospheric CO_2 contribution to exacerbate the acidification process.

1.0.2 What we need to know about ocean acidification

- What is the status of pH, dissolved inorganic carbon (DIC), and total alkalinity (TA) in Washington marine waters including Puget Sound and the outer coast? What are the long-term trends?
- What are the temporal and spatial scales of variability of the corrosive waters in Washington marine waters?
- What is the relative importance of local drivers to the acidification process, including those affected by human activities?
- How do marine organisms at different life stages respond to changes in pH, DIC, and TA?
- How do marine ecosystems respond to changes in pH, DIC, and TA?

1.1 Definition of Ocean Acidification

The International Panel on Climate Change (IPCC) Workshop on Impacts of Ocean Acidification on Marine Biology and Ecosystems (2011, p. 37) defines Ocean

Acidification (OA) as *"a reduction in the pH of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of carbon dioxide from the atmosphere, but can also be caused by other chemical additions or subtractions from the ocean."* Washington State is particularly vulnerable to pH decline because regional drivers—upwelling, hypoxia, nitrogen oxides (NO_X)/sulfur oxides (SO_X), and watershed inputs of nutrients—can combine with the global drivers to exacerbate the acidification process.

1.2 Chemistry of Ocean Acidification

Over the past two and a half centuries, humans have injected vast amounts of CO_2 into Earth's atmosphere, primarily through the burning of fossil fuels and land use changes. Since the pre-industrial era, global atmospheric CO_2 levels have risen from approximately 280 parts per million (ppm) to 394 ppm, higher than they have been at any time over the past 800,000 years (IPCC Core Writing Team et al., 2007). About one quarter of this *anthropogenic*, or human generated, CO_2 has been absorbed by the ocean, which naturally equilibrates with the atmosphere (Le Quéré et al., 2009, 2010). Once viewed as a useful "sink" for excess atmospheric carbon, it is now understood that the 550 billion tons of CO_2 that has entered the oceans in this manner is having a profound long-term impact on marine chemistry and biology. Through a series of reactions driven by the uptake of anthropogenic CO_2, open ocean surface waters have become ~30% more acidic since the mid-1700s (Caldeira and Wickett, 2003; Feely et al., 2004). At the current rate of CO_2 emissions, the acidity of the surface oceans is projected to rise by 100–150% over pre-industrial levels by the end of this century (Orr et al., 2005; Doney et al., 2009; Feely and Dickson, 2009).

When CO_2 enters the ocean it reacts with water to form carbonic acid (equation 1), which undergoes a series of chemical reactions that reduce seawater pH, lowers the concentration of carbonate ion (CO_3^{2-}), and increases the concentration of bicarbonate (equation 2).

$$CO_{2(gas)} \rightleftarrows CO_{2(aqueous)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \quad (1);$$

and $$H^+ + CO_3^{2-} \rightleftarrows HCO_3^- \quad (2).$$

The hydrogen ions (H^+) are what gives an acid its "kick," and is the term used to describe the acidity of seawater. It is often measured on the *pH* scale, which is the negative log of the H^+ ion concentration (**Figure 1.1**).

A portion of the H^+ released by H_2CO_3 reacts with the ocean's reserves of CO_3^{2-} to produce additional bicarbonate (HCO_3^-) (equation 2). CO_3^{2-} is an essential building block used by marine *"calcifiers"*—organisms that build shells or skeletons composed of calcium carbonate ($CaCO_3$). As CO_3^{2-} levels are depleted, animals like oysters, corals, and pteropods (an important source of food for juvenile salmon) have to use more energy to pull this molecule out of solution, compromising their ability to make their shells or skeletons (Fabry et al., 2008; Guinotte and Fabry, 2008) (**Figure 1.2**).

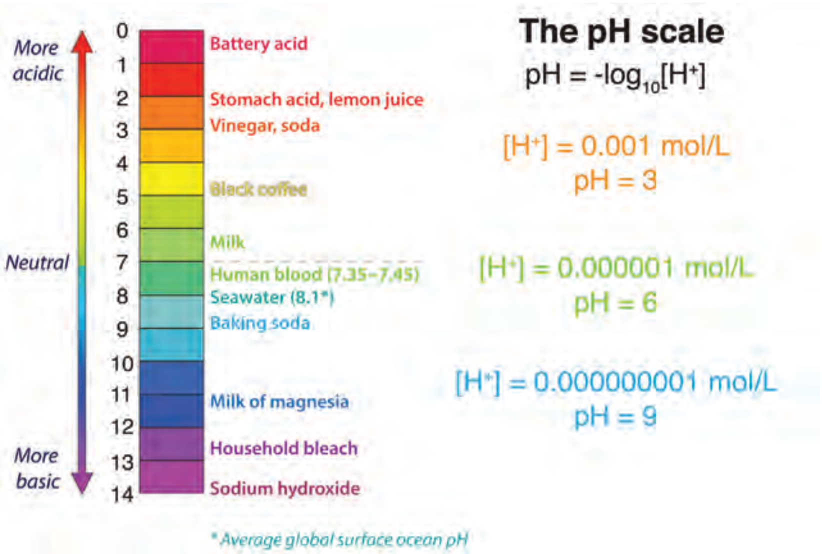

Figure 1.1: Diagram of the pH scale, labeled with the average pH values for some common solutions, including seawater. pH is defined as the negative log of the hydrogen ion concentration in a solution. Neutral pH is 7.0, solutions that have pH values < 7.0 are acidic, and those that have pH values > 7.0 are basic. The term "ocean acidification" refers to the direction of change toward more acidic conditions with increasing atmospheric CO_2 concentrations. Like the Richter scale, the pH scale is *logarithmic*. This means that a pH of 7 is ***10 times more acidic*** than a pH of 8.

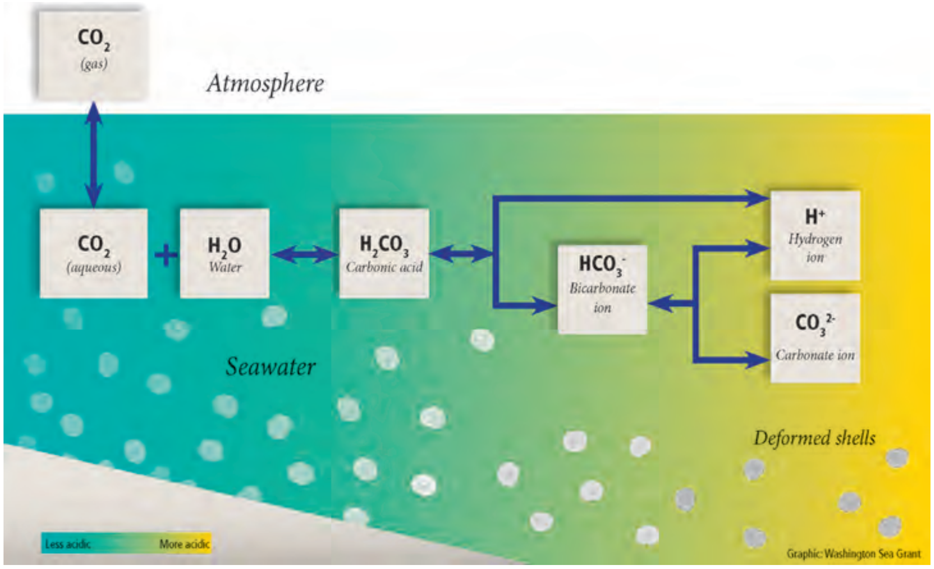

Figure 1.2: The effect of dissolved CO_2 on marine carbonate chemistry.

The decline in pH also reduces the saturation states of the calcium carbonate biominerals, aragonite (Ω_{arag}) and calcite (Ω_{cal}) (Caldeira and Wickett, 2003; Feely et al., 2004). Saturation state of aragonite and calcite carbonate minerals is calculated as the product of the concentrations of calcium (Ca^{2+}) and CO_3^{2-} ions divided by the apparent solubility product, K_{sp}*:

$$\Omega_{arag} = [Ca^{2+}]\ [CO_3^{2-}]/K_{sp}{}^*{}_{arag} \qquad (3)$$

$$\Omega_{cal} = [Ca^{2+}]\ [CO_3^{2-}]/K_{sp}{}^*{}_{cal} \qquad (4)$$

where K_{sp}* reflects seawater conditions and is a function of temperature, salinity, and pressure. At Ω_{arag} values greater than 1.0, aragonite does not readily dissolve, and shell maintenance is thermodynamically favored over dissolution. Ω_{arag} levels below 1.0 can be "corrosive" to organisms that produce aragonite shells, unless they have a mechanism for preventing dissolution (Feely et al., 2004; Fabry et al., 2008). Other biologically important forms of $CaCO_3$ are calcite and high-magnesium calcite. Although these forms differ in solubility relative to aragonite, their saturations states respond to declining pH in a similar manner (Mucci, 1983; Andersson et al., 2003).

Prior to the industrial era, the average global Ω_{arag} level of surface seawater was about 3.4. The current average is ~3.0, and may reach ~2.3 by the end of this century, at which point the calcification rates for some organisms may be significantly (30–60%) reduced (Fabry et al., 2008; Guinotte and Fabry, 2008; Feely et al., 2009).

Though the term *ocean acidification* (Caldeira and Wickett, 2003) only refers to the pH reduction associated with the long-term ocean uptake of anthropogenic CO_2, the process it describes has a direct impact on all three interrelated phenomena described in this section:

1. Declining pH (trending toward the acidic end of the pH scale),
2. Lowering of the concentration of carbonate ion, *and*
3. Reducing the saturation state of biologically important forms of calcium carbonate.

1.3 Global Trends

Direct atmospheric and open-ocean surface water measurements clearly show the relationship between atmospheric CO_2 levels, pCO_2 (i.e., the *partial pressure* of CO_2 in solution), and pH since 1989 (**Figure 1.3**).

Since the beginning of the industrial era, the pH of open-ocean surface waters has decreased by about 0.1 pH units (**Figure 1.4**), equivalent to an overall increase of ~30% in the hydrogen ion concentration. By the end of this century, surface ocean pH is expected to decline by another 0.3–0.4 pH units (**Figure 1.4**), with aragonite saturation state decreasing below the current range of annual variability within 12–40 years throughout the global oceans (Cooley et al., 2012; **Figure 1.5**). As anthropogenic CO_2 absorbed from the atmosphere has mixed into the upper ocean over the course of the

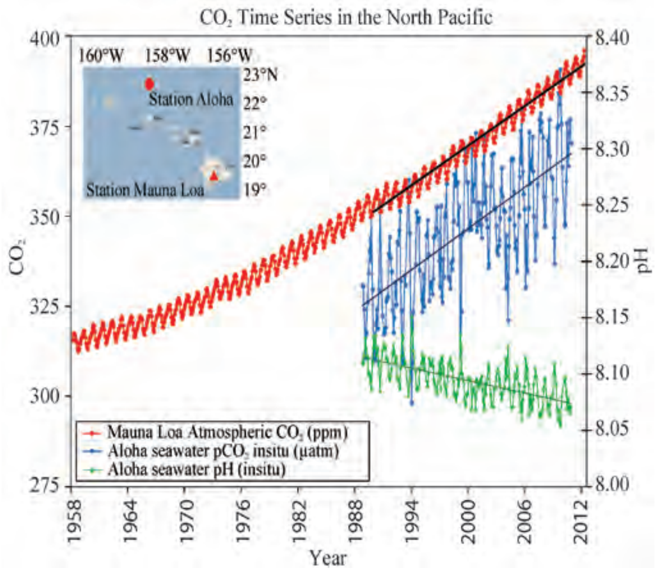

Figure 1.3: Time series of atmospheric CO_2 at Mauna Loa (in ppm; mole fraction in dry air) and surface ocean pH and pCO_2 (µatm) at Ocean Station Aloha in the subtropical North Pacific Ocean. Note that the increase in oceanic CO_2 over the last 19 years is consistent with the atmospheric increase within the statistical limits of the measurements. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL (http://www.esrl.noaa.gov/gmd/ccgg/trends); HOTS/ALOHA data: Dr. John Dore, University of Hawaii (http://hahana.soest.hawaii.edu).

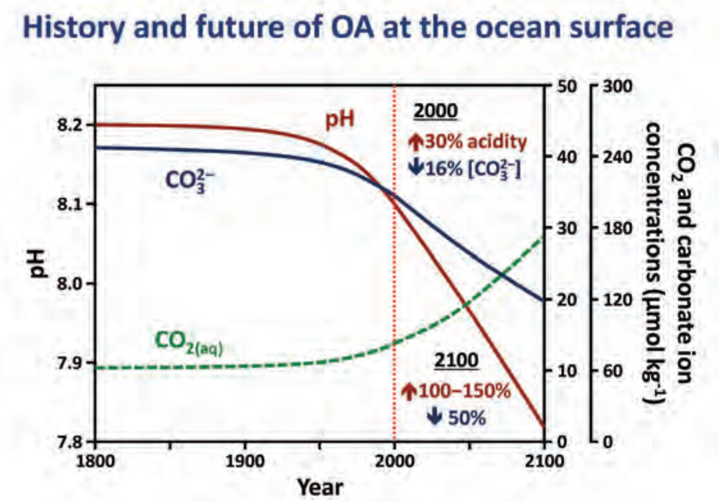

Figure 1.4: Schematic diagram of the changes in pH, CO_3^{2-}, and $CO_{2(aqueous)}$ of the surface oceans under a high CO_2 emission scenario out to 2100 (after Wolf-Gladrow et al., 1999). The pH has declined by about 0.1 (equivalent to a hydrogen ion concentration increase of about 30%) since the beginning of the industrial era.

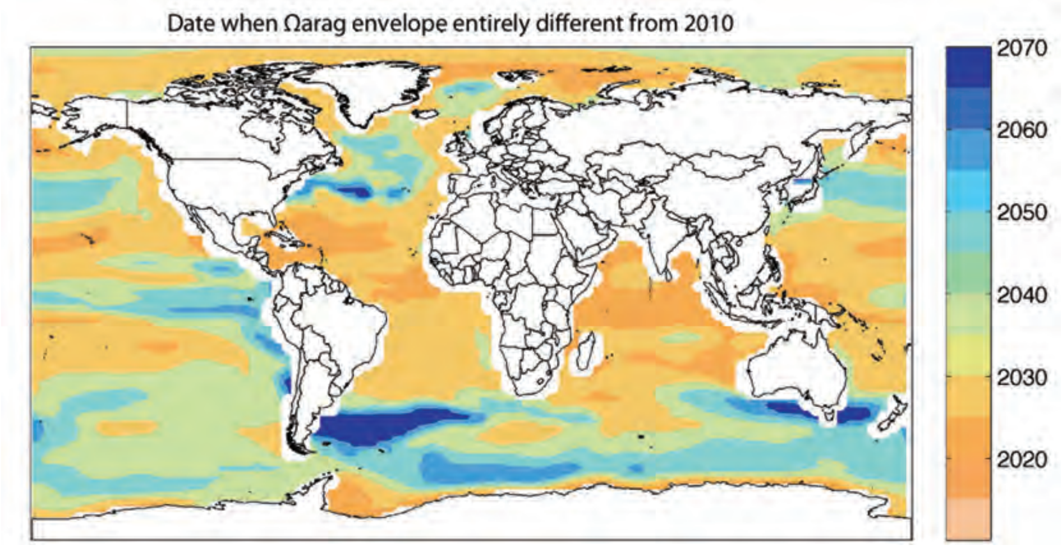

Figure 1.5: Transition decades when the future surface aragonite saturation state will no longer overlap that of 2010 (from Cooley et al., 2012). In the eastern North Pacific the transition would occur sometime around 2030.

industrial era, the depths of the aragonite and calcite *saturation horizons* (i.e., the depths where the carbonate ion concentrations are low enough to cause calcium carbonate shells to dissolve) have become shallower by 30–100 m in the northeastern Pacific. In many parts of the open ocean, the aragonite saturation horizon in the northeastern Pacific is within 150-400 m of the ocean surface and is rising at 1–2 m yr^{-1} (Feely et al., 2004, 2012).

Models have suggested that corrosive waters would rise to depths affecting western U.S. shelf ecosystems, home to rich fisheries and diverse communities, over the next several decades to a century (Orr et al., 2005; Hauri et al., 2009; Rykaczewski and Dunne, 2010). More recently, other investigators (Gruber et al., 2012; Hauri et al., 2012) have employed a high-resolution combined physical-biogeochemical model of the California Current System to show that by 2050, waters with aragonite saturation state > 1.5 will have largely disappeared and more than half the waters will be undersaturated year-round in the IPCC A2 CO_2 emission scenario. However, the first detailed observations of carbon chemistry in the California Current Ecosystem in 2007 revealed that anthropogenically acidified waters, corrosive with respect to aragonite, were already upwelling onto the continental shelf to depths of 20–120 m in most areas, and all the way to the surface along a transect in northern California (Feely et al., 2008).

1.4 Geological Context

Concentrations of atmospheric CO_2 have reached very high concentrations several times during the past 300 million years, and during a number of these periods, ocean pH was also lower than it is today (Hönisch et al., 2012). However, there was only one time over this entire period that the *rate* of pH change was even close to what our oceans are currently experiencing. During the Paleocene-Eocene Thermal Maximum, or PETM, some 55 million years ago, the pH of the oceans was estimated to have declined by as much 0.45 units over roughly 5000 years. This decline has been attributed to a rapid change of atmospheric CO_2 concentrations to 1800 ppm, which also pushed global average temperatures up by ~6° C (Hönisch et al., 2012). Such rapid pH change can outpace the natural capacity of the ocean to buffer the excess CO_2 levels through dissolution of benthic calcium carbonate sediments and rock weathering (Archer et al., 1997).

Although marine life obviously recovered following the PETM, there is evidence for a dramatic shift in biodiversity: about half of benthic foraminifera (tiny shelled protists) species went extinct over a 1000-year period (Zachos et al., 2008). Today, the ocean is acidifying at a rate *nearly 10 times faster* than the one that drove this extinction 55 million years ago, and the natural processes that ultimately will restore the oceanic pH and carbonate chemistry balance cannot compensate rapidly enough, since full ocean circulation and dissolution of carbonate sediments require tens to hundreds of thousands of years to reach equilibrium (Archer et al., 1997).

1.5 Regional Drivers of Ocean Acidification

Although atmospheric CO_2 is the major driver of acidification globally, near the coasts—particularly highly populated or developed areas—other drivers that generate additional CO_2 in the water column also contribute significantly to acidification. The schematic in **Figure 1.6** from Kelly et al. (2011) depicts both anthropogenic sources and natural processes that potentially could contribute to coastal ocean acidification. These inputs and their relative importance will vary with space and time, and some may not be appreciable drivers in all locations. The next section will explain how several of these additional drivers could contribute to further acidification of surface waters in Washington State.

1.6 Ocean Acidification in Washington-Oregon Coastal Waters

The waters of the Washington-Oregon coast are strongly influenced by seasonal upwelling, which typically begins in early spring and lasts until late summer or fall, when winter storms return. Upwelling brings corrosive, low-pH seawater with Ω_{arag} values < 1.0 and pH values < 7.75 onto the continental shelf. These corrosive waters can reach mid-shelf depths of ~20 to 100 m along the coast (**Figure 1.7**). This shoaling of CO_2-rich waters is typical of strong coastal

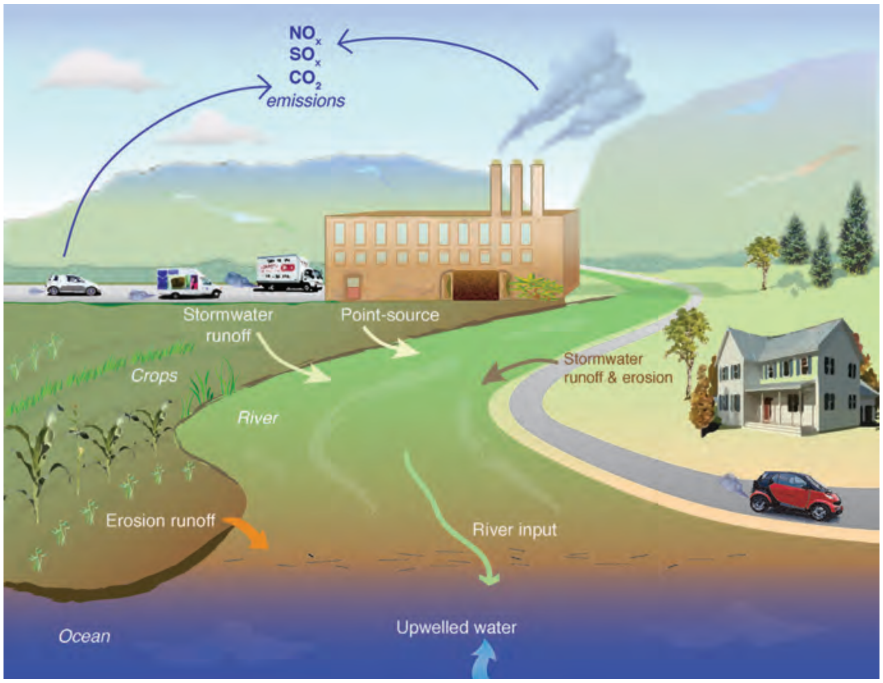

Figure 1.6: **Diagram of the local sources of chemical species that could potentially contribute to the acidification of coastal waterways, fjords, and estuaries (adapted from Kelly et al., 2011).**

upwelling conditions (Feely et al., 2008). The pCO_2 values in the upwelled water ranges from 850 to 950 μatm (microatmospheres) near the shelf-break with higher values inshore, possibly enhanced by respiration processes on the shelf (R. Feely, *unpublished data*, 2012). These results indicate that the upwelling process causes most of the water column below 60 m to be corrosive with respect to aragonite. The uptake of anthropogenic CO_2 has caused the aragonite saturation horizons to shoal by 50 to 100 m since preindustrial times, so they are within the density layers that are currently being upwelled onto the continental shelf along the west coast of North America (Feely et al., 2012). Because the calcite saturation horizon is located between 225 and 400 m in this part of the northeastern Pacific (Feely et al., 2004), it is still too deep to shoal onto the continental shelf.

As recently as seven years ago, oceanographers thought that seawater with pH and Ω_{arag} levels low enough to harm marine life would not impact Washington until the end of this century (Orr et al., 2005). So they were quite surprised when they sampled water along the West Coast in 2007, and found corrosive water (Ω_{arag} values < 1.0 and pH values < 7.75) in the ocean upper layer (20–120 m), and not just in certain spots, but all along the continental shelf (Feely et al., 2008; **Figure 1.7**).

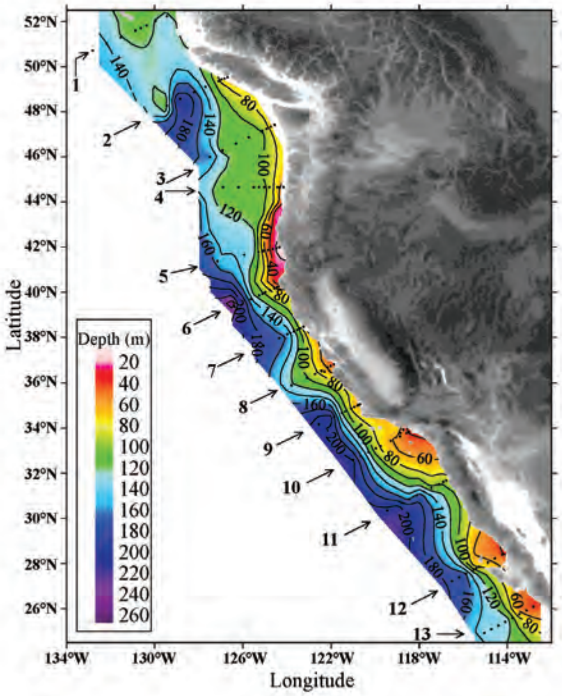

Figure 1.7: Depth distribution in meters of corrosive water ($\Omega_{arag} < 1.0$, pH < 7.75) along the western North American continental margin in May–June 2007 (from Feely et al., 2008).

1.6.1 Upwelling

Strong seasonal upwelling occurs along the West Coast from British Columbia to Mexico. Deeper waters are drawn upward (upwelled) to replace surface waters displaced by strong seasonal northerly winds (**Figure 1.8**). Deep water naturally has lower pH and Ω_{arag} than surface water for two reasons: during the time it has been out of contact with the surface, biological respiration has consumed oxygen and generated CO_2 (just as humans do when they breathe). In addition, mineral saturation state is a function of both temperature and pressure; thus the deeper and/or colder the water, the lower the Ω_{arag} value (Feely et al., 2004). The aragonite saturation horizon typically occurs well below the depth at which most calcifying marine life is found. Why was the upwelled water so much more corrosive than expected? It turns out that pH decline driven by atmospheric CO_2 has caused the saturation horizon to *shoal*, or rise upward, by consuming carbonate ions, thereby reducing saturation states (Feely et al., 2008). By 2007, the aragonite saturation horizon along the West Coast had shoaled into the upwelling region between 150 and 200 meters from the surface, and it has continued to move upward at a rate of 1–2 m yr^{-1} (Feely et al., 2004, 2012). Water that is upwelling onto the coast of Washington and Oregon now contains approximately ~31 µmol kg^{-1} anthropogenic CO_2 and has been out of contact with the atmosphere for approximately 30–50 years (Feely et al., 2008). Waters presently moving toward the upwelling centers from the open ocean, which have had more recent contact with the atmosphere, are carrying even higher concentrations of anthropogenic CO_2. Therefore, upwelled waters will be increasingly corrosive well into the future, even if emissions of atmospheric carbon were halted today.

Upwelled waters are not confined to the Washington coast. These acidified, oxygen-depleted waters enter Puget Sound via the Juan de Fuca submarine canyon in the summer and fall months, and cause the bottom water pH to decline, particularly in the deep stratified layer in Hood Canal (Feely et al., 2010). While upwelling is a significant driver of ocean acidification in our region, other natural and anthropogenic drivers are also contributing to the corrosive conditions frequently observed both on the coast and in Puget Sound (see below).

1.6.2 Respiration and hypoxia

The near-surface coastal waters off Washington and Oregon are unusually productive. This is due to a combination of upwelling in this part of the California Current System and rivers (Columbia River and the combined inputs from the Salish Sea through the Strait of Juan de Fuca) delivering high levels of nitrogen to the shallow *photic zone*, where it fertilizes intense algae blooms that take up CO_2 and raise pH via photosynthesis (the reverse direction of equation 5) (Hickey and Banas, 2003; Hales et al., 2006; Hutchins et al., 2009). The organic material generated by these blooms sinks back into deeper water, where it is largely remineralized (the forward direction of equation 5) back to CO_2 by microbial respiration (**Figure 1.9**). This releases large amounts of CO_2 directly into the water column, where it has the same effect on pH and Ω_{arag} as dissolved atmospheric CO_2.

$$C_6H_{12}O_6 + 6\ O_2 \rightleftarrows 6\ CO_2 + 6\ H_2O \qquad (5)$$

As illustrated in equation 5, respiration is an oxygen-consuming process that depletes

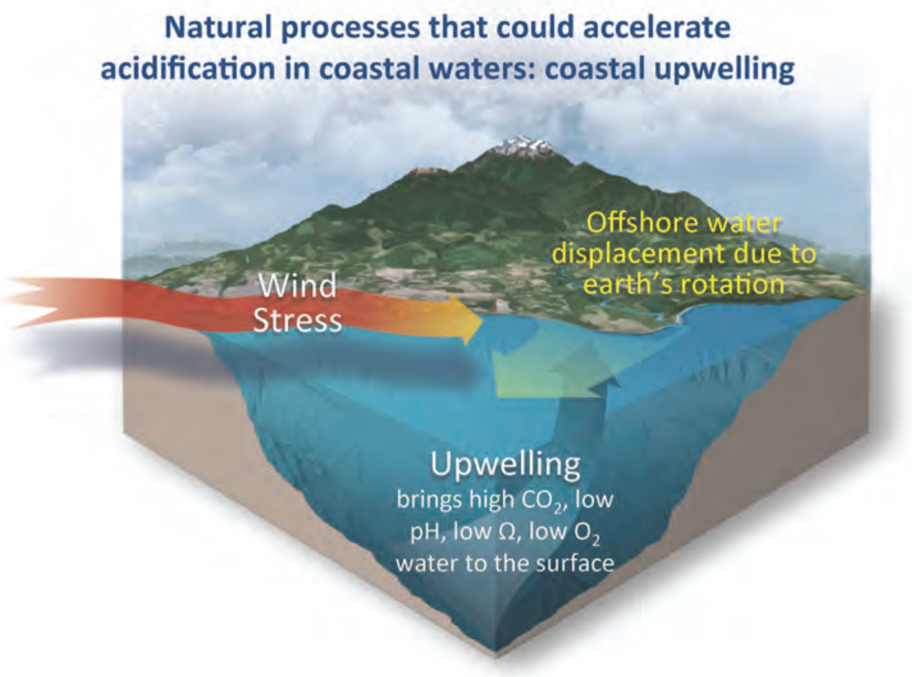

Figure 1.8: Upwelling is the replacement of surface ocean water by colder, saltier, nutrient- and CO_2-rich but oxygen-poor, intermediate-depth ocean water.

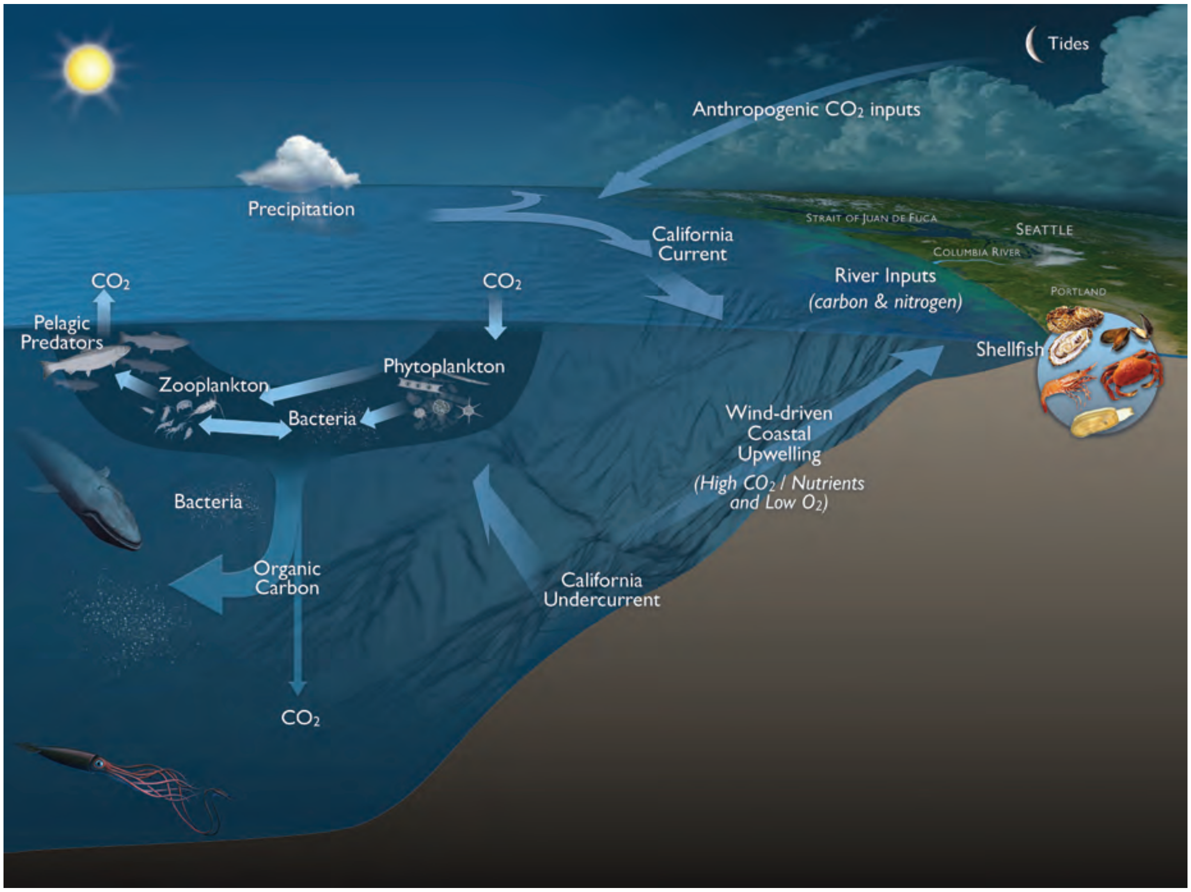

Figure 1.9: Schematic diagram of the pathways for carbon uptake and remineralization in the coastal waters of Washington State.

the water column of oxygen that would otherwise be available to marine animals living in and above the sediment (such as worms, bivalves, crabs, and fish). During periods of high productivity in the summer and early fall months, dissolved oxygen (DO) levels often dip to *hypoxic* (<65 µmol kg^{-1}) and even *suboxic* (<5 µmol kg^{-1}) levels; such events have been increasing in frequency and intensity since 2000 (Grantham et al., 2004; Hales et al., 2006; Chan et al., 2008). The term *hypoxia* is used to describe DO levels that are low enough to be stressful or fatal to marine macrofauna.

The linked processes of respiration and hypoxia are now acknowledged to be important drivers of ocean acidification, particularly when the land nearby is highly populated or agriculturally developed. Where human activity increases the amount of nutrients such as nitrate, phosphate, and iron flowing off the land, the result is *eutrophication* (literally “excessive growth,” referring in this setting to blooms of marine algae). Anthropogenic nutrient inputs into localized areas of Puget Sound may contribute to the overall acidification in certain areas, such as the southern part of Hood Canal, for reasons that are explained in Chapter 3 (Feely et al., 2010). Eutrophication has been linked with enhanced ocean acidification in other coastal areas (Cai et al., 2011; Sunda and Cai, 2012). Hypoxic events are expected to occur more frequently as climate change warms the ocean surface, which leads to stratification of the water column, discouraging penetration of oxygen from the surface (Bopp et al., 2002; Matear and Hirst, 2003; Stramma et al., 2008; Rykaczewski and Dunne, 2010). This effect will tend to enhance acidification in Washington coastal subsurface waters.

1.6.3 Other non-CO_2 sources of acidification in coastal regions

In addition to carbon dioxide, other acid gases (e.g., NO_X and SO_X) are also released into the atmosphere from fossil fuel burning, biomass burning, and agricultural practices (Mackenzie, 1995; Doney et al., 2007). After some chemical reactions in the atmosphere, these species are quickly deposited on the land surface or in the coastal oceans as the dissociation products of nitric acid (HNO_3) and sulfuric acid (H_2SO_4), which fall out as dry deposition or acidic rainwater downwind of primary source regions. Anthropogenic deposition of these nitrogen and sulfur species in surface waters can lead to reduced pH and alkalinity. Estimates based on both observations and models suggest that in coastal regions these gases can contribute up to 10–50% of the CO_2-derived acidification near major source regions (Doney et al., 2007). In some regions, the addition of ammonia from agricultural processes can lead to more alkaline (basic) waters (Doney et al., 2007).

1.6.4 Watershed inputs

Washington's marine waters are affected by several major rivers (the Columbia, Frasier, and Skagit) and thousands of smaller rivers and streams draining the watershed that is bounded to the east by the Cascade Mountains. Freshwater itself varies in pH from ~6.5 to ~8.5, depending on the materials dissolved in the water, and Ω_{arag} is also generally lower in freshwater due to the lower alkalinity. Thus, places where freshwater mixes with the marine water (river mouths and estuaries) can be quite corrosive to calcifying organisms (Salisbury et al., 2008).

In addition, waterways collect material that falls into them, runs off the soil surface, or leaches in through the ground. As the river and stream waters run downhill into marine environments, they deliver these products from one ecosystem (terrestrial) to another (estuarine). In the Pacific Northwest, water flow is typically large during the rainy winter—and for some of the larger rivers, during spring snowmelt—but flows decline during the summer drought period (Babson et al., 2006). Large rivers such as the Columbia River have experienced dramatic flow modification due to impoundment behind dams and diversion for agricultural, domestic, and industrial use (Naik and Jay, 2005).

Many harmful materials carried by rivers are regulated through restrictions on total maximum daily loads (TMDLs; section 303(d) of the Clean Water Act). The TMDL process is well established as a method to aid in the control of pollutants, such as pathogens, nutrients, sediment, mercury, and other metals, from both point and non-point sources, to protect aquatic life (Keller and Cavallaro, 2008). However, the water quality standards process does not track a number of carbon species including dissolved organic carbon (DOC), particulate organic carbon (POC), DIC, and TA. These species can have a substantial influence on the marine carbon system in coastal waters (Frankignoulle et al., 1998; Alin et al., 2012).

The mechanism by which organic carbon inputs influence water chemistry is addressed more fully in Chapter 4, but generally pertains to microbial breakdown of organic materials, which releases CO_2 into the water column. Organic carbon inputs have some natural sources, such as from leaf litter and wildlife. Human activities can also increase the amount of POC (material too large to pass through a 0.45 µm filter) through land use change and development (Frankignoulle et al., 1998), and the amount of DOC (able to pass through a 0.45 µm filter, but still susceptible to microbial breakdown) associated with the density of roads in the watershed (Tallis, 2009). Levels of dissolved oxygen and pH, which are monitored and regulated through TMDLs, frequently co-vary with DIC, because of the concurrent use of oxygen and release of CO_2 during respiration.

1.7 Conclusions

Atmospheric CO_2 is indisputably the most important driver of ocean acidification in the open-ocean waters of the North Pacific, and unless global carbon emissions are rapidly brought under control, it will dominate at the local level as well within the coming decades. For now, however, acidification in Washington State coastal waters is driven by a combination of factors, particularly in the deep waters of the Washington outer coast, Puget Sound, and the estuaries that are so important to Washington's shellfish industry.

The following chapters will provide an in-depth analysis of the factors that combine to make Washington waters particularly vulnerable to acidification. The knowledge gained from the initial surveys, and finally, the biological impacts and potential ramifications of acidification for several key Washington species, are also discussed in the following chapters. For the purpose of geochemical discussions, this scientific summary breaks Washington waters into three distinct geographic domains: Washington's outer coast (Chapter 2), Puget Sound and the Strait of Juan de Fuca (Chapter 3), and the Columbia River and other Washington shallow estuaries (Chapter 4). The responses and sensitivities of biological systems to acidification are discussed in the subsequent two chapters: general physiological principles and observed responses within taxonomic groups (Chapter 5), and the ecological context for acidification (Chapter 6).

1.7.1 Observation and research needs

Below is a listing of the primary observation and research needs for the Washington coast and Puget Sound. These observation and research needs will be described in more detail in each of the following chapters.

1. Obtain high-quality, regional survey data to describe spatial and temporal patterns.
2. Instrument moorings in key existing and new locations to assess regional impacts and provide early warning of corrosive conditions.
3. Instrument shore-based platforms to monitor nearshore conditions to assess regional impacts and provide early warning of corrosive conditions.
4. Expand capabilities of existing platforms to collect data from the shallow and deep water layers.
5. Conduct laboratory studies of biological responses to ocean acidification.
6. Conduct coupled physics/chemistry/biology process studies in the field.
7. Develop forecast models of future changes and ecosystem responses.

2

Ocean Acidification on Washington's Outer Coast

Jan A. Newton
Richard A. Feely
Simone R. Alin

2.0 Key Points

2.0.1 What we know about ocean acidification on Washington's outer coast

- A combination of different drivers contributes to acidification on Washington's outer coast: atmospheric CO_2 input, deep-water respiration, upwelling, Columbia River inputs, and coastal hypoxia, though these have not all been quantified.
- Deeper open ocean waters—particularly in the North Pacific Ocean—that have been out of contact with the atmosphere for decades are naturally high in CO_2 as a result of biological respiration, which consumes dissolved oxygen and releases CO_2.
- An increase in DIC in seawater has been measured and ascribed to anthropogenic sources.
- Due to anthropogenic input of CO_2 to the Pacific Ocean, the aragonite saturation horizon has shoaled upward 50–100 m.
- Upwelling is a key seasonal feature that draws deep, corrosive waters toward the surface along the coastal margin, predominantly during summer, to within 20–120 m of the surface.
- The Columbia River plume is a dominant oceanographic feature in this region, delivering a large supply of freshwater, nutrients, and particulates to the coastal ocean. The river water is naturally low in pH and high in pCO_2, and river-borne nutrients can stimulate primary productivity in surface waters and respiration in bottom waters. It also influences the retention of corrosive waters either against or away from the coast.
- Coastal hypoxia is a sign of high respiration rates and, thus, higher amounts of DIC in subsurface waters.

2.0.2 What we need to know about ocean acidification on Washington's outer coast

- What are the carbon sources and sinks?
- What mechanisms drive the observed spatial and temporal variation in pCO_2 and pH, and what is the relative magnitude of these drivers?
- What is the effect of the Columbia River plume on pCO_2 and pH?

2.1 Drivers of Ocean Acidification on Washington's Outer Coast

A combination of drivers renders the Pacific coast of North America especially vulnerable to the presence of corrosive, acidified waters. Subsurface waters of the Pacific are naturally corrosive from accumulated CO_2 due to natural respiration processes and oxidation of organic matter. Anthropogenic additions of atmospheric CO_2 have further reduced the pH and the carbonate saturation states of Pacific coast waters (Feely et al., 2008, 2010). Offshore ocean conditions in our region are strongly influenced by the California Current System (Hickey, 1989), which experiences seasonal upwelling of these deep, highly corrosive waters onto the continental shelf, sometimes all the way to the surface (Feely et al., 2008). The seasonal impingement of the Columbia River plume in the south is also an important contributor to regional ocean conditions (Hickey et al., 2005, 2009). Respiration of organic matter in bottom waters is stimulated by the fertilizing effect of upwelled and river-borne nutrients and ultimately leads to low oxygen (hypoxia) and high pCO_2 levels in benthic coastal environments. The contribution of each of these drivers to acidification on the Washington coast is discussed in the following subsections. While most of our knowledge comes from the open coastal ocean, the nearshore regions of the coast are expected to be impacted by these same drivers. The intertidal zone may be subjected to somewhat different processes, due to the shallowness and strong mixing found in the surf zone. Data from this area are discussed further in Chapter 6, due to the important role of biological processes in this domain.

2.1.1 Upwelling

The waters of the Washington-Oregon coast are strongly influenced by seasonal upwelling, which has been well documented (e.g., Huyer, 1983; Hickey and Banas, 2003; Hickey et al., 2010). Upwelling is an important driver of acidification in this region. Upwelling is caused by prevailing winds from the north that are most common during summer, and its intensity can be gauged by an Upwelling Index available through NOAA (**Figure 2.1**). These winds cause deep, cold, salty, oxygen-poor, CO_2-rich, nutrient-rich (and recently corrosive) waters to be drawn up to the surface. In the winter, winds from the south drive downwelling, which allows warmer, fresher, oxygen-rich, nutrient-poor ambient surface waters to pile up along coast and impinge onshore.

The upwelling-driven transport of corrosive waters along the Washington coast has been well characterized (Feely et al., 2008, 2010; Hauri et al., 2009). Seawater samples taken from the *upwelling zone* (the source of upwelled water) between 150 and 200 m have Ω_{arag} values < 1.0 and pH values < 7.75; during the summer, these corrosive waters can rise up to mid-shelf depths of ~20 to 100 m along the coast (see Chapter 1, **Figure 1.7** from Feely et al., 2008). In August 2011, the pCO_2 in the upwelled water ranged from 850 to 950 μatm near the shelf break and higher values inshore, possibly enhanced by respiration processes on the shelf (R. Feely, *personal communication*). These studies indicate that, due to upwelling, most of the water column in nearshore regions below 60 m is corrosive with respect to aragonite.

Whether upwelling will increase or decrease with climate change has not been established (Bakun, 1990). Interannual variation in the strength, duration, and timing of upwelling is evident (Legaard and Thomas, 2006). Upwelling is often, but not always, decreased in El Niño years (Smith et al.,

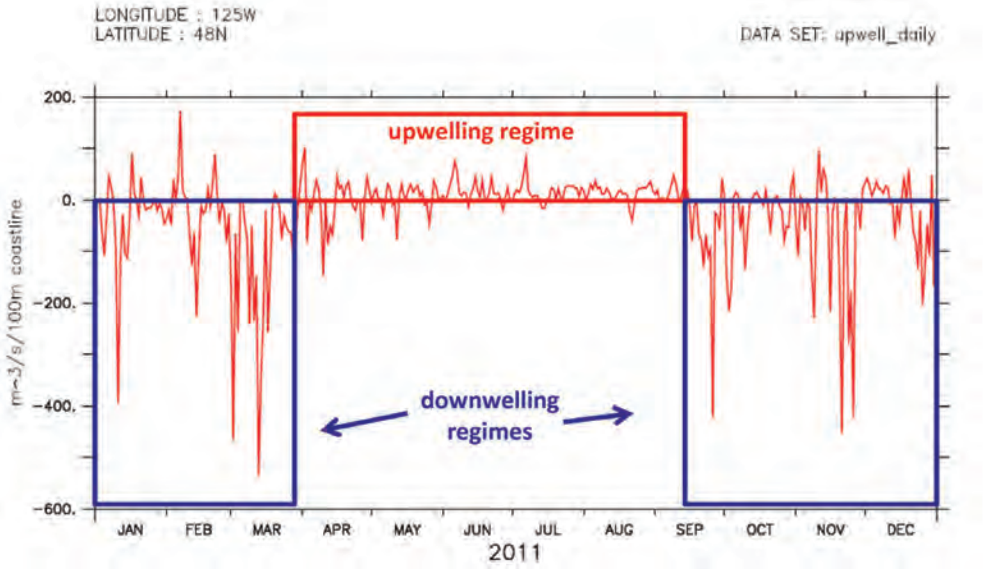

Figure 2.1: Upwelling index over an annual cycle at 48°N, 125°W along Washington's outer coast, showing spring and fall transition. Note that during the predominant up- or down-welling periods, reversals occur and will influence surface waters briefly. Data courtesy of the Environmental Research Division, NOAA NMFS Southwest Fisheries Science Center: las.pfeg.noaa.gov/las6_5/servlets/dataset.

2001). The relationship between upwelling and periodic climate patterns, such as the El Niño/La Niña-Southern Oscillation (ENSO) and Pacific Decadal Oscillation (PDO), needs further exploration.

2.1.2 Anthropogenic CO_2

The human contribution to acidification on Washington's outer coast is almost entirely due to atmospheric CO_2 from global sources. Anthropogenic land-based inputs of chemical compounds other than CO_2 (see Chapter 1) are relatively small in this region; for example, the amount of nitrogen in the Columbia River plume is low compared with the nitrogen signal in upwelled waters (Hill and Wheeler, 2002; Bruland et al., 2008). Ambient atmospheric CO_2 levels are lower off the coast than over Puget Sound (**Figure 2.2**) primarily due to the lack of vehicle traffic, but there is a measurable upward trend with time visible in the outer coastal data (**Figure 2.3**).

2.1.3 Columbia River

The Columbia River accounts for 77% of the freshwater input to the Pacific from the U.S. West Coast north of San Francisco (Barnes et al., 1972) and the Columbia River plume is a dominant oceanographic feature of Washington's outer coast (Hickey et al., 2005, 2009). Its plume can be pushed northward

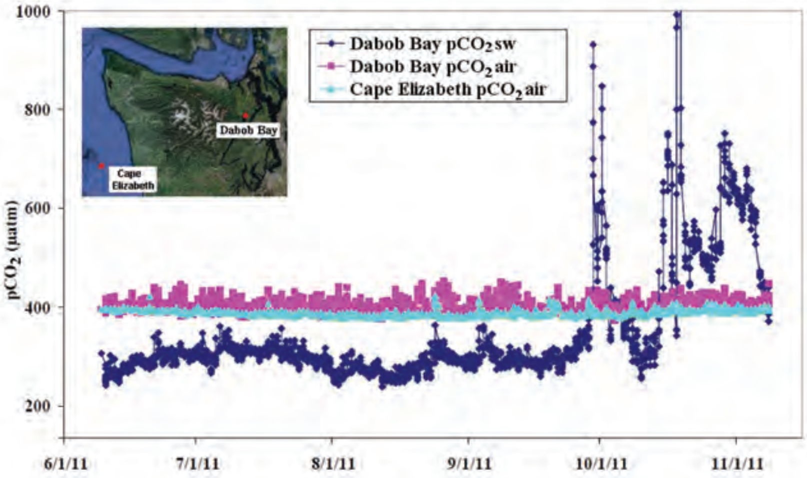

Figure 2.2: Atmospheric pCO_2 (the partial pressure of CO_2 in units of µatm) measurements by NOAA Pacific Marine Environmental Lab (PMEL) from the University of Washington buoy in Dabob Bay (in magenta) and NOAA National Data Buoy Center (NDBC) buoy off Cape Elizabeth on the outer Washington coast (in cyan). The surface seawater (sw) pCO_2 measurements at Dabob Bay are displayed in blue diamonds. The higher atmospheric pCO_2 values at Dabob Bay relative to the outer Washington coast reflect the local sources of CO_2 in the atmosphere, which can enhance the summertime flux of carbon dioxide into the local waters by about 75%.

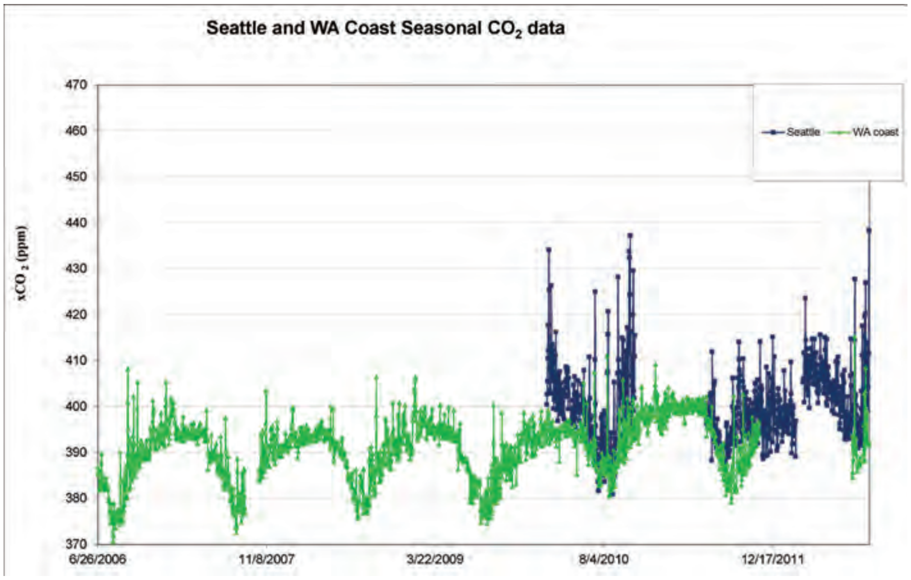

Figure 2.3: Atmospheric xCO_2 (the mole fraction of CO_2 in units of ppm in dry air) measurements from NOAA PMEL for Seattle in blue (Space Needle) and the outer Washington coast in green (Cape Elizabeth NOAA NDBC buoy) showing full time record for coast (since 2006) and available data for Seattle (2010 and 2011). Note that the outer coast has an apparent upward trend with time. Graphics provided by Ellen Lettvin, Pacific Science Center; NOAA PMEL data exhibited in Pacific Science Center CO_2 kiosk and in collaboration with C.L. Sabine, NOAA PMEL.

along the Washington coast when winds are from the south, which brings it in contact with coastal Washington waters, either near the coast or just offshore. The Columbia River can influence the pH of coastal waters in at least three ways. First, the pH of the Columbia River water is generally lower than surface seawater (R.A. Feely, *unpublished data*). Second, although nutrient concentrations in the Columbia River plume are typically low compared with upwelled water (Hill and Wheeler, 2002; Bruland et al., 2008), iron and silicates supplied by the plume can stimulate intense primary productivity along the Washington coast in summer, both nearshore and offshore (Hickey et al., 2010). As described in the section on Respiration and Hypoxia in Chapter 1, microbial decomposition of organic carbon (e.g., carbon produced by algal blooms) leads to increased pCO_2 levels, which drive down the pH. Third, during the summer, when the river plume frequently flows northward and occupies the nearshore water column, depending on wind and current conditions, it can temporarily shield the southern Washington coast from upwelled water or insulate recently upwelled waters near the coastline (Hickey and Banas, 2003; Hickey et al., 2005). Since upwelled waters can be corrosive, this effect can either prevent or prolong exposure. Overall, however, the effect of the Columbia River on acidification, and its relative importance compared to the Juan de Fuca eddy to the north (which also fuels primary productivity; MacFadyen et al., 2005, 2008) is not well described. Hickey et al. (2010, p. 23) assert that "to allow quantitative comparison of these processes, models and data collection must expand in scale, to encompass the interactions between freshwater inputs, and retention features over hundreds of kilometers of coastline."

2.1.4 Hypoxia

The linked processes of respiration and hypoxia are acknowledged to be important drivers of ocean acidification. Because hypoxic events are influenced by ocean conditions such as upwelling, changes in ocean dynamics can affect the degree, timing, and location of hypoxia, and its association with the carbon dynamics. Washington's outer coast experiences seasonal hypoxia coincident with periods of high primary productivity fueled by summer upwelling of nutrients. The historical record going back to 1950 shows that seasonal hypoxia is a recurring oceanographic feature in the northern California Current System, although the hypoxic "dead zones" that formed off the Pacific Northwest coast in the summer of 2006 were particularly severe (Connolly et al., 2010).

2.2 Current Monitoring System on Washington's Outer Coast

A few systems are currently in place that provide high-quality data on a suite of variables relevant to acidification and carbonate chemistry of Washington's coastal waters. However, these are either limited in time (survey cruises) or space (La Push buoy) and thus do not give a comprehensive view. Four monitoring platforms are either operational or coming online:

1. NOAA's Ocean Acidification Program:
    a. NOAA conducts periodic survey cruises to measure comprehensive carbon variables—pCO_2, pH, DIC, and TA—as well as temperature, salinity, DO, nutrients and chlorophyll (a metric for phytoplankton biomass).
    b. NOAA's wave glider is in its second year of field testing in Washington waters. The NOAA Pacific Marine Environmental Laboratory (PMEL) carbon group has teamed up with **Liquid Robotics Inc.** to integrate a $MAPCO_2$ system, a **SeaFET pH sensor** and a **SeaBird CTD** into a Wave Glider vehicle. The Wave Glider represents an innovative approach to ocean persistent presence; it harnesses ocean wave energy to provide essentially limitless propulsion while solar panels continually replenish the batteries used to power the Wave Glider's control electronics and payload systems. The Wave Glider vehicle is propelled by the purely mechanical conversion of ocean wave energy into forward thrust, independent of wave direction. (**http://www.pmel.noaa.gov/co2/story/Carbon+Wave+Glider**).
2. The NANOOS Buoy at La Push, funded by both NOAA Ocean Acidification and the U.S. Integrated Ocean Observing System (IOOS) implemented regionally by the Northwest Association of Networked Ocean Observing Systems (NANOOS) Programs, measures pCO_2 and pH, and also takes water column profiles of temperature, salinity, dissolved oxygen, nitrate, and chlorophyll. Data are relayed in near-real time to the NANOOS web portal for viewing or download. This buoy was deployed during the spring to fall months of 2010 and 2011 and was re-deployed in May 2012 for sustained year-round operations.
3. The National Data Buoy Center (NDBC) Buoy at Cape Elizabeth measures surface water pCO_2 levels (funded via NOAA's Global Carbon Cycle Program). This platform will be phased out as the more comprehensive La Push buoy comes online.

Other observing assets and opportunities exist in the region (e.g., annual NANOOS cruises, other buoys (including the Olympic Coast National Marine Sanctuary coastal buoys), and gliders; see the NANOOS website: **http://www.nanoos.org**), but none of them are currently equipped to collect or analyze carbon system variables. A major National Science Foundation (NSF) funded program, Ocean Margin Ecosystems Group for Acidification Studies (OMEGAS), has deployed pH and temperature sensors in the coastal waters of Oregon and California that could have relevance for Washington.

2.3 Observing and Research Needs for Washington's Outer Coast

Adequate monitoring is essential to understand and track ocean acidification trends on Washington's outer coast. Enhanced observational platforms would supply the data necessary to understand seasonal and inter-annual dynamics of ocean acidification. These data could also be used to develop and test models that may yield forecasting tools for hatchery and natural resource management.

2.3.1 Observing needs

1. Moorings to provide high-resolution time series data:
    a. Continued operation of the La Push buoy, which is currently supported by NOAA and IOOS.
    b. Additional moorings equipped with CO_2 sensors at the mouth of the Strait of Juan de Fuca, and outside the mouth of the Columbia River.
2. Sustained periodic coastal surveys to improve predictive relationships for estimating pH and carbonate saturation levels. Ship-based hydrography is the only method for obtaining high-quality measurements at high spatial and vertical resolution for a suite of physical, chemical, and biological parameters over the full water column.
3. Additional shipboard surveys are needed to characterize the Columbia River plume effect.
4. Nearshore and intertidal monitoring.
5. Operational modeling that is nested within larger scale models is needed to understand seasonal and inter-annual dynamics of outer coast conditions, including the Columbia River plume (an operational model assimilates real-time data to continuously calculate current conditions). Operational models generate information on shorter-term timescales that are useful both to hatchery managers (hourly to weekly) and to scientists studying longer-term trends. (Note: current modeling capability for the Washington coast does not include carbon parameters or pH, nor is it operational.)

2.3.2 Research needs

1. Determine spatial and temporal patterns in carbon parameters and pH; identify what is driving variation and quantify the contributions of specific drivers of acidification.
2. Develop a budget for carbon sources and sinks; derive a basic understanding of carbon sources and sinks, flows, and transformations. Include the effect of the Columbia River plume on carbon parameters and pH.
3. Use data and models to improve current predictive forecasting of risk of corrosive waters.
4. Conduct coupled physics/chemistry/biology measurements.
5. Conduct process studies to address above unknowns, such as identified in *research need 2*, above.

3

Ocean Acidification in Puget Sound and the Strait of Juan de Fuca

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3.0 Key Points

3.0.1 What we know about ocean acidification in Puget Sound and the Strait of Juan de Fuca

- Ocean acidification in Puget Sound and the Strait of Juan de Fuca is strongly influenced by oceanic input; the nature of ocean input varies seasonally and inter-annually.
- Flushing (renewal of basin waters) is influenced by density differences between freshwater and oceanic inputs; the strength of flushing varies spatially within Puget Sound and inter-annually.
- Puget Sound is retentive. Waters stay in some parts of Puget Sound for a long time due to sills that "reflux" water back into Puget Sound.
- NOAA/University of Washington (UW) data from moored sensors in Dabob Bay and at Twanoh indicate that surface pCO_2 levels are highly variable spatially and temporally. NOAA/UW data from Puget Sound cruises show strong regional and seasonal variation, with well-mixed but corrosive conditions during wintertime and strong gradients with more corrosive waters in the deeper layer during the summer and fall.
- Subsurface waters in many parts of Puget Sound are undersaturated with respect to aragonite throughout the year.
    - Ocean acidification accounts for 24–49% of the DIC increase in the subsurface waters of Hood Canal.
    - The remaining DIC increase is due to respiration processes within Puget Sound.
- Nitrate concentrations in Puget Sound are increasing. Washington State Department of Ecology data reveal a presumed anthropogenic nutrient fingerprint in Puget Sound, implying that respiration may exceed the natural signal.
- Nutrient-fueled hypoxic events contribute to the high DIC levels in stratified waters.
- The contribution of regional atmospheric inputs of CO_2 and NO_X/SO_X to acidification is not known.

3.0.2 What we need to know about ocean acidification in Puget Sound and the Strait of Juan de Fuca

- What are the carbon dioxide and pH inputs and outputs?
- What mechanisms drive the observed extreme variation in DIC and pH?
- What are the effects of nitrogen loading on DIC and pH?
- What are the effects of regional atmospheric CO_2, NO_X, and SO_X emissions on seawater DIC and pH?

- What are the relative contributions of these drivers to regional acidification?
- How does freshwater affect TA, DIC, and pH measurements?

3.1 Distinguishing Features of Puget Sound and the Strait of Juan de Fuca

Puget Sound, the second largest estuary in the United States, has over 3,000 km of shoreline (Shipman, 2008). Carved by retreating glaciers at the end of the last ice age 11,000–15,000 years ago (Kruckeberg, 1991), Puget Sound is a deep, fjord-like, semi-enclosed estuary that communicates with Pacific Ocean at its northern end via the Strait of Juan de Fuca. Puget Sound is unique in the United States; most estuaries in this country are coastal plain or drowned river estuaries, lacking significant restrictions to the coastal ocean and lacking the great depths and strong tidal currents that characterize Puget Sound. The average depth of Puget Sound is 62 m and its maximum depth is 280 m (Thomson, 1994).

Characteristics of the incoming Pacific Ocean water, such as temperature, salinity, oxygen, and nutrients, vary on a seasonal and inter-annual basis. The largest variation is from the seasonal wind shifts between upwelling and downwelling conditions on the outer coast. Upwelled waters, typically observed in summer, are cold and salty, with lower oxygen and higher nutrient content (Hickey and Banas, 2003). Upwelling can be confused with, but also can compound effects of, human-related eutrophication. Upwelled waters are also CO_2-rich and contribute significantly to acidification in the deeper layers of Puget Sound (Feely et al., 2008, 2010). Conditions in the Sound are strongly tied to climate on many scales, including seasonal, inter-annual, and long-term climate change (Adelsman and Ekrem, 2012).

Net circulation of marine waters is a density-driven exchange between salt water from the Pacific Ocean that underlies and mixes with fresh water runoff from the surrounding watershed (Cannon et al., 1990; Thomson, 1994). Less dense than seawater, the fresh water forms a surface layer that moves towards the ocean while the ocean water forms a deeper layer that moves toward the land. Strong tidal exchanges drive much of the mixing and currents in Puget Sound; these are strongest near Admiralty Inlet, where the tidal currents range from approximately 0.5 to 1.0 m s^{-1} (e.g., Geyer and Cannon, 1982). Puget Sound estuarine waters thus reflect input from, and the variation in, water from both oceanic and watershed sources. Additionally, Puget Sound is quite diverse within itself, e.g., strong gradients in salinity and circulation are evident throughout the four interconnected basins of Puget Sound (Whidbey, Main, Hood Canal, and South Sound) (Newton et al., 2003; Moore et al., 2008).

Ridges or sills on the bottom of the Sound affect the movement of seawater. These sea-bed features cause turbulence in the overlying water flow that increases the mixing of the fresher (upper) layers and saltier (deeper) layers such that some of the out-flowing water returns, or refluxes, back into the Sound (see Ruckelshaus and McClure, 2007). Tidal pumping of water in and out of basins increases this mixing. An implication of the mixing and return flow is that some of the materials that have been transported into, or are suspended within Puget Sound waters can persist for a long time. Thus, planktonic (free-drifting) organisms in Puget Sound tend to have a long residence time before being exported out, which contributes to the high productivity of the Sound. However, this condition also promotes retention of nutrients and other substances received from adjacent watersheds (sometimes referred to as watershed loads), which has implications for the magnitude of their effect in the local system.

3.2 Drivers of Ocean Acidification in Puget Sound and the Strait of Juan de Fuca

Acidification in Puget Sound and the Strait is strongly influenced by the oceanic signal—corrosive water moves in from the coast at depth and resides in the subsurface basin layers. In coastal estuarine environments within Puget Sound, inputs of nutrients and organic matter can further reduce pH and carbonate saturation state by stimulating microbial respiration. In developed or urbanized regions, localized high concentrations of atmospheric CO_2, NO_X, and sulfur dioxide (SO_2) can also acidify marine waters (see Chapter 1, Sections 1.5 and 1.6). These terrestrial inputs, whether from natural sources or due to human activity, can combine to intensify ocean acidification in estuaries and nearshore areas. Because circulation is sluggish in many of the restricted inlets of Hood Canal and South Sound, terrestrial inputs can have relatively localized impacts. Layered over an acidification signal in upwelled coastal water, these additive effects may have contributed to corrosive conditions in Puget Sound. Some of the lowest pH levels and aragonite saturation states yet observed in Washington coastal waters have been measured in the southern part of the Hood Canal basin (Feely et al., 2010). All of these drivers will be discussed in more detail in the following subsections.

3.2.1 Contribution of coastal waters

Orr et al. (2005) calculated that the increase in acidity of the *surface waters* of the North Pacific that can be attributed to the uptake of anthropogenic CO_2 from the atmosphere since the beginning of the industrial age is 0.1 pH units. Feely et al. (2008) determined that the anthropogenic contribution to the acidity of *upwelled corrosive waters* along the Pacific Northwest coast accounts for a pH decrease of ~0.05 units (based on World Ocean Circulation Experiment/Joint Global Ocean Flux Study Global CO_2 Survey data). Further decline in ocean pH caused by the deposition of nitrogen and sulfur compounds (from fossil fuel combustion and agriculture) to the ocean surface layer has also been estimated (Doney et al., 2007).

Based on these three studies, a reasonable estimate of the range of the present-day pH decrease in Puget Sound that is due to drivers acting *outside* Puget Sound is between 0.05 and 0.15 (Feely et al., 2010). The remaining change in pH between when seawater enters the Sound and when it reaches the deep basins of Puget Sound must therefore be due to remineralization of organic matter stimulated by natural or anthropogenic nutrient inputs *within* Puget Sound.

The relative contribution of global vs. regional drivers varies seasonally. In the winter, when primary productivity in Puget Sound is low, 49% of the total DIC increase (above pre-industrial levels) observed in Hood Canal has been attributed to the influx of coastal waters. In the summer, when Hood Canal phytoplankton blooms lead to an increased local respiration signal, the estimated oceanic contribution drops to 24% (Feely et al., 2010).

3.2.2 Terrestrial nutrient inputs

Historically, anthropogenic contributions to nutrient loading in Puget Sound were not considered to be significant, given the typically high concentrations of nutrients coming into the system from the Pacific Ocean (Mackas and Harrison, 1997; Newton and Van Voorhis, 2002). It was furthermore expected that strong mixing in the Main Basin, which limits exposure of phytoplankton to light and therefore reduces growth, protected Puget Sound from anthropogenic eutrophication (Winter et al., 1975). These characteristics of central Puget Sound contributed to the success of the diversion of sewage from Lake Washington to West Point (Puget Sound) in the late 1950s (Edmondson, 1991).

Harrison et al. (1994) evaluated the issue of anthropogenic eutrophication in the Strait of Juan de Fuca, Strait of Georgia, and Puget Sound, and judged potential impacts from eutrophication of the Main Basin of Puget Sound to be relatively low. However, they reported that the more poorly flushed bays and inlets of Puget Sound, particularly in the southern end, showed depleted surface nitrate concentrations and very low oxygen concentrations at depth. They asserted that the “early warning signs of eutrophication” were already evident in these poorly flushed bays and inlets of southern Puget Sound. This conclusion has been reinforced by more recent assessments of surface waters in certain parts of Puget Sound with restricted circulation and developing shorelines (Newton and Van Voorhis, 2002; Simonds et al., 2008).

The effects of eutrophication on ocean acidification have been explored recently by observational and modeling studies. Using data collected in the northern Gulf of Mexico and the East China Sea, two regions heavily influenced by nutrient–laden rivers, Cai et al. (2011) concluded that eutrophication was associated with the development of hypoxia and the acidification of subsurface waters. Moreover, model simulations, using data collected from the northern Gulf of Mexico, suggested that the decline in pH was greater than that expected from eutrophication and ocean acidification alone. They attribute an additional decline of 0.05 pH units to a reduction in the ability of carbon dioxide-rich waters to buffer changes in pH.

Aside from the effect on pH from contribution of CO_2 from microbial respiration of organic matter, the authors suggest that eutrophication could increase the susceptibility of coastal waters to ocean acidification. Additional model runs for the Gulf of Mexico and the Baltic Sea by Sunda and Cai (2012) confirmed this result and indicated that CO_2 inputs were predicted to reduce current pH values by 0.25–1.1 units, effects that increased with decreasing temperature and salinity.

Because there have been no high-quality, long-term, time series measurements of carbon, nitrogen, and sulfur species in Puget Sound that have been linked with models of carbon dynamics, it is not possible to *directly* determine the level to which human activity in this region is contributing to acidification. Nitrogen inputs (both natural and anthropogenic) are suspected of being regional drivers of acidification. The Washington State Department of Ecology has extensive nitrogen loading data for Puget Sound and has recently published a report summarizing these nutrient loads over the period 1999–2008 (Mohamedali et al., 2011). The comparison of human to "natural" sources of nitrogen in Puget Sound from that report, reproduced here as **Table 3.1**, shows a considerable contribution from human sources. Nitrogen inputs are from a number of sources, such as sewage input (from septic systems and wastewater treatment facilities), agricultural and domestic fertilizers, and red alders (which harbor nitrifying microbes). The relative contribution of various nitrogen loads to the status of acidification in Puget Sound has not been established. However, we do have evidence that human loads of nitrogen may be altering the nitrate content of the surface marine water in Puget Sound. Independent of substantial spatial and temporal variations in seawater properties of Puget Sound, surface nitrate (NO_3) concentrations are increasing, according to Washington State Department of Ecology data showing a 3 micromolar ($\mu mol\ l^{-1}$) increase in surface NO_3 over 10 years (**Figure 3.1**; C. Krembs, *personal communication*). This increase appears to be non-oceanic in source, based on the associated silicate to dissolved inorganic nitrogen ratios, which have decreased, instead of holding steady, as would be predicted for oceanic input. This surface increase in NO_3 represents the *net increase* (i.e., the amount that is *not* taken up by phytoplankton) in the top 30 m, so the nitrogen increase could be appreciably more than 3 $\mu mol\ l^{-1}$. It is not known whether there is an increase in NO_3 below 30 m, because sampling for nitrate has not routinely extended below 30 m. Different areas of Puget Sound would be expected to react differently to nitrogen inputs depending on the degree of ocean input relative to land-based or human-sourced nitrogen inputs, as well as features such as mixing, flushing, and natural productivity of the area. Basins with strong stratification and long residence times should be the most susceptible to land-based and human-sourced inputs of nitrogen.

Table 3.1: **Comparison of natural and 1998–2008 average annual dissolved inorganic nitrogen (DIN) loads from rivers and wastewater treatment plants (WWTPs) into the Puget Sound and the Straits. Source: Mohamedali et al. (2011).**

	Average Annual DIN Load (kg/d)			
Subbasin/Region	Natural Conditions	Human Nonpoint Sources (in rivers)[1]	Human Point Sources (WWTPs)[2]	Total Human
South Sound	1,820	2,300	2,540	4,840
Commencement Bay	1,230	880	2,440	3,320
Elliott Bay	760	880	0	880
Puget Main	850	0[4]	22,700	22,700
Sinclair Dyes Inlet	140	90	1,010	1,100
Whidbey	9,490	3,260	3,470	6,730
Admiralty	20	110	40	150
Hood Canal	570	240	1	240
Strait of Juan de Fuca	350	130	310	440
Strait of Georgia	2,350	3,790	1,760	5,550
Puget Sound Subtotal[3]	**14,900**	**7,700**	**32,200**	**40,000**
Straits (US) Subtotal[3]	**2,700**	**3,900**	**2,100**	**6,000**
Total[3]	**17,600**	**11,600**	**34,300**	**46,000**

[1] Human nonpoint sources = (1999-2008 annual average river loads) – (natural conditions loads)

[2] Human point sources = 1999-2008 annual average wastewater treatment plant (WWTP) loads

[3] These loads have been rounded to the nearest 100 kg/d.

[4] Estimated natural DIN loads into the main basin of Puget Sound were comparable to current nonpoint sources, so the calculated value for human nonpoint sources is zero based on the difference between current and natural loads. Current loads were estimated using more information, while natural loads were estimated from fewer ambient data from the Cedar River.

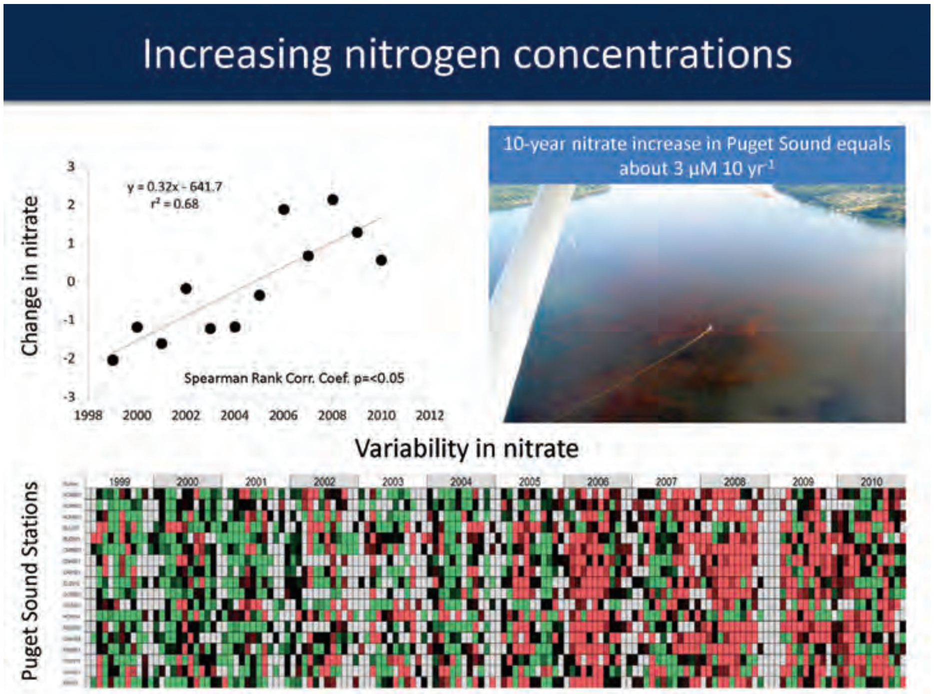

Figure 3.1: Change in NO$_3$ in µM (=µmol L^{-1}) in 0–30 m waters from Washington State Department of Ecology monitoring stations over 10 years yields a statistically significant increase. The "heat map" of the anomalies (red: above 10-year trend; green: below 10-year trend; grey: equal to the 10-year trend; black: no data) shows this decadal increase is Sound-wide. Figure from C. Krembs, Washington State Department of Ecology presentation to the Blue Ribbon Ocean Acidification Panel, 23 May 2012.

What is *not* known is the magnitude of the effect that the anthropogenic nitrogen inputs have on pH or aragonite saturation levels. Resolving this issue is not trivial; it will require new knowledge of residence times, export production (the amount of particulate organic carbon that sinks out of the euphotic zone and is remineralized at depth), and oceanic boundary conditions (baseline pH and carbon species signals from the coast). While model estimates exist for some of these parameters, the analyses needed to definitively answer this question have not been performed, and the data to verify results are lacking.

Another factor affecting our understanding of terrestrial inputs and carbon chemistry is that the rivers entering Puget Sound may have a large impact on surface seawater alkalinity. Freshwater inputs also have been associated with increases in pCO$_2$ and lower pH values (Frankignoulle and Borges, 2001). Further analysis of the data from Puget Sound and Strait of Juan de Fuca waters is needed to quantify correlative relationships between pH and carbon species and other variables, and to identify the underlying mechanisms responsible.

3.2.3 Hypoxia

The linked processes of respiration and hypoxia are acknowledged to be important drivers of acidification. Hypoxia is a natural consequence of the strong stratification, slow flushing, and restricted mixing typical of Hood Canal (Newton et al., 2002, 2007; Newton, 2007) and the South Sound (Albertson et al., 2002, 2007). It is also subject to climate forcing (Brandenberger et al., 2008). Recent, prolonged hypoxia in Hood Canal and more seasonal or episodic hypoxia in South Puget Sound are being studied to determine whether human additions of nutrients are exacerbating this condition (Roberts et al., 2008; Newton et al., 2011).

The degree of stratification within a marine water column is significant because of the physical barrier it presents with respect to vertical water movement (mixing and entrainment). Turbulent eddies, driven by winds and tides, cause vertical mixing of phytoplankton, dissolved oxygen, nutrients, pollutants, etc. If, however, the water is stratified—that is, if its density increases significantly with depth—then the ability of turbulence to cause vertical mixing is greatly reduced. Thus, stratification effectively isolates the surface water from the deep water. This can have significant implications for water quality; it can isolate zones where dissolved oxygen in the seawater becomes depleted and causes fish kills; it can isolate zones where nutrients become scarce and thus human additions of nutrients (e.g., sewage input, agricultural and domestic fertilizers) can cause additional algal growth in excess of the natural system; it can concentrate pollutants and contaminants up in the surface water, where much of the plankton (including sensitive eggs and larvae) is concentrated, instead of mixing and diluting these out and away from the surface zone.

Stratification is spatially and temporally variable in Puget Sound, with the most persistent and strong stratification found in Hood Canal, Whidbey Basin, and parts of South Puget Sound. Hypoxia is typically found in persistently stratified areas. Hypoxia indicates where respiration of organic material has occurred, and thus, this also is where pCO_2 is high and pH is low. Thus, respiration as indicated by hypoxia is an additional driver of acidification.

3.2.4 Inputs from regional atmospheric CO_2

Atmospheric carbon loads in the Puget Sound region are associated with the urban corridors; for example, in Seattle, xCO_2 (the mole fraction of CO_2 in units of ppm in dry air) values occasionally exceed 490 ppm (Chapter 2, **Figure 2.2**). Whether this local enhancement has resulted in a measurable decrease in the pH of local surface waters is not known. There is significant variation in the surface seawater pCO_2 signal in Puget Sound (**Figure 3.4**). Much of the variation is due to upward mixing of deep waters, but respiration generates a strong signal as well, as do freshwater inputs and seawater temperature changes. While patterns in pCO_2 levels do seem to correlate with certain processes, such as upward mixing of deep waters and phytoplankton blooms

(**Figure 3.5**), these associations have not been described quantitatively. Moreover, quantifying the effect from diffusion of atmospheric CO_2 into seawater would involve knowing the timescales of diffusion and mixed layer processes, which would be influenced by wind and temperature. Such calculations have not been made, although suitable data may exist. In general, the gas exchange processes across the air-sea interface are slow relative to the mixing and biological processes in coastal regions.

3.2.5 Additional ocean acidification drivers

The emission of NO_X and SO_X gases from fossil fuel combustion, and their subsequent dissolution in seawater present another source of acidification in seawater. The effect from these gases is expected to be more important in coastal waters than in the open ocean (Doney et al., 2007) because of the proximity of coastal waters to the sources of emissions. The emission of NO_X and SO_X gases from maritime transport is potentially a substantial portion of the total contribution. The significance of these acid gases for ocean acidification in the Puget Sound region is likely to be small, but is not known. The Strait of Juan de Fuca is a major shipping corridor, and there are several very large ports within Puget Sound. Therefore, this topic deserves further attention for its regional role.

Wastewater discharges from industrial sources can reduce the pH of receiving marine waters. State and federal regulations apply to such wastewater discharges. The contribution of wastewater discharges to ocean acidification conditions is not known and is potentially small, but localized effects could occur, especially in retentive areas and those of limited flushing. For example, effluent from the Rayonier Pulp mill, which operated in Shelton from 1927 to 1957, had a suspected effect on the native oyster population (White et al., 2009), though note that this result predates current wastewater regulations. The effect from existing pulp mills on water quality in Puget Sound is not known and is potentially small, but because of the potential for localized effects, it merits further research.

3.3 Current Monitoring Capacity in Puget Sound and the Strait of Juan de Fuca

Puget Sound does not have a sustained, comprehensive monitoring program to provide high-quality measurements of the suite of variables relevant to acidification and carbonate chemistry. While pH is being monitored by the Washington State Department of Ecology and others via potentiometric sensors, these sensors do not provide the accuracy and precision required to measure ocean acidification. The following monitoring platforms currently collect data on carbonate system variables. All data streams noted below have been made available through the NANOOS Visualization System (NVS: **http://www.nanoos.org**) by the data providers; the NOAA data are also available through NOAA PMEL's Ocean Acidification page (**http://www.pmel.noaa.gov/co2/story/Observations+and+Data**):

1. **Land-based systems:** Two shellfish hatcheries and one shore-based station have pCO_2 and pH and ancillary sensors (temperature, salinity, etc.), and collect calibration water samples on seawater intakes:
    a. Dabob Bay Hatchery (Taylor Shellfish Farms), maintained in conjunction with the Pacific Coast Shellfish Growers Association.
    b. Lummi Hatchery (Lummi Natural Resources), maintained in conjunction with the Pacific Coast Shellfish Growers Association.
    c. Seattle Aquarium, maintained in conjunction with NOAA PMEL's Carbon Program.
2. **Open water monitoring platforms:** Two buoys are equipped with pCO_2 sensors for surface measurement of seawater and atmosphere, and take full water-column profiles for temperature, salinity, oxygen, chlorophyll, etc. and meteorological measurements:
    a. Dabob Bay: UW-NANOOS profiling buoy with NOAA PMEL sensors.
    b. Twanoh: UW-NANOOS profiling buoy with NOAA PMEL sensors. NANOOS funding currently is not sufficient to maintain these two buoys, and the carbon measurements currently are not supported by NOAA's Ocean Acidification Program.
3. **Cruise-based sampling:** Two programs can contribute to assessment of Ocean Acidification:
    a. University of Washington annual PRISM/NANOOS cruises. Since 1998, the UW has conducted semi-annual or annual cruises on the R/V *Thompson*. First as part of the PRISM program and now adopted by NANOOS, these cruises are staffed by students and run on State-donated ship days for student training, with participation from regional partners, including the Washington Department of Ecology. Since 2008, the UW invited the participation of NOAA PMEL scientists to measure ocean acidification variables. These cruises cover ~40–50 stations in greater Puget Sound and the Strait of Juan de Fuca. Comprehensive oceanographic sampling is conducted for temperature, salinity, oxygen, chlorophyll, transmissivity, nutrients, and other variables. There is no funding for carbon system sampling or analysis. The U.S. Environmental Protection Agency (EPA) hosted this cruise on their Ocean Survey Vessel (OSV) *Bold* in August of 2008.
    b. University of Washington Friday Harbor Laboratory (FHL) Pelagic Ecosystem Function Time Series. These data currently are collected at four depths at two stations in the San Juan Channel and the Strait of Juan de Fuca. Water samples are analyzed for DIC and alkalinity. Data

are accompanied by water column profiles for temperature, salinity, oxygen, chlorophyll, and nutrients. This time series is conducted as part of the UW-FHL fall quarter Research Apprenticeship student cruises, and recently has been extended through the rest of the year through collaborations with the Northwest Indian College and Western Washington University, with partial funding through UW College of Environment and NSF's Center for Coastal Margin Observations and Prediction for tribal Science, Technology, Engineering and Math (STEM) enhancement. There is no sustained funding for this time series beyond 2013.

There exist other opportunities and observing assets that are of relevance to water quality but are not currently equipped to collect or analyze carbonate system variables. These include: the Washington State Department of Ecology seaplane, which collects samples to monitor water quality; four additional UW profiling buoys; and other buoy and shore-based platforms (see assets at NANOOS Visualization System (**http://www.nanoos.org**)).

3.4 Recent Observations

3.4.1 Spatial variability

Data collected during ship transects of Puget Sound in February and August 2008 (UW PRISM-NANOOS cruises; **Figures 3.2** and **3.3**) revealed that marine waters below the surface in Puget Sound were undersaturated with respect to aragonite throughout the year (Feely et al., 2010). During February 2008, the entire water column in both the Main Basin and Hood Canal was corrosive, meaning that waters were undersaturated with respect to the aragonite form of the biomineral calcium carbonate ($\Omega_{arag} < 1.0$, corresponding to a pH < 7.75 (Feely et al., 2010)). During August 2008, aragonite saturation and pH values in the upper ~20 m were substantially higher, due to biological drawdown of CO_2, while deeper waters (> 20 m depth) hovered just above or below the saturation threshold ($\Omega_{arag} = 1.0$) in the Main Basin and were substantially lower than 1.0 (undersaturated) in Hood Canal bottom waters, especially at the southern end of the basin (minimum $\Omega_{arag} < 0.4$, minimum pH = 7.35; Feely et al., 2010).

Since the initial surveys in 2008, carbon measurements have been repeated on cruises in October of 2009, 2010, and 2011 at stations from the Strait of Juan de Fuca through Puget Sound, including Hood Canal. Carbonate-system variables were measured at a limited number of stations due to lack of funding for analysis. Because of the extremely low pH and Ω_{arag} values observed in southern Hood Canal during the 2008 cruises, sampling on subsequent cruises was extended to a site around the Great Bend toward Lynch Cove. In all three October surveys, the entire water column from the Strait of Juan de Fuca to the Great Bend was undersaturated with respect to aragonite and was corrosive (Alin and Feely,

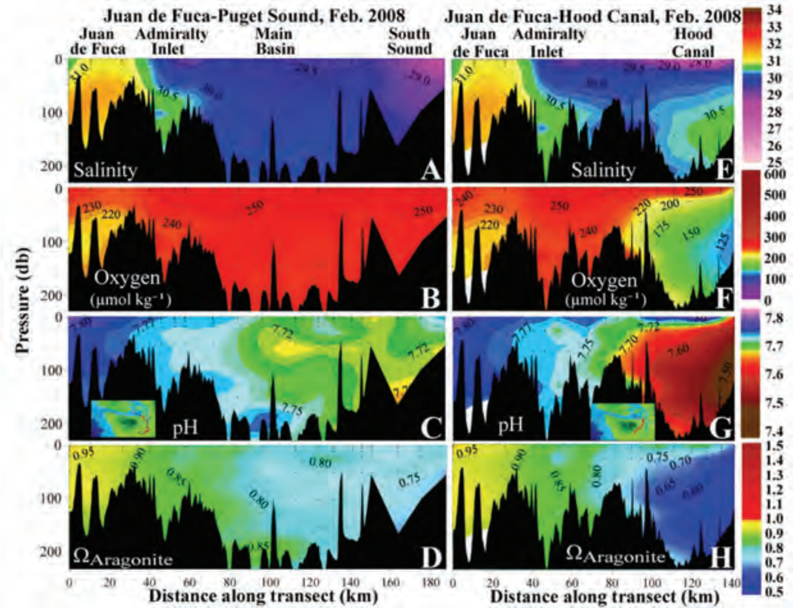

Figure 3.2: Distribution of a) salinity, b) oxygen, c) pH, and d) Ω_{arag} along a transect from the Strait of Juan de Fuca through the Main Basin and into South Sound; and e) salinity, f) oxygen, g) pH, and h) Ω_{arag} from the Strait of Juan de Fuca to the southern end of Hood Canal during February 2008. Note that color scales for winter cross-sections span smaller ranges for all parameters than summer cross-sections. Black dots represent sampling depths (from Feely et al., 2010).

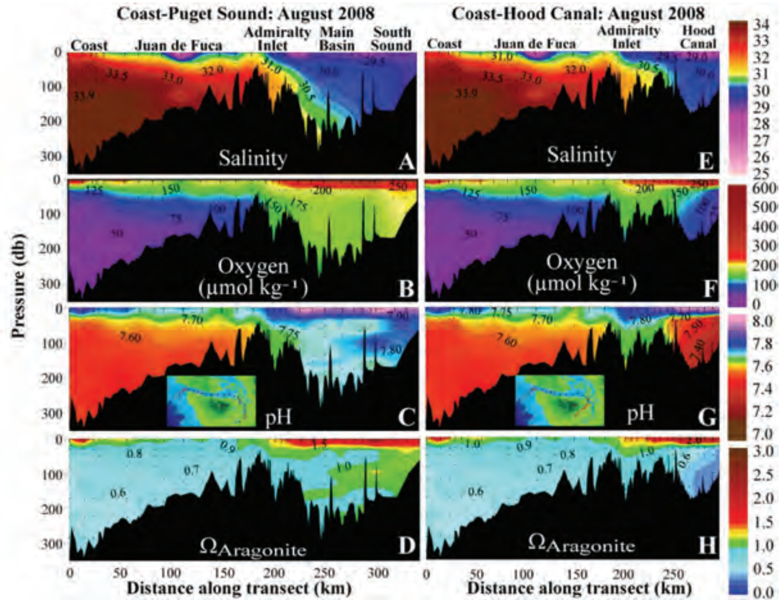

Figure 3.3: Distribution of a) salinity, b) oxygen, c) pH, and d) Ω_{arag} along a transect from the coast through Puget Sound's Main Basin and into South Sound; and e) salinity, f) oxygen, g) pH, and h) Ω_{arag} on a transect from the coast to the southern end of Hood Canal during August 2008. Note that color scales for summer cross-sections span larger ranges for all parameters than winter cross-sections. Black dots represent sampling depths (from Feely et al., 2010).

unpublished data). During all October cruises, the cruise-wide minimum values observed for pH and Ω_{arag} were observed at a station in the Great Bend at depth below the pycnocline. The pH and Ω_{arag} values throughout Hood Canal during the 2009 and 2011 October cruises were comparable to or lower than those observed in August 2008, with slightly higher values observed in 2010 in deep Hood Canal waters compared with 2008. The lowest values measured to date in Puget Sound (pH = 7.06; minimum Ω_{arag} = 0.19) were obtained in October 2011 at a station in the Great Bend. These minimum pH and Ω_{arag} values occurred at water depths of ~5–10 m in all three years (2009–2011) and appear to be the result of strong production and respiration in surface waters in Lynch Cove.

3.4.2 Temporal variability

High-resolution observations: To further observe ocean acidification status in Puget Sound, autonomous buoys that are part of NANOOS have been outfitted with sensors for pCO_2 and pH. The scale of variation in pCO_2 in the atmosphere and surface waters is different, but both records reflect dynamic processes. The variation in seawater pCO_2 appears to be associated with processes such as destratification (i.e., upward mixing of deep high-CO_2 waters; **Figure 3.4**) and increased primary production (drawing CO_2 levels down; **Figure 3.5**), which can vary on short timescales. Note the seasonal drawdown of atmospheric CO_2 during the summer growing season. Assembling a time series from these data is leading to a better understanding of range of variation and the mechanisms involved with ocean acidification in Puget Sound.

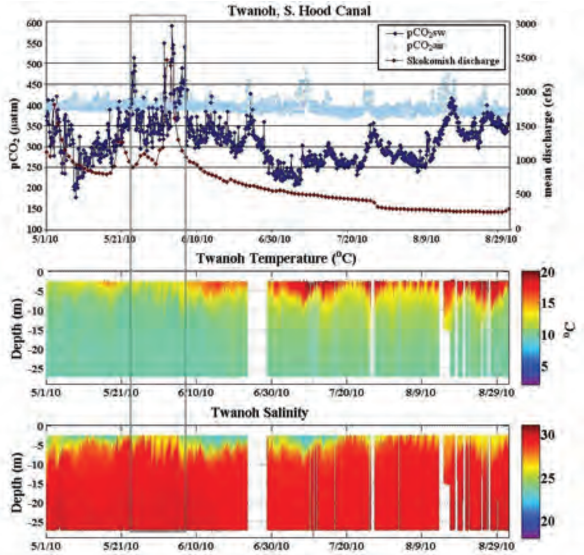

Figure 3.4: Seasonal record of seawater and air pCO_2 from NOAA PMEL sensors on a NANOOS profiling buoy at Twanoh in S. Hood Canal. Also shown are the Skokomish River discharge (U.S. Geological Survey), and water column profiles of seawater temperature and salinity. Higher seawater pCO_2 coincides with destratification deep mixing events, as bounded by the grey box. The CO_2 data are courtesy C.L. Sabine (NOAA PMEL); oceanographic data are courtesy A. Devol and J. Newton (UW).

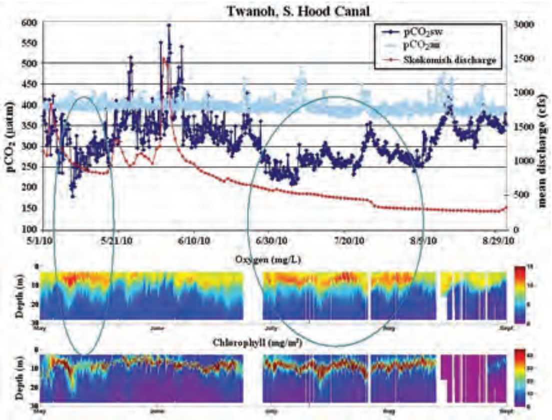

Figure 3.5: Seasonal record of seawater and air pCO_2 from NOAA PMEL sensors on a NANOOS profiling buoy at Twanoh in South Hood Canal. Also shown are water column profiles of seawater dissolved oxygen and chlorophyll. Drawdown of seawater pCO_2 appears to coincide with phytoplankton blooms, as evidenced by high surface oxygen and chlorophyll concentrations within green ellipses. The CO_2 data are courtesy C.L. Sabine (NOAA PMEL); oceanographic data are courtesy A. Devol and J. Newton (UW).

Observations of water mass signatures: A time series initiated in summer 2010, based at the UW Friday Harbor Laboratories, is focused on two stations: one in San Juan Channel and one in the Strait of Juan de Fuca just outside Cattle Pass. These two stations are characterized by different water masses, with the former influenced by water from the Strait of Georgia and Fraser River and the latter influenced by surface water flowing out of Puget Sound and deeper water flowing in from the Pacific Ocean. Graduate student C. Sullivan (UW School of Marine and Environmental Affairs) has analyzed the data through December 2010 (Sullivan, 2012). Observations showed substantial variation in time, with evidence of seasonal changes in coastal dynamics and local wind mixing as well as fluvial (river) influence. These data captured the change in oceanic carbonate chemistry due to the transition from upwelling to downwelling conditions in the coastal ocean.

Coupled observations of biological, physical, and chemical variables: Observations of high mortality among larval stages of oysters in the Pacific Northwest have raised concern that changing water chemistry due to ocean acidification could be causing the negative effects observed in shellfish populations. To help address this question, pilot studies coupling biological, physical, and chemical measurements were conducted in Totten Inlet in South Puget Sound and in Dabob Bay near the north end of Hood Canal, both important areas for oyster production and farming (Alin et al., 2012). Comparison between the two sites suggests that different mechanisms may be associated with oyster mortality. The major factor influencing water chemistry in Dabob Bay is wind-driven localized upwelling, whereas in Totten Inlet, nearshore carbonate chemistry appears to be dominated by biological respiration. At both sites, the decrease in pH and carbonate saturation states corresponded with the end of oyster larval settlement, and the time when predominant shell mineralogy in juvenile oysters transitions from aragonite to calcite, which is more resistant to corrosion.

Atmospheric observations: Ambient atmospheric CO_2 levels in Seattle and over Dabob Bay and Twanoh vary substantially across daily and monthly time scales (**Figures 2.2**, **3.4**, and **3.6**). Increases are associated with traffic and weather events in Seattle (**Figure**

3.6) with values being highest during worker commute hours, and on warm, calm days.

3.5 Observing and Research Needs for Puget Sound and the Strait of Juan de Fuca

Monitoring studies of Puget Sound and the Strait of Juan de Fuca must be expanded to include carbonate system variables. Sustained funding is needed to deploy enhanced observational platforms at spatial and temporal scales that are capable of characterizing the water chemistry within different sub-areas of Puget Sound and the Strait of Juan de Fuca. The high-resolution data provided by such platforms can lead to improved predictive relationships for estimating pH and carbonate saturation levels in areas of concern. Such observations will help to determine the factors that regulate the observed variation in acidification in Puget Sound and the Strait of Juan de Fuca, and to identify areas of sensitivity and resilience. Already, Taylor Shellfish has used the monitoring data from their Dabob Bay hatchery to ameliorate the effects of acidification events and increase oyster seed production. Tribal and state resource managers require this type of information to make informed decisions about resource management.

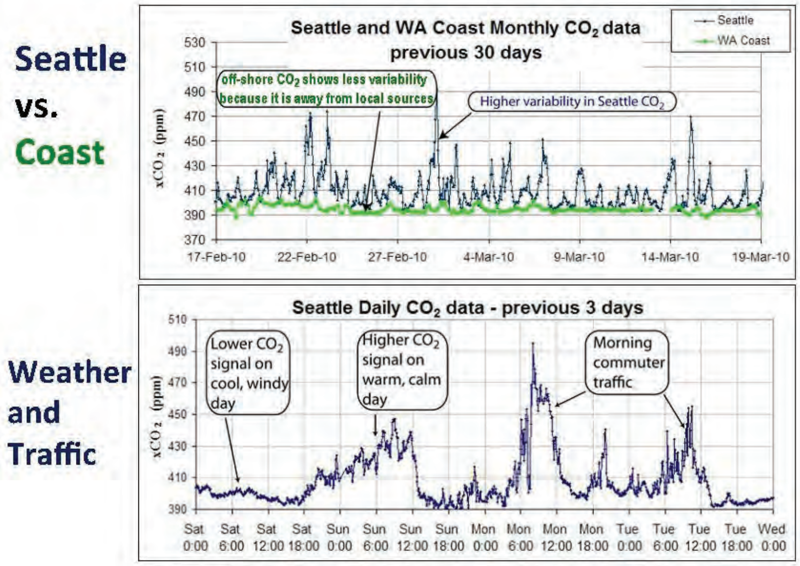

Figure 3.6: Atmospheric xCO_2 (the mole fraction of CO_2 in units of ppm in dry air) measurements from NOAA PMEL for Seattle in blue (Space Needle) and the outer Washington Coast in green (Cape Elizabeth NOAA NDBC buoy) for 30 days in 2010 (upper) and 3 days (lower) to show higher resolution detail for Seattle. Also shown are comments on variation and associated activities. Graphics provided by E. Lettvin, Pacific Science Center; NOAA PMEL data exhibited in Pacific Science Center CO_2 kiosk and in collaboration with C.L. Sabine, NOAA PMEL.

3.5.1 Observing needs

1. Obtain high-quality survey data throughout the region.
    a. Conduct biannual cruises, which provide the highest quality spatially-defined data, throughout all of Puget Sound.
    b. Develop new measurement capabilities for the Washington State Department of Ecology seaplane monitoring program. Sampling constraints that limit water volume must be overcome to allow analysis of carbonate system variables. Monthly samples will provide higher temporal resolution than can be obtained on biannual cruises.
2. Deploy new instrument moorings and expand capabilities among existing moorings. Focus on key locations such as the ocean boundary, major basins within Puget Sound, nearshore environments and river mouths (e.g., Bellingham Bay and Skagit Basin). Equip moorings with carbon sensors to provide high-resolution time series data (e.g., hourly measurements) that can serve as input to predictive models.
3. Expand shore-based platforms to monitor nearshore conditions affecting nearshore species and ecosystems. Locate installations at marine science centers and other sites where public education can be added.
4. Expand capacity of existing Joint Effort to Monitor the Strait (JEMS) monitoring platforms across the Strait of Juan de Fuca to collect data from the shallow and deep water layers representing outflow from and inflow to Puget Sound, respectively.

3.5.2 Research needs

1. Describe spatial and temporal patterns in pCO_2 and pH. Quantify the contribution of local drivers of acidification.
2. Develop budgets for carbon and nitrogen sources and sinks. Use observations and numerical models to derive a basic understanding of sources and sinks to:
    a. Quantify the effects of nitrogen and carbon loading on pCO_2 and pH;
    b. Quantify the effects of regional atmospheric CO_2 on local seawater pCO_2 and pH;
    c. Quantify the contribution of regional NO_X and SO_X to acidification;
    d. Quantify the effect of freshwater on alkalinity and pH measurements; and
    e. Quantify the impact of existing carbon sinks as potential mitigation options.
3. Develop predictive forecasting of the risk of corrosive waters.
4. Conduct coupled physics, chemistry, and biology measurements.
5. Conduct manipulative experiments and process studies to address unknowns, such as those identified in *research needs 2a–d*.

4

Ocean Acidification in the Columbia River Estuary and Other Washington Shallow Estuaries

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Jennifer Ruesink
Richard A. Feely
Simone R. Alin

4.0 Key Points

4.0.1 What we know about ocean acidification in the Columbia River and shallow estuaries

- The Columbia River and its estuary are major features within Washington, and their large size makes them unique within the state. The Columbia River contributes 77% of the freshwater input to the Pacific Ocean from the U.S. West Coast north of San Francisco (Barnes et al., 1972). The estuary is characterized by turbid waters, low levels of dissolved inorganic nitrogen and little phytoplankton productivity, but appreciable amounts of iron and silicate. About 4 km wide, the Columbia River estuary is only 18 m deep at the bar.
- Shallow estuaries (< 20 m) typically are very well mixed. The mixing between fresh and salt water is governed by the balance of river flow and tidal forcing. Especially when rivers are weak relative to the tides, the density layers are more vertical than horizontal in orientation. For this reason, shallow estuaries in Puget Sound, for example Totten Inlet, are functionally different than the deeper portions of Puget Sound such as the Main Basin and Hood Canal, and are more similar to outer coast estuaries such as Willapa Bay.
- Shallow estuaries can have a strong freshwater influence, due to the relative size of the receiving basin. River input is an important factor and there is some evidence for low pH in low salinity waters, as is evident for Willapa Bay.
- Rivers transport substances from terrestrial to estuarine habitats via particles, dissolved organics, and nutrients from both natural and human sources. All can lead to reduced pH and aragonite saturation, and increased pCO_2 in estuaries.
- The shallowness of the estuary can enhance some biological processes due to the large amount of habitat exposed to sunlight at levels sufficient for biological production. Shallow estuaries, both within Puget Sound and on the outer coast, can be highly productive because they support both benthic (sea-bed) and pelagic (suspended in water) photosynthesizers. High rates of primary production, in turn, can lead to high respiration rates and CO_2 production via microbial degradation of organic matter.

4.0.2 What we need to know about ocean acidification in the Columbia River and shallow estuaries

- What are the inputs and outputs of carbon and pH?
- What mechanisms drive the observed extreme variation DIC and pH?
- What are the effects of freshwater on TA, DIC, and pH?

- What are the effects of regional land use on seawater DIC and pH?
- What are the relative contributions of these drivers to regional acidification?
- How does freshwater input affect total alkalinity variations?

4.1 Distinguishing Features of the Columbia River Estuary and Other Washington Shallow Estuaries

Many shallow estuaries tend to be well mixed, with a physical structure that is very different from those of deep, density-stratified estuaries such as Puget Sound's Main Basin, Hood Canal, Dabob Bay, or the Strait of Juan de Fuca. Washington's outer coastal estuaries, such as Willapa Bay, tend to be shallow and well mixed, due to their basin geomorphology and also the relative balance between river inflow and tidal forcing. Portions of Puget Sound, such as Totten Inlet, resemble this shallow, well-mixed physical structure more than they do the stratified portions of Puget Sound, and thus are described here.

As shown in Hickey and Banas (2003; their Figure 12), the density layers in shallow coastal plain estuaries are more typically vertical, as opposed to the horizontal density layers typically found in the coastal ocean and Puget Sound's deep basins.

Willapa Bay is a shallow coastal plain estuary with strong freshwater-ocean gradients. More than 50% of the surface area and volume of the bay is intertidal (Banas et al., 2007). The highest primary production (Newton and Horner, 2003) and the highest oyster production (Ruesink et al., 2003) in the estuary occur nearer the mouth rather than up-estuary, consistent with an oceanic contribution of upwelled nitrogen during summer and the presence of oceanic phytoplankton as an indicator during these events (Newton and Horner, 2003).

Puget Sound contains many shallow estuaries, such as Penn Cove, Totten Inlet, Sequim Bay, and Samish Bay. Totten Inlet, one of the many finger inlets in South Puget Sound, is typical of shallow estuaries in Puget Sound, and lacks the degree of freshwater input observed in Willapa Bay. Density layers in Totten Inlet are more horizontal than vertical. While freshwater and terrestrial inputs are less in Totten Inlet compared with Willapa Bay, its flushing is slower due to the weaker density gradient, which stimulates estuarine circulation.

The Columbia River estuary is unique in Washington State. The Columbia River constitutes the major freshwater input (77%) to the Pacific Ocean from the U.S. West Coast north of San Francisco (Barnes et al., 1972). The estuary is about 4 km wide and the depth over the bar is 18 m. The physical structure within the estuary normally alternates between two conditions: one that is weakly stratified, occurring during low flow periods with strong tides, and one that has a salt-wedge, and thus stratification. The salt-wedge travels up and down the river, commensurate with the balance between river flow and tides.

The Columbia River tends to be very turbid, thus, in situ productivity by phytoplankton is low. Most of the estuarine ecosystem is supported by exogenous organic material supplied by the river. During summer, the river plume has very little nitrate, but contains high amounts of silicate and iron.

4.2 Drivers of Ocean Acidification in the Columbia River Estuary and Other Washington Shallow Estuaries

The same drivers of ocean acidification described for Puget Sound (Chapter 3) are relevant to these estuaries, although the relative contributions could differ. The contribution of coastal water conditions is strong for Willapa Bay because of its direct connection to the ocean. While less immediate for Totten Inlet because of its more distal location, ocean inputs are likely still an important factor. Terrestrial nutrient inputs are very important to shallow estuaries and are discussed below in the context of land-based inputs. Hypoxia is less a factor in shallow estuaries, due to mixing within the water column, but it has been noted in some estuaries with strong density stratification, such as Penn Cove (in that case contributed by the Skagit River plume). For the outer coast, regional atmospheric inputs are likely not a significant factor because the urban corridor is distant, but the same concepts discussed in Chapter 3 do apply to the Puget Sound shallow estuaries. Below, we focus on the two drivers that are likely the most significant for shallow estuaries: influence from land-based and freshwater inputs.

4.2.1 Contribution of land-based inputs

Several types of land-based inputs enter estuaries and alter water chemistry in a manner relevant to ocean acidification. These include particulate organic carbon, dissolved organic carbon, and nitrogen species. The supply of carbon compounds contributes to acidification through microbial degradation of organic material, which consumes oxygen and releases carbon dioxide. While the immediate effect of nutrient enrichment may be uptake of carbon dioxide or bicarbonate from seawater, as primary production is stimulated, the longer-term effects include oxygen depletion and production of carbon dioxide when primary producers decompose and are remineralized at depth.

In European estuaries where estuarine carbon budgets have been carefully constructed, a major input is particulate organic carbon of anthropogenic origin. Levels of pCO_2 in these estuaries can exceed 5000 μatm, more than an order of magnitude higher than current-day atmospheric values (Frankignoulle et al., 1998). Carbon dioxide and oxygen concentrations in these estuaries were found to be strongly inversely correlated, and peak carbon dioxide concentrations occurred in the turbidity maximum zone, at salinities < 10, where materials of freshwater origin tend to be concentrated. The carbon dioxide released from estuaries of salinity < 34 was found to represent about 10% of the total anthropogenic carbon released to the atmosphere in Europe.

Similar measurements of carbon dioxide concentrations in Washington's estuaries are not available. However, similar to patterns reported for European estuaries, the general pattern of supersaturated carbon dioxide within estuaries appeared to be the case for surface water in Willapa Bay on 10 September 2010 (**Figure 4.1**, J. Ruesink and A. Trimble, *unpublished data*). Although the sampling transect extended across waters of relatively high salinities overall, supersaturated surface water conditions with respect to atmospheric CO_2 occurred at salinities < 30.

4.2.2 Freshwater influence

The inverse relationship between salinity and pCO_2 in estuaries should be reflected in a positive correlation between salinity and pH. Seawater pH measurements in Washington's marine waters are collected frequently as part of the Washington State Department of Ecology's water quality monitoring. Measurements are made at particular points on a monthly basis using a device that does not have the accuracy or precision recommended for ocean acidification measurements, but may have utility for identifying broad patterns. **Figure 4.2** shows three patterns from multiple years

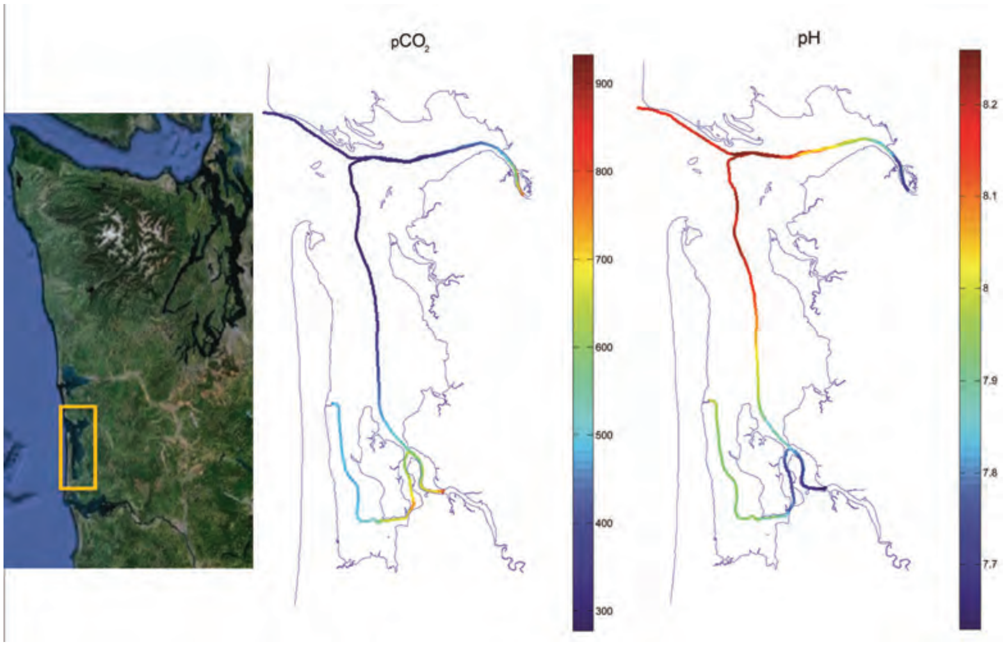

Figure 4.1: Surface sampling for pCO_2 and pH measured during September 2010 in Willapa Bay. The survey, originating at Oysterville on the Long Beach Peninsula, has a survey arm in the southeast up the Naselle River estuary, then goes north and bifurcates with an arm to the east extending up the Willapa River estuary, and an arm to the west out to the Pacific Ocean. Funded by Washington Sea Grant, the UW study also documented watershed carbon inputs (J. Ruesink and A. Trimble, *unpublished data*).

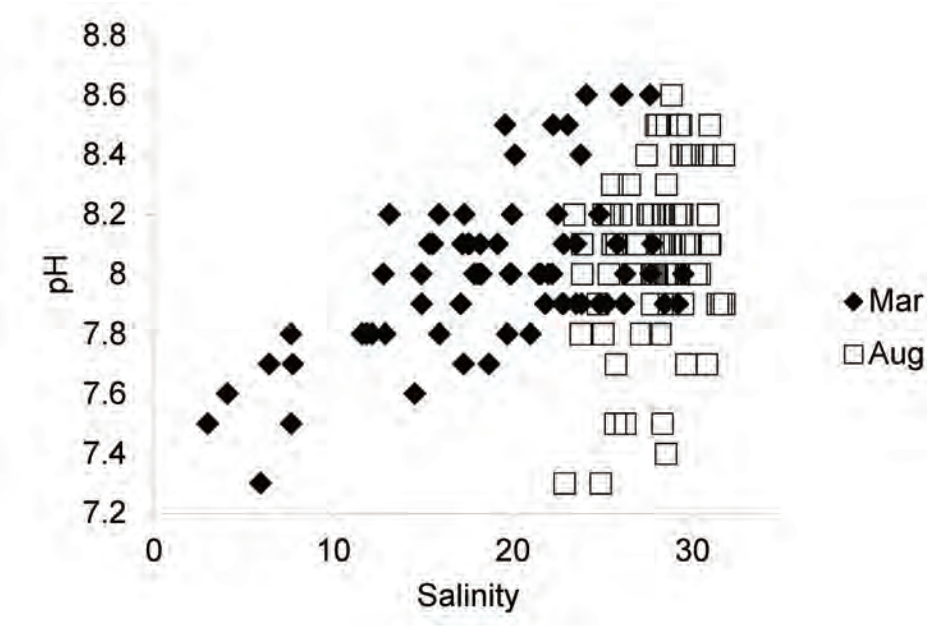

Figure 4.2: Plot of pH versus salinity as measured by Washington State Department of Ecology at five stations in Willapa Bay during 1990-2008.

of sampling at five stations in Willapa Bay (1990–2008): 1) the expected positive correlation between salinity and pH throughout the year (results are statistically significant at $P < 0.001$); 2) stronger salinity gradients during March than August, associated with reduced freshwater input in summer; and 3) overall lower salinity-specific pH in August than March (results are statistically significant at $P < 0.01$), possibly associated with enhanced respiration under warmer conditions. Investigation of these relationships at other sampling locations within Puget Sound and Grays Harbor may reveal spatial patterns useful for assessing areas with particular vulnerability to ocean acidification effects.

4.3 Current Monitoring Capacity in the Columbia River Estuary and Other Washington Shallow Estuaries

The Columbia River estuary is the site of the Center for Coastal Margin Observation and Prediction (CMOP), funded by NSF. There are several monitoring assets in the estuary. Three of these are, or will be, equipped with carbon chemistry sensors. The two shallow estuaries that have or have had carbon chemistry observations are also major sites of shellfish growing areas: Willapa Bay and

Totten Inlet. However, most of the observations in these estuaries are not being sustained beyond an initial study grant. The data streams noted below, except for research studies in Willapa Bay and Totten Inlet (further described in items 5b and c, below), have been made available through the NANOOS Visualization System (NVS: **http://nanoos.org**) by the data providers.

1. **Land-based systems:** Two shore-based stations have pCO_2 and pH and ancillary sensors (temperature, salinity, oxygen) plus take calibration water samples on seawater intakes.
    a. Nahcotta and Bay Center, both within Willapa Bay, maintained by Pacific Shellfish Institute in conjunction with the Pacific Coast Shellfish Growers Association.
2. **Freshwater measurements:** Several targeted studies by the Washington Department of Ecology contain information on organic carbon concentrations found in rivers and wastewater treatment effluent within Puget Sound and shallow estuaries (Mohamedali et al., 2011) and across watersheds with different land uses (Herrera Environmental Consultants 2011, Appendix L; **https://fortress.wa.gov/ecy/publications/summarypages/1103010.html**).
3. Existing data could therefore be analyzed to address anthropogenic vs. background levels of organic carbon entering estuaries as part of river inputs. Future efforts could follow organic and inorganic carbon concentrations along salinity gradients to link measurements made in freshwater and in estuaries.
4. **Columbia River estuary monitoring platforms:** Three fixed shore platforms will be equipped with sensors for pCO_2 and pH sea surface measurement during 2012. These also take temperature, salinity, oxygen, chlorophyll, nutrient, colored dissolved organic matter and turbidity measurements.
    a. Stations SATURN 03, 04, and 05, all within the Columbia River estuary and in a salinity gradient up-river, operated by Oregon Health and Sciences University as part of CMOP.
5. **Cruise-based sampling:** One ongoing program and two research studies can contribute to ocean acidification assessment.
    a. University of Washington annual PRISM/NANOOS cruises. Described in Chapter 3, these cruises occupy stations in some but not many shallow estuaries in Puget Sound. However, there is no funding for carbon system sampling or analysis.
    b. Willapa Bay-directed Washington Sea Grant research. Through this funding, Drs. Ruesink and Trimble outfitted a vessel to measure pCO_2 and pH during the period of their research grant (2009–2011) and made surveys throughout Willapa Bay.
    c. Totten Inlet- and Dabob Bay-directed Puget Sound Partnership study. A partnership between NOAA, University of Washington, Pacific Shellfish Institute, Taylor Shellfish Farms, and Puget Sound Restoration Fund conducted sampling of carbon chemistry, oceanographic properties,

and biological measurements including larval abundance and settlement. The study was conducted during 2009–2010 in both Totten Inlet, a shallow estuary with native Olympia oysters, and Dabob Bay, a deep fjord with Pacific oyster aquaculture.

There are other opportunities and observing assets that are of relevance to water quality but are not currently equipped to collect or analyze carbon system variables. These include the Washington State Department of Ecology seaplane monitoring, which collects samples to monitor water quality in Puget Sound, and other buoy and shore-based platforms operated by several entities (see assets at NANOOS Visualization System (**http://www.nanoos.org**).

4.4 Recent Observations

4.4.1 Freshwater influence

As shown in **Figure 4.1**, survey data from Willapa Bay reveal a spatial pattern in which the highest pCO_2 and lowest pH are found in the two river estuaries of Willapa Bay, thus associated with freshwater. The correlation between pCO_2 and salinity is shown in **Figure 4.3** for estuaries of the Willapa and Naselle rivers. The consistency of this relationship is important to confirm for Washington estuaries since different rivers may have different water chemistries, due to differences in land-use practices, watershed characteristics, and origin (glacier vs. snow fed).

4.4.2 Respiration signal

Shallow estuaries can be highly productive due to the extent of habitat exposed to sunlight sufficient for photosynthesis. Both benthic and pelagic photosynthesizers can exist in these habitats. High primary production and growth of phytoplankton creates the potential for very high respiration rates and thus CO_2 production through microbial degradation in subsurface waters.

Totten Inlet, a shallow estuary, is a key shellfish growing area for mussels, clams, and oysters, and also houses shellfish nurseries, a hatchery, oyster brood stock repositories, and a natural population of Olympia oysters. The Puget Sound Partnership funded NOAA, UW, Pacific Shellfish Institute (PSI), and Puget Sound Restoration Fund (PSRF) scientists to study one station each in Totten Inlet and Dabob Bay, a deep fjord in Puget Sound off Hood Canal, for two years to better understand water chemistry and how it pertains to oyster reproduction and settlement. Measurements included oceanographic variables, water chemistry, and oyster larvae spatfall. Important differences were found between the two study locations, with the Dabob station showing an influence on pCO_2 from local upwelling of cold, salty, pCO_2–rich deep water, versus Totten Inlet with different dynamics suggesting the role of biological respiration. **Figure 4.4** displays the temporal pattern in seawater temperature and pCO_2 at the Totten Inlet station (Alin et al., 2012). While the analysis is preliminary, it is evident that pCO_2 increased to very high values when temperature was still increasing, indicating that upwelling of

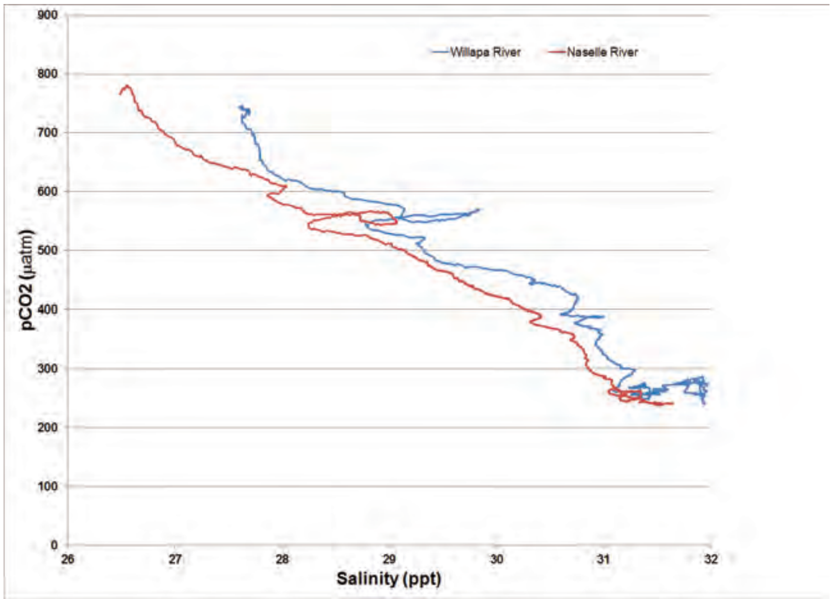

Figure 4.3: Survey data from Willapa Bay showing pCO_2 (in units of µatm) versus salinity in the Willapa River estuary (blue) and the Naselle River estuary (red) as part of the same study presented in Figure 4.1 (J. Ruesink and A. Trimble, *unpublished data*).

high pCO_2 deeper (typically colder) waters was likely not the cause, but instead that increased biological respiration may have influenced the high values. The pCO_2 was greater than that seen in deep oceanic-sourced waters, again suggesting that local respiration may have been the cause for the high pCO_2 values.

Data from both stations sampled during 2009 and 2010 suggest a dynamic link between larval settlement, organic production and respiration, water mass movement, and carbon chemistry. To further evaluate tidal and diel (24 h) fluctuations in Totten Inlet, volunteers from PSI collected nutrient, dissolved oxygen, and inorganic carbon samples every two hours for a full diel cycle on 29 June 2011 and 9 September 2011. NOAA scientists found significant water chemistry fluctuations at the study site on these dates related to tidal and solar variations throughout the diel cycle. Project partners continue working toward understanding more about this complex estuarine environment, although this work is not funded to continue.

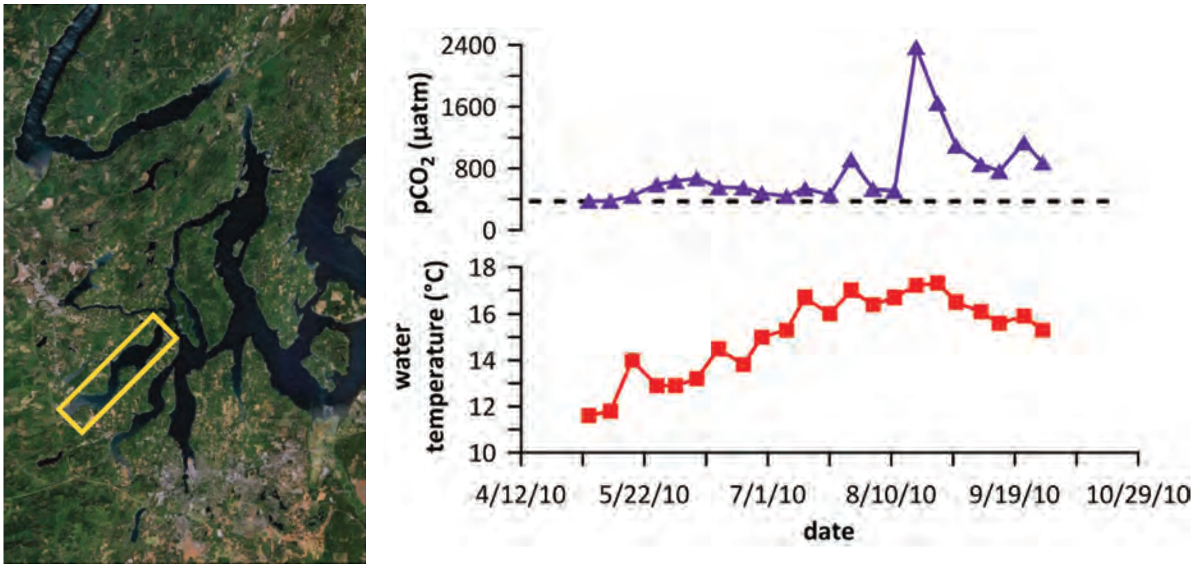

Figure 4.4: Data for pCO_2 and temperature at Totten Inlet, South Puget Sound, during summer 2010 from a 2 year study funded by the Puget Sound Partnership to NOAA PMEL, University of Washington, Pacific Shellfish Institute, and Puget Sound Restoration Foundation partners (Alin et al., 2012).

4.5 Observing and Research Needs for the Columbia River Estuary and Other Shallow Estuaries

Monitoring of the Columbia River estuary and shallow estuaries must be increased. While platforms are supported in the Columbia River estuary, sustained funding is needed to deploy enhanced observational platforms throughout some of the shallow estuaries, both in Puget Sound and on the outer coast; especially those of significance to oyster rearing. The high-resolution temporal and spatial data provided by such platforms can lead to improved predictive relationships for estimating pH and carbonate saturation levels, for the benefit of shellfish production and natural resource management. Observations are needed in order to understand variation in ocean acidification in response to freshwater input and land use, as well as to identify sensitive and resilient areas. Tribal and state resource managers can use this information to make informed decisions regarding resource protection.

4.5.1 Observing needs

1. Obtain high-quality, regionally representative survey data.
   a. Conduct survey cruises, which provide the highest quality spatially defined data.
   b. Develop new measurement capabilities that incorporate gliders to survey pCO_2 and pH.
2. Sustain high-resolution time series: Deploy new instrument moorings and expand capabilities among existing moorings. Focus on key locations, such as those along the Columbia River salt gradient and in estuary types classified based on land-use, hydrography, and other features. Moorings should be equipped with carbon sensors to provide high-resolution time series data (e.g., hourly measurements) that can be used as input to predictive models.

4.5.2 Research needs

1. Describe spatial and temporal patterns in carbon species and pH; quantify local drivers of variation in seawater carbonate chemistry.
2. Develop budgets for sources and sinks and carbon and nitrogen, to:
   a. Quantify the effect of freshwater on TA, DIC, and pH
   b. Quantify the effect of land use on local seawater carbon species and pH.
3. Develop capabilities to make predictive forecasts of risk of corrosive waters.
4. Conduct coupled measurements of physical, chemical, and biological variables, particularly in Willapa Bay and Totten Inlet, where some data already exist and where shellfish growing is important.
5. Conduct manipulative experiments and process studies to address unknowns, such as those identified in *research needs 2a–b*.

5

Responses of Species and Assemblages to Ocean Acidification

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5.0 Key Points

5.0.1 What we know about responses of species and assemblages to ocean acidification

- Acidification-driven changes in carbonate chemistry can cause diverse physiological responses among organisms.
- Organisms vary in their response to acidification; negative effects are evident, particularly among calcifying (shell-building) species.
- The process of shell formation and maintenance in marine organisms is vulnerable to acidification.
- Co-occurring environmental stressors can modify or exacerbate the effects of acidification.

5.0.2 What we need to know about responses of species and assemblages to ocean acidification

- How will acidification affect species of importance in Washington State?
- Which local species are most vulnerable to the effects of acidification?
- How will co-occurring stressors influence species' responses to acidification?

This Chapter summarizes published evidence of biological responses to ocean acidification. Call-out boxes are used to present specific examples. We note at the outset that, while research is accelerating, many taxonomic groups remain under-studied and our understanding of biological response to ocean acidification remains incomplete.

5.1 General Physiological Processes Affected by Ocean Acidification

5.1.1 Biological roles of key molecules

As described in Chapter 1, the term *ocean acidification* refers to reductions in the pH of seawater caused by oceanic uptake of CO_2 from the atmosphere and by other chemical additions to or subtractions from the ocean (Field et al., 2011). As shown in **Figure 1.2**, the chemical reactions that follow the dissolution of CO_2 in seawater influence the concentration of other key molecules: hydrogen (H^+) and bicarbonate (HCO_3^-) ion concentrations increase, carbonate ion (CO_3^{2-}) concentrations decrease, and the saturation state of biologically important forms of calcium carbonate ($CaCO_3$) declines. These changes in the chemistry of seawater can affect a wide range of physiological processes in marine organisms, and do so via a number of different mechanisms and pathways. We offer a few examples here to illustrate the biological importance of individual variables in the seawater carbonate system.

Hydrogen ion (H^+) concentration: All animals including humans can accumulate CO_2 in their blood if their respiratory organs do not function sufficiently to expel it (Schmidt-Nielsen, 1997). The accumulation of CO_2 in interstitial body fluids is termed *hypercapnia* and leads to blood acidosis (low pH in blood). Aquatic animals alter their blood chemistry to maintain a temperature-specific internal pH despite fluctuations in the environment (Schmidt-Nielsen, 1997), but such homeostasis can be energetically costly (e.g., Dissanayake and Ishimatsu, 2011). If homeostasis is not maintained, low blood pH reduces oxygen transport and impedes the ability to engage in aerobic activity (Pörtner et al., 2004; Brewer and Peltzer, 2009).

The sperm of marine organisms could be particularly sensitive to changes in seawater pH (Reuter et al., 2011) because they are single-celled, have a high surface-to-volume ratio, and require high motility to successfully reach eggs that have been released into seawater. Other organisms appear to be affected because reduced seawater pH alters chemical cues, or the organism's capacity to detect these cues. Thus, chemo-responsive behavior can be disrupted (de la Haye et al., 2012; Ferrari et al., 2012a).

Bicarbonate ion (HCO_3^-) concentration: Bicarbonate ion is the primary form of inorganic carbon in seawater at pH between about 7 and 10 (Zeebe and Wolf-Gladrow, 2001; Kaiser et al., 2005). Therefore, despite changes in equilibrium levels of carbon dioxide, carbonate ion, and bicarbonate ion associated with acidification, bicarbonate ion is expected to remain relatively abundant and perhaps will even increase slightly in a higher CO_2 environment. Bicarbonate ion is used by many marine algae as a carbon source for photosynthesis; for instance, bicarbonate ion accounts for 80–90% of the carbon fixed by the green seaweed known as sea lettuce (Beer, 1996).

Carbon dioxide (CO_2): Carbon dioxide concentrations in seawater will increase under conditions of ocean acidification. Seagrasses are a group that use carbon dioxide to fuel photosynthesis, and under present-day conditions can experience carbon limitation. Experiments have demonstrated that high concentrations of CO_2 in seawater at low pH (see section 6.2) can immediately increase seagrass photosynthetic rates under full-light conditions (Zimmerman et al., 1997), and can augment shoot production and flowering in longer-term experiments (Palacios and Zimmerman, 2007).

Carbonate (CO_3^{2-}): Carbonate ions are required for precipitation of shells in many aquatic organisms. Carbonate ion concentration is low in proportion to other inorganic carbon species and will decline as pH declines (Zeebe and Wolf-Gladrow, 2001; Kaiser et al., 2005, p. 54). In two tropical coral species, calcification rates were correlated with the concentration of carbonate ion but not with the concentration of HCO_3^- or dissolved inorganic carbon (de Putron et al., 2011). Although molluscs are not closely related to corals and precipitate their shells through different cellular mechanisms (see below), they too can be sensitive to carbonate ion concentration. In the case of Pacific oysters (*Crassostrea gigas*), larval survival and growth declined in association with low carbonate ion availability, and were less affected by pH or aragonite saturation state

(Ω_{arag}), when these environmental variables were manipulated separately (Gazeau et al., 2011; Barton et al., 2012). Because many calcifying organisms appear to be sensitive to acidification (Kroeker et al., 2010), the topic of shell formation is described in more detail below.

5.1.2 Shell formation

The process of shell formation is termed biocalcification. Not all organisms build shells in the same way, and multiple mechanisms of biocalcification are known. Calcium carbonate is the primary mineral found in shells of marine animals. Calcium carbonate can exist in different forms, or polymorphs, among which are *calcite*, *aragonite*, and *high-magnesium calcite*. These different polymorphs exhibit different properties, including their resistance to dissolution under conditions of low pH and low carbonate saturation state. Calcite is most resistant to dissolution. Aragonite is less resistant to dissolution, and high-magnesium calcite varies in its resistance to dissolution depending on the magnesium concentration. Aragonite is the polymorph found in the larval stages of most bivalves. Adult bivalves vary in the calcium carbonate polymorph deposited in the shell. Although carbonate saturation state is often used to describe the solubility of these different shell minerals under different carbon chemistry conditions, it is important to note that the solubility of a biomineral may differ from that of the corresponding mineral polymorph. At best, the carbonate saturation state provides an estimate of how readily calcium carbonate shell material will dissolve; several other factors ultimately determine how sensitive an animal shell is to dissolution, including the extent of the protective organic coating (the periostracum), the amount of organic matter in the shell, the microstructure of the shell, and trace elements that have been incorporated into the shell.

Creation of biominerals in most organisms is a *biologically controlled* process (Dove et al., 2003). Biocalcification generally occurs within a calcifying space in which the carbonate saturation state can be manipulated by the calcifying organism. The location of biocalcification differs among organisms and can be *intra*-cellular (as found in marine phytoplankton such as coccolithophores), *inter*-cellular (as found in most corals), and *extra*-cellular (as found in gastropods and bivalves). Intra-cellular shell formation occurs within the controlled biological environment of the cell; for example, a coccolithophore produces its coccolith (or calcified plate) internally and then transports it to the exterior surface of the cell, where it is deposited. Inter-cellular biocalcification occurs in a biologically controlled environment between cells; for example, a coral polyp “sits” on top of its calcium carbonate skeleton, creating a controlled microenvironment between its soft-tissue and the underlying mineral that is favorable for biocalcification. This differs from the arrangement typical of extra-cellular biocalcification, in which shell material is deposited external to the soft tissues of the organism, for example in oysters and other bivalves.

Although carbonate saturation levels greater than 1.0 predict that shell formation in many marine waters is thermodynamically favored, the presence of magnesium in seawater greatly reduces the rate of calcium carbonate deposition by physically interfering with the crystallization process (Stanley, 2008). Shell-forming organisms must therefore expend energy to create conditions favorable for biocalcification by physiologically altering the chemistry of their calcifying space. There are two generally accepted processes that require energy for the formation of shell: 1) pumping H^+ out of the calcifying space to raise the pH, in order to increase the carbonate saturation state to a level that is favorable for calcification, and 2) generating the organic matrix that helps organize and shape the shell material as it forms (Dove et al., 2003; Weiss, 2010).

The energy required for formation of an organic matrix, which consists primarily of protein, has been estimated by Palmer (1992). More recently, Ries (2011) provided a model of the expense of pumping protons under different pCO_2 conditions. From these studies, we can infer that a significant energetic expense can be incurred by shell-forming organisms when carbonate chemistry conditions are altered by acidification. Furthermore, molluscs (e.g., snails and bivalves) can only deposit new shell on the leading edge of growth, or on the interior surface of their shells. Consequently, loss of exterior shell from chemical corrosion creates a significant challenge for the organism (Green et al., 2009; Nienhuis et al., 2010; Melzner et al., 2011). Additional work is needed to better parameterize the energetic costs of shell formation under corrosive conditions, to determine differential sensitivities of organisms relative to modes of calcification, and to better link whole-animal physiology to the shell formation process.

5.2 Response to Acidification by Taxonomic Group

Physiological responses to ocean acidification conditions can influence biological processes other than shell formation and can result in changes in growth, development, reproduction, and behavior. Even if organisms are able to overcome challenging chemical conditions through their ability to modify internal fluid chemistry, doing so under increasingly corrosive conditions could impose energetic costs that reduce growth or survivorship. The direct effects of pH and carbon chemistry on growth and survival of marine organisms are the subject of vigorous research, the majority of which is conducted under laboratory conditions. Studies conducted in natural settings are less common, but provide valuable information that helps contextualize results obtained from laboratory investigations and corroborate field observations. Early research efforts have largely focused on shell-forming organisms that are known or suspected to be directly affected by acidification. Globally, these are corals (tropical species receiving far more attention than slow-growing cold water species), some zooplankton (most notably, the pteropods that serve as an important source of food for many high-latitude species, including juvenile Alaskan salmon), a small number of phytoplankton species, and bivalves.

In the following sections we summarize known and projected responses of selected taxonomic groups to projected ocean acidification conditions. Representatives of each group appear in Washington waters, although the species may differ from those used as examples here.

5.2.1 Microbes

Marine microbes represent a diverse group of taxa that includes bacteria, Archaea, microbial eukaryotes (e.g., phytoplankton, fungi, and protists), and their associated viruses. Microbes account for more than 90% of biomass in the ocean (Whitman et al., 1998) and for approximately 50% of the planet's annual net primary production (Ducklow et al., 2010). Microbes are present in the plankton as free-living cells, or attached to substrates such as phytoplankton cells and as biofilms on surfaces. Microbes strongly influence all biological communities via their role in energy and nutrient cycling. In marine environments, they can create energy by fixing carbon via photosynthesis (*autotrophy*) or can consume organic material from other sources (*heterotrophy*). Heterotrophic microbes are responsible for creating hypoxic conditions that follow phytoplankton blooms, during which process the microbial decomposition of organic matter created by phytoplankton consumes dissolved oxygen and releases CO_2 via respiration. In biofilms, microbes can provide some of the cues that benthic invertebrates use to settle out of their planktonic life stages (Lidbury et al., 2012). In addition, microbes can be pathogenic and infect other organisms.

Little is known about the response of individual marine microbial taxa to increasing pCO_2. Primary questions regarding the potential for physiological tolerance, acclimation, and adaptation to increasing pCO_2 have not yet been answered. Among the studies that have been performed, substantial variation in response to increasing pCO_2 has been observed (Joint et al., 2011). This variation likely derives at least in part from diversity inherent among taxa and strains. One survey found diverse bacterial assemblages composed of similar lineages to be present over a range of pH conditions, raising the possibility that tolerance to changes in pH could exist among some microbes (Joint et al., 2011).

Microbes are essential to nutrient cycling and nitrogen fixation in the ocean. Consequently, microbial response to increasing pCO_2 could cause changes in nutrient cycling in the ocean, particular nitrogen cycling. Rates of nitrification and denitrification are governed by different processes, but both could increase in response to CO_2 enrichment, potentially leading to more rapid nitrogen cycling or changes in the inventory of total fixed nitrogen (Hutchins et al., 2009). Changes in the abundance of specific forms of nitrogen (e.g., ammonium versus nitrate) could lead to substantial changes in phytoplankton communities (Hutchins et al., 2009).

Given the strong interactions between microbes and other species in marine communities, the response of microbes to ocean acidification will be influenced both by the physiology of the microbes themselves and by the response of other species (Allgaier et al., 2008; Liu et al., 2010). We draw on a recent meta-analysis (Liu et al., 2010) to characterize some general responses of the microbial community to ocean acidification. In doing so, we recognize that the analysis is based on relatively few studies and that substantial deficiencies remain in our understanding of microbial responses to ocean acidification. The meta-analysis performed by Liu et al. (2010) found that, in general, under high CO_2 conditions:

- The growth rate and photosynthetic rate (CO_2 fixation rate) of cyanobacteria increases. Cyanobacteria play an important role in the marine carbon cycle and are responsible for up to 50% of marine carbon fixation.
- Nitrogen fixation increases. Microbes play an important role in the marine nitrogen cycle; for example, cyanobacteria in the genus *Trichodesmium* may be responsible for almost half of marine nitrogen fixation (Mahaffey et al., 2005).
- Elemental ratios of carbon, nitrogen and phosphorous in microbes change in ways that reduce their quality as a food source for higher trophic levels.

Research published since this meta-analysis appeared indicates that microbial nitrification (the conversion of ammonium to nitrate) decreases with decreasing pH under both experimental and natural conditions (Beman et al., 2011; Kitidis et al., 2011). Conversely, Fulweiler et al. (2011) report that in a New England estuary, nitrification rates were highest at low pH and declined as pH increased. Optimum pH for nitrification in this estuary was observed to be site-specific, ranging from 7.0 to 8.3 (Fulweiler et al., 2011). Clearly, more research is required to resolve apparent discrepancies between studies and to better describe temporal and spatial variation in nitrification under conditions of changing pH. This issue is important because the availability of nitrogen can limit biological productivity in marine environments.

Two recent studies on bacterial biofilms, one from a natural experiment in a carbon dioxide vent environment and the other from a laboratory experiment, suggest that the species composition of bacterial communities changes with carbon dioxide concentrations (Witt et al., 2011; Lidbury et al., 2012).

5.2.2 Phytoplankton

Phytoplankton are free-living cells that use photosynthesis to create organic compounds from the carbon dioxide dissolved in seawater. Although phytoplankton are part of the marine microbial community, here we call them out because of their fundamental importance. Phytoplankton are essential to the function of the Earth system: they generate approximately 50% of the oxygen we breathe, produce biomass that forms the basis of marine food webs, fuel the “biological pump” that transports carbon from the surface of the ocean to the deep interior, and contribute to global biogeochemical cycles. Substantial alterations in the distribution, abundance, growth rates, and species composition of phytoplankton populations will influence the composition and productivity of marine ecosystems and will potentially influence the release of oxygen to the atmosphere, the absorption of CO_2 by the ocean, and the global cycling of carbon, nitrogen, and other chemical compounds.

Most marine phytoplankton have carbon concentrating mechanisms that allow the organism to actively take up carbon, either as CO_2 or bicarbonate ion (The Royal Society, 2005). Because phytoplankton can actively concentrate carbon dioxide, changes in the pH and CO_2 content of seawater may have less effect on photosynthesis than might otherwise be expected (The Royal Society, 2005).

Phytoplankton species have shown diverse responses to elevated pCO_2 under laboratory conditions. Among the responses reported are increased growth rate (Borchard et al., 2011), decreased growth rate (Riebesell et al., 2000), increased calcification rate (Iglesias-Rodriguez et al., 2008), decreased calcification rate (Riebesell et al., 2000), decreased cell size (Borchard et al., 2011), changes in carbon-to-nitrogen ratios (influencing their nutritive value; Lohbeck et al., 2012), and changes in the production of toxic compounds (Fu et al., 2008; Sun et al., 2011; Tatters et al., 2012). The broad taxonomic diversity encompassed by phytoplankton contributes to the observed variation in response, but strain-specific differences also have been reported (Ridgwell et al., 2009).

Many phytoplankton taxa exist as "naked" cells surrounded by only a cell membrane and cell wall. Other taxa are surrounded by hard structures such as calcified scales or shells ("frustules") containing silica. The outer covering of the cell will influence the cell's response to seawater pH. For example, the calcified outer scales of some phytoplankton could be affected by exposure to low pH (Langer et al., 2009). Furthermore, the mechanisms that transport dissolved substances into and out of the cell are sensitive to pH, with the result that changes in seawater pH could affect cellular processes (The Royal Society, 2005).

Genetic variation and adaptive capacity could modify the responses of phytoplankton species to acidification. A recent study demonstrates the existence of adaptive capacity in the phytoplankton species *Emiliania huxleyii* (Lohbeck et al., 2012), but an earlier study of the green alga *Chlamydomonas* failed to detect genetic adaptation to elevated pCO_2 after 1000 generation of experimentally imposed selection in a laboratory setting (Collins and Bell, 2004). Importantly, the response of phytoplankton to low pH and high pCO_2 will be influenced by interactions with temperature, nutrients, sunlight, and ultraviolet radiation (Feng et al., 2008), as well as by competitive interactions with other species (Collins and Bell, 2006). Several of the phytoplankton species that have been studied with respect to ocean acidification occur in, or are related to species that occur in, Washington waters. Directed studies of phytoplankton species isolated from Washington waters are underway, but it is too early to predict with confidence the likely responses of phytoplankton communities to ocean acidification in Washington.

BOX 5.1 HARMFUL ALGAL BLOOMS AND TOXICITY

Harmful algal blooms (HABS) are produced by rapid growth and entrainment of toxin-producing phytoplankton. Although the occurrence of such blooms predates the occupation of coastlines by humans, some have speculated that the frequency and intensity of blooms could be intensified under conditions of climate change and ocean acidification. In Washington, harmful algal blooms occur along the outer coast and in Puget Sound. Although the blooms are not known to be toxic to shellfish, their impacts on human health via consumption of shellfish can cause the closure of recreational and commercial shellfish fisheries. Some HABS can cause harm to finfish such as salmon (Horner et al., 1997; Gilbert et al., 2005; Kudela et al., 2005; Chadsey et al., 2012).

Recent research has demonstrated that the toxicity of some HAB-forming phytoplankton increases under conditions of high CO_2 in seawater. Two species of the diatom *Pseudo-nitzchia* were shown to produce more toxin when grown in seawater with high CO_2 and low nutrients (Sun et al., 2011; Tatters et al., 2012), as was the dinoflagellate species *Karlodinium* (Fu et al., 2010). These findings suggest that HABS on Washington's outer coast and inside Puget Sound could become more toxic under conditions of ocean acidification, with consequent impacts on food webs, ecosystems, human health, and economy.

5.2.3 Macroalgae and seagrasses

Marine macroalgae (seaweeds) and seagrasses are multicellular photosynthetic organisms. They produce oxygen through photosynthesis, create essential biological habitats in shallow environments, and contribute to marine food webs.

Marine macroalgae typically grow attached to hard substrata. Because they rely on photosynthesis for growth, macroalgae are restricted to upper areas of the ocean where sunlight is sufficient for photosynthesis. Most macroalgae use bicarbonate ion as a substrate for photosynthesis. Carbon concentrating mechanisms are thought to be less common among macroalgae than among phytoplankton (The Royal Society, 2005), so macroalgae may be more vulnerable to carbon limitation than are phytoplankton.

Macroalgae are taxonomically and phylogenetically diverse, and their response to ocean acidification is likely to reflect such diversity. Most macroalgae are fleshy (uncalcified), while others are calcified. The relative abundance of fleshy versus calcified species has been observed to change in response to natural acidification at CO_2 vents, with fleshy algae increasing and calcified algae decreasing as pH declines from 8.1 to 7.8 (Porzio et al., 2011). At these CO_2 vents, all calcified macroalgae disappeared at a pH of about 6.7 (Porzio et al., 2011).

Seagrasses are photosynthetic flowering plants that are more closely related to land

BOX 5.2 POTENTIAL FOR LOCAL MITIGATION BY SEAGRASSES AND MACROALGAE

Photosynthetic organisms convert CO_2 to organic compounds such as carbohydrates through a process termed carbon fixation. Marine primary producers—phytoplankton, seaweeds, and seagrasses—contribute approximately 50% of global carbon fixation and up to 70% of global carbon storage (Beardall and Raven, 2004; Chung et al., 2011). Most seagrasses and macroalgae are able to use HCO_3^- to fuel photosynthesis, and evidence suggests that they have the potential for increased photosynthesis and growth when concentrations of HCO_3^- are sufficient to reduce carbon limitation, as predicted under conditions of ocean acidification (Koch et al., 2012). At the same time, many seagrasses and non-calcified (fleshy) algae appear to be robust to associated declines in pH and increases in pCO_2 (Palacios and Zimmerman, 2007; Porzio et al., 2011; Johnson et al., 2012). These attributes, combined with the rapid growth rates characteristic of some species, have caused some to propose that seaweeds and seagrasses could offer mitigation potential through their ability to metabolically consume carbon (Nellemann et al., 2009; Chung et al., 2011; Duarte et al., 2011; Unsworth et al., 2012). An analysis of kelp-bed ecosystems in the northeast Pacific estimates that the kelp carbon pool (that is, the amount of carbon tied up in kelp biomass) is roughly 10 times larger in intact kelp forests compared with equivalent areas from which kelps have been lost (Wilmers et al., 2012), and that the capacity for carbon sequestration by kelp is substantial.

The local drawdown of carbon by seaweeds and seagrasses holds some promise for local and short-term mitigation effects in Puget Sound and other areas of Washington State. Among the seaweeds and seagrasses native to or established in Washington State, several (e.g., *Ulva* spp., *Palmaria palmata*, *Porphyra* spp., *Laminaria* spp., *Nereocystis luetkeana*, *Macrocystis integrifolia*, *Sargassum muticum*, and *Zostera* spp.) are characterized by high or very high photosynthetic rates (Chung et al., 2011; Duarte et al., 2011). High photosynthetic rates tend to be associated with high carbon assimilation rates, but this relationship is complicated because variable amounts of fixed carbon are re-released to the environment through respiration, carbon "leakage," and decomposition of decaying tissues. Consequently, mitigation potential in local environments will be determined by rates of assimilation and re-release of carbon. Local oceanographic processes will influence carbon dynamics and mitigation potential; for example, carbon drawdown could be more effective in semi-enclosed bays and estuaries than in highly flushed environments, and carbon burial is more likely in areas of rapid sedimentation. The utility of mitigation by seaweeds and seagrasses in Washington has not been tested and merits investigation. Until evidence is available, the potential benefits offered by seaweeds and seagrasses argues strongly for their preservation and restoration in Puget Sound to offset declines that have occurred or are suspected to have occurred.

plants than to macroalgae. Although seagrasses and macroalgae are often found growing together, seagrasses differ from macroalgae in many aspects of physiology, morphology, growth, and reproduction. Because of differences in photosynthetic pathways, photosynthesis in seagrasses is more likely to be carbon-limited under present-day conditions than is photosynthesis in macroalgae. (Beer and Koch, 1996). As a consequence, it has been suggested that seagrasses could respond positively to carbon enrichment associated with ocean acidification. In a review of biological effects of acidification, Hendriks et al. (2010) found that across six CO_2 enrichment studies (in which pCO_2 levels up to 2000 ppm were tested), seagrass growth increased significantly. However, others have reported that under conditions of elevated pCO_2, some seagrasses lose the ability to produce anti-herbivore compounds and consequently suffer higher rates of herbivory and lower overall productivity (Arnold et al., 2012).

5.2.4 Zooplankton

Zooplankton species link the primary production of algae and plants to groups higher in the food web, such as fish. The species composition and abundance of zooplankton influence the population dynamics of groups higher in the food web, for example fish and whales, as does zooplankton size and nutritional content. To date, there has been limited research on the impacts of acidification on zooplankton. Major research needs on this topic include determination of: 1) how acidification will affect population dynamics of the dominant zooplankton species in Puget Sound, Washington's coastal waters, and the northeast Pacific including the Gulf of Alaska and Bering Sea, and 2) how acidification will affect the energy content (total calories, body composition) of the dominant zooplankton species of the region.

Copepods and krill are the dominant, non-gelatinous, medium-to-large sized zooplankton in Washington marine waters (Brand et al., 2007; Harvey et al., 2010). While locally based research on the response of both groups to acidification is underway, findings are yet to emerge. The single published study on the response of a krill species to acidification found no effect on the embryonic development or behavior up to 1000 µatm pCO_2, but no successful hatch of krill eggs at 2000 µatm pCO_2 (Kawaguchi et al., 2011). At present, pCO_2 levels around 2000 µatm are not common in marine waters, but such concentrations could occur in the future in deeper areas inhabited by both krill and copepods.

The response of copepods to acidification varies with species and life stage, but includes evidence for decreased growth, egg production and hatching success, and increased mortality (Kurihara et al., 2004; Dupont and Thorndyke, 2009; Fitzer et al., 2012; Mayor et al., 2012; Zhang et al., 2012). Experiments on copepods also provide evidence for increased feeding and respiration rates at high levels of pCO_2, and for a trade-off between reproductive effort and self-maintenance (Fitzer et al., 2012; Li and Gao, 2012). While the presence and nature of the response to high CO_2 environments is variable among species, the observed responses indicate that, over the next century, ocean acidification will likely affect the life cycle of some local copepod species.

Pteropods are shelled molluscan zooplankters that are important components of marine food webs offshore of Washington State and in Alaskan waters. Pteropods are consumed by a variety of species, ranging from other zooplankton to fish, seabirds, and whales. For example, pteropods can comprise 45% of the diet of Gulf of Alaska pink salmon (Aydin et al., 2005). Because Alaskan marine ecosystems support a large fishing industry that is based in Washington State, and because salmon from Washington State migrate into waters of the Gulf of Alaska and the northeast Pacific to grow and mature, acidification in these northern ecosystems will have impacts in Washington State. Among all pteropod species studied to date, calcification and growth rates decline as pH decreases (Comeau et al., 2009a, b, c, 2010a, b; Lischka et al., 2011). How pteropod population dynamics will be affected by acidification is unknown because the effects of low pH conditions on metabolism, mortality, and reproductive success are unclear (Comeau, et al., 2010b; Lidbury et al., 2012; Maas et al., 2012; Seibel et al., 2012). Zooplankton samples collected off of Vancouver Island suggest a local decline in abundance of subarctic pteropods (*Limacina*), an increase in abundance of subtropical pteropods (*Clio*), and no significant change in the abundance of predatory pteropods over the past few decades (Mackas and Galbraith, 2011).

Gelatinous zooplankton, commonly known as jellyfish and comb jellies, are becoming more abundant in some areas of the North Pacific, but the impacts of ocean acidification on gelatinous zooplankton are virtually unknown. While an association between increasing abundance of gelatinous zooplankton and declining pH had been demonstrated in the central North Sea (Attrill and Edwards, 2008; Richardson and Gibbons, 2008; Richardson et al., 2009), the strength of this relationship is weak. The single laboratory study of the response of a gelatinous zooplankton (moon jellyfish, *Aurelia labiata*) to ocean acidification was conducted locally, and showed no effect of acidification on asexual reproduction and polyp survival (Winans and Purcell, 2010).

5.2.5 Molluscs

Molluscs include three familiar shell-forming groups—bivalves (oysters, clams, mussels, scallops); gastropods (snails, abalone); and cephalopods (octopus, squid) —and several others that are less familiar. In Washington, Pacific oysters have helped to raise awareness of ocean acidification and its potential biological effects (**Box 5.3**), particularly because oyster hatchery production has declined in apparent association with low seawater aragonite saturation levels (Barton et al., 2012).

BOX 5.3 OYSTER SEED CRISIS

The Washington State shellfish industry currently employs 3200 people and contributes $270 million to the state's economy each year (22 April 2012 press release; **http://www.cantwell.senate.gov/public/index.cfm/press-releases**). Washington State is a national leader, growing about 88% of the West Coast's farmed shellfish $107 million annual harvest. Beginning in the mid-2000s, two of the three primary oyster hatcheries supplying Pacific oyster larvae for growers in the Northwest began experiencing production failures. The Taylor Hatchery on Dabob Bay, Washington, and Whiskey Creek Shellfish Hatchery on Netarts Bay, Oregon, at the time supplied the majority of larvae to growers along the entire U.S. West Coast. Oyster hatcheries often experience an occasional failure of the production cycle, but the failures beginning in the mid-2000s were persistent. Anecdotally, the Whiskey Creek Hatchery noted that they often had problems during the month of August, but never to the extent and magnitude of the most recent failures. Pathogens such as *Vibrio tubiashii* were initially suspected as the culprit, and high counts of *Vibrio* were initially found in the Whiskey Creek Hatchery. However, the failures continued, even after new water treatment equipment reduced the *Vibrio* counts. During this period, natural recruitment of Pacific oysters in Willapa Bay, the primary source of wild seed for growers, was also too low to be commercially viable (Dumbauld et al., 2011). The underlying causes of low levels of Pacific oyster recruitment in Willapa Bay have not been determined, although sensitivity of reproduction to low environmental temperatures has long been recognized (Kennedy et al., 1996), and natural recruitment is typically variable. The concurrent failures of some natural populations to produce adequate recruits and the production failures in the hatcheries have been termed the Oyster Seed Crisis (**http://www.seafoodchoices.org/seafoodsummit/documents/Dewey,Bill.pdf**), due to a bottleneck in the availability of juvenile oysters (seed) for planting.

Washington shellfish growers received assistance from Senator Cantwell in 2010, who secured $500,000 to deploy seawater monitoring equipment near major hatcheries. After the sensors were deployed, production of young oysters rose from 20 to 70% of historical levels (B. Dewey, *personal communication*; 22 April 2012 press release; **http://www.cantwell.senate.gov/public/index.cfm/press-releases**). In Oregon, Whiskey Creek Hatchery began monitoring pH to test whether an association among seawater carbonate chemistry, upwelling, and production failure could be detected. Together with collaborators at Oregon State University and NOAA PMEL, they were able to take highly precise measurements of carbon chemistry. High resolution CO_2 monitoring equipment was later installed at the hatchery, allowing the growers to take advantage of natural daily variability in seawater pH to selectively draw water into the hatchery when conditions were favorable. Whiskey Creek Hatchery has also recently had success with chemical buffering of incoming seawater to maintain desired pH levels.

A primary lesson learned through these monitoring efforts has been the limited value of pH measurement in isolation of other variables. In both the Taylor and Whiskey Creek hatcheries, measurements of pH alone were not sufficient to identify seawater conditions that would support normal larval growth. These lessons demonstrate the importance of high-resolution monitoring equipment that yields real-time estimates of calcium carbonate saturation state.

BOX 5.4 FIELD EVIDENCE LINKING OYSTER LARVAL PERFORMANCE TO WATER CHEMISTRY (Barton et al., 2012)

In 2009, the Whiskey Creek Hatchery in Netarts, Oregon, and the Taylor Shellfish Hatchery on Dabob Bay in Washington, experienced unprecedented problems raising Pacific oyster larvae. Water monitoring for ocean acidification conditions began as part of efforts to understand underlying causes and solve problems. Because hatchery personnel take detailed notes on larval size, survival, and development, it was possible to relate the performance of different cohorts of larvae to the water conditions that they experienced during their development in the Whiskey Creek Hatchery using data collected in the hatchery under conditions of ambient seawater. Scientists examined the data for associations between natural fluctuations in aragonite saturation state of incoming seawater and the condition of oyster larvae. They found that both larval production and mid-stage growth were significantly impaired when the Ω_{arag} of seawater in which they were spawned and reared for the first 48 h of life was low.

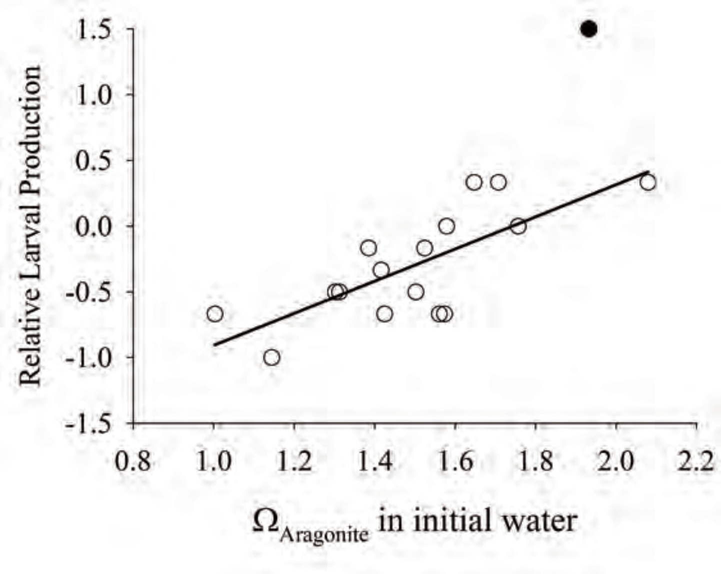

Figure 5.1: The measure of Whiskey Creek Hatchery output as a function of the saturation state of the water that larvae were spawned in and retained for the first 48 h, while developing the D-hinge shell, from Barton et al. (2012). Individual circles indicate cohorts of larvae produced during the summer of 2009. The production term is a standardized measure of biomass as estimated from stocking densities of tanks and the number of tanks a specific cohort occupied following D-hinge stage until competency to settle (or the stage at which they are shipped to growers). A value of zero indicates that mortality rates in the cohort matched growth and resulted in cohorts not increasing in total biomass.

Our treatment of molluscs focuses here on bivalves and gastropods, which have received proportionately more study than other species. Bivalves include a number of reef-building and suspension-feeding species that provide important ecosystem services including 1) improvement of water clarity (Wall et al., 2008); 2) removal of nitrogen and carbon through incorporation in tissue and shell production (Newell and Koch, 2004; Lindahl et al., 2005); 3) deposition of particulate nitrogen and carbon to the seafloor in shallow habitats, thereby supporting primary production and promoting nutrient trapping (Newell et al., 2005); 4) production of alkalinity (buffering capacity) in dense filter-feeding bivalve aggregations, such as oyster reefs (Waldbusser et al., *in press*); and 5) provision of important nursery habitat to other finfish and invertebrates (Coen et al., 2007, 2011; Grabowski and Peterson, 2007; Dumbauld et al., 2009). Gastropods include grazers and predators that structure marine benthic communities or have commercial and conservation value (see **Boxes 5.5** and **5.6**).

BOX 5.5 RESPONSE OF ADULT DOGWHELKS TO ACIDIFICATION (Nienhuis et al., 2010)

In an experiment with non-feeding adult dogwhelks (*Nucella lamellosa*) conducted over six days, individuals continued to create new shell material across all pCO_2 treatments (ambient, 785 ppm, 1585 ppm), but shell dissolution increased with pCO_2, even though in all cases Ω_{arag} was probably > 1.0. The researchers were able to draw these conclusions by noting that shell weight gain declined with pCO_2, and this difference across treatments was of similar magnitude to results from empty shells.

BOX 5.6 SENSITIVITY OF ABALONE LARVAE TO ACIDIFICATION (Crim et al., 2011)

Elevated seawater pCO_2 impairs larval development and reduces larval survival in northern abalone (*Haliotis kamtschatkana*), a Washington State Candidate species and federal Species of Concern. Abalone are among a group of gastropods that release eggs and sperm into the seawater, and fertilized eggs develop into non-feeding larvae that metamorphose into juveniles in about eight days. Developing *Haliotis* embryos were placed into three pCO_2 treatments (400, 800, 1800 ppm) within 4 h of fertilization. Larval morphology was strongly affected by elevated pCO_2, with the percentage of normal larval shells dropping from 97% (at ambient levels of 400 ppm) to 60% (800 ppm) to 0% (1800 ppm). Larval survival was reduced by 40% under both elevated pCO_2 conditions relative to ambient, but surviving larvae metamorphosed equivalently across treatments.

Larval bivalves appear to be more sensitive to acidification than adults (Kroeker et al., 2010), although growth and survival of juvenile bivalves have also been observed to be negatively affected by elevated pCO_2 (Talmage and Gobler, 2011). The sensitivity of shell-forming larvae to ocean acidification conditions may be due to the mineralogy of the larval shell (Weiss et al., 2002; but see Kudo et al., 2010). Some species, including the Pacific oyster (*Crassostrea gigas*) and local clam species, go through the entirety of larval development as free-swimming plankton. In contrast, the Olympia oyster (*Ostrea lurida*) is a brooding species that retains larvae within the mantle cavity for approximately the first week of early development. Inside brooding adults of another brooding oyster species (*Ostrea chilensis*), the pH of internal fluids has been observed to drop below 7.0 due to respiration by the adult when its shell is closed against external conditions (Chaparro et al., 2009). Despite similarities in life histories among many bivalves, sensitivity to acidification varies considerably in studies in which several species are simultaneously exposed to similar treatments (Miller et al., 2009; Talmage and Gobler, 2009, 2011; Parker et al., 2010). This suggests that species-specific differences in organismal form and life history can determine sensitivity to ocean acidification conditions, and that organismal responses cannot be derived from strictly thermodynamic arguments.

One recent meta-analysis of molluscan responses to acidification found no consistent change in growth or calcification across species (Kroeker et al., 2010). In a separate meta-analysis of bivalves, reduced calcification was observed under enriched pCO_2, but survival and growth were not consistently affected (Hendriks et al., 2010). While these meta-analyses indicate the challenge of finding general patterns across species, there remain clear examples, particularly for bivalve larvae, in which performance was seriously impaired when the larvae were grown under elevated pCO_2. For instance, larvae of a U.S. West Coast mussel (*Mytilus californianus*) grew more slowly under conditions of elevated pCO_2 (Gaylord et al., 2011), and European mussels (*Mytilus edulis*) exhibited impaired hatching, survival, and growth when seawater pH declined by 0.5 units (Gazeau et al., 2011). A consistent result from several laboratory studies of oyster larvae is that elevated pCO_2 tends to reduce survival and growth, summarized in **Figures 5.2A** (depicting survival) and **5.2B** (depicting size).

These figures show published data for four species of oysters subjected to treatments of elevated pCO_2 during larval development. The preponderance of negative values in both figures demonstrates the tendency for elevated pCO_2 to reduce the survival of normal larvae and larval size, relative to baseline conditions (usually ~380 ppm). Although ranking oyster species by their sensitivity to acidification is not yet possible, there have been two studies in which larvae of two oyster species were exposed to elevated pCO_2 simultaneously. In these studies, *C. virginica* was more sensitive than *C. ariakensis* (Miller et al., 2009), and *S. glomerata* was more sensitive than *C. gigas* (Parker et al., 2010). Response to elevated pCO_2 may

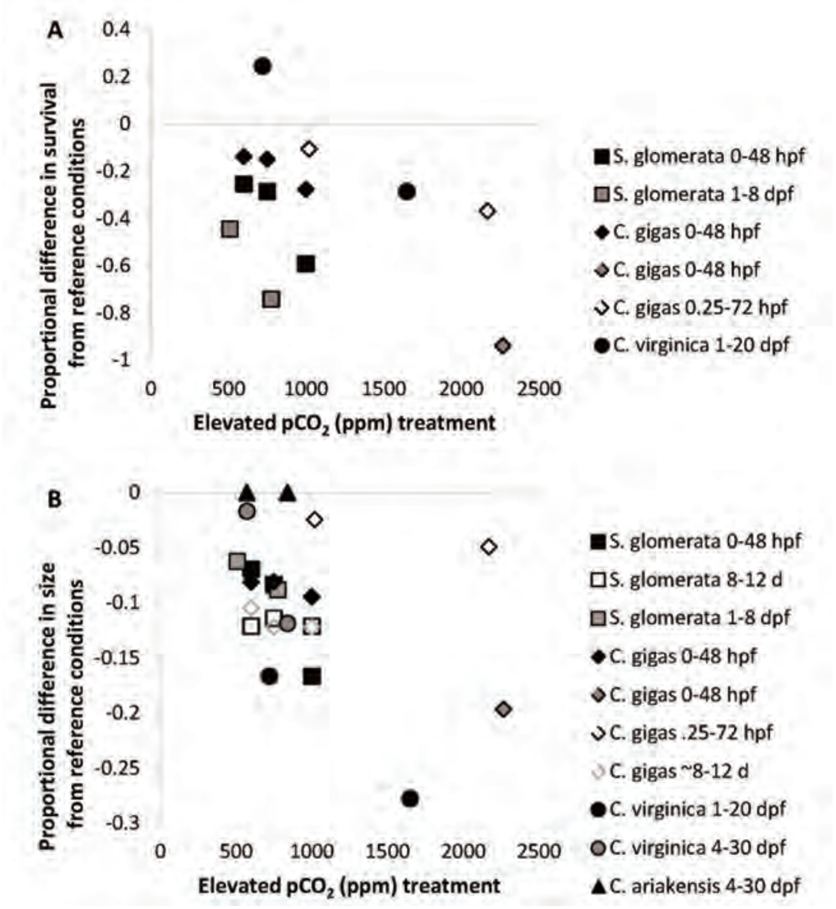

Figure 5.2: Compilation of published laboratory studies of survival (A) and growth (B) of oyster larvae under elevated pCO$_2$ conditions (hpf = hours post fertilization; dpf = days post fertilization). Plot points are distinguished by species (shape) and by study (shading), with the x-axis showing pCO$_2$ enrichment levels (ppm). The y-axis shows the proportional difference relative to reference conditions, usually around 380 ppm pCO$_2$. The proportional difference in survival is the difference in % surviving at the end of the study between treatment and reference conditions, divided by the % survival in reference conditions; proportional difference in growth is calculated similarly (Miller et al., 2009; Parker et al., 2009, 2010, 2012; Talmage and Gobler, 2009; Watson et al., 2009; Gazeau et al., 2011).

have a genetic component: larvae of *S. glomerata* bred for rapid growth and disease resistance performed better under elevated pCO$_2$ than did offspring of wild parents (Parker et al., 2009). Response to elevated pCO$_2$ may also be phenotypically plastic, given that larvae of *S. glomerata* from parents raised in a high-pCO$_2$ environment demonstrated growth and survival that were not strongly reduced by high pCO$_2$ during larval development, whereas larvae from parents raised at current levels of pCO_2 were negatively affected by high pCO_2 (Parker et al., 2012). Sensitivity to naturally fluctuating conditions in a hatchery setting recently has been reported (Barton et al., 2012; **Box 5.4**).

The methods used in the above experiments differ in terms of which larval phase was exposed to elevated pCO_2 and for how long, as well as variation in baseline water chemistry. In some cases, exposure to elevated pCO_2 conditions commenced with spawning, and experiments concluded before larvae reached the feeding stage. Other experiments were of longer duration, and phytoplankton were added as a food source for larvae during later stages of development. The aragonite saturation (Ω_{arag}) level of reference conditions was not consistent among these studies (baseline Ω_{arag} varied from 1 to 3), and Ω_{arag} always dropped in response to elevated pCO_2, in most cases to below 1.0. However, Gazeau et al. (2011) report that for early embryonic (non-feeding) development of *C. gigas*, the concentration of carbonate ion is more important than Ω_{arag} per se.

In addition to changes in shell formation that can be measured by size or thickness, water chemistry can also influence the chemical composition of the shell and therefore allow shells to be used as bio-recorders of their environment. A recent example comes from the outer coast of Washington (see **Box 5.7** Stable Isotopes in Mussel Shells).

BOX 5.7 STABLE ISOTOPES IN MUSSEL SHELLS (Pfister et al., 2011)

Mussels (*Mytilus californianus*) dominate the mid-intertidal zone of wave-exposed shorelines of Washington. Some of the chemical elements that constitute shell can be measured for the relative amounts of different isotopes. Carbon-13 is a stable (non-radioactive) isotope with one more neutron than the more common form of carbon-12. Similarly, oxygen-18 is a heavier stable isotopic form relative to oxygen-16. Hydrogen, nitrogen, and sulfur are other elements commonly measured for stable isotopic ratios in living and non-living materials. Carbon and oxygen stable isotopes were measured in mussel shells collected from Tatoosh Island, Washington dating to the late 2000s, 1970s–1980s, and approximately 1300 years ago, the last from specimens in the Makah Tribal Museum. These shells demonstrated a strong decline in the relative amount of carbon-13 versus carbon-12 over the past decade, which was unprecedented over the previous millennium. Oxygen-18 relative to oxygen-16, which reflects water temperature and salinity, did not change in the shell time series. The change in carbon isotopic ratio was consistent with increased anthropogenic CO_2 in the atmosphere.

BOX 5.8 THE EFFECT OF ACIDIFICATION ON EXTERNAL FERTILIZATION IN A SEA URCHIN (Reuter et al., 2011)

In this study, researchers mixed sea urchin (*Strongylocentrotus franciscanus*) sperm and eggs together across a range of sperm concentrations and at three pCO_2 levels (400, 800, 1800 ppm). Fertilization was allowed to proceed for 30 seconds and then stopped chemically. Eggs were examined for evidence of fertilization and for polyspermy. Polyspermy occurs when more than one sperm fertilizes an egg, a process that is generally blocked by chemical changes in the egg that occur following fertilization. Development cannot proceed normally if more than one sperm fertilizes an egg. At elevated pCO_2, much higher sperm concentrations were required for successful fertilization relative to controls. At the same time, low pH may also be responsible for a delay in the egg's ability to prevent more than one sperm from fertilizing, since polyspermy increased with pCO_2. These results show that acidification could both shift and narrow the optimal range of sperm concentrations for fertilization in this broadcast spawner.

5.2.6 Crustaceans

Marine crustaceans play important roles in marine food webs and have commercial importance in Washington State. For example, the combined average 1990-2002 ex-vessel value of the coastal and Puget Sound Dungeness Crab fisheries was ~$25 million (Washington State Department Fish and Wildlife). A limited amount of research suggests that acidification, alone or in combination with other stressors, could affect marine crustaceans, and decreases in survival, growth rate, and egg production have been reported in some species (Whiteley, 2011). It is not yet possible to draw generalized conclusions from this body of work given its limited extent, especially when compared with the diversity of the crustaceans and the diversity of habitats in which they are found. Whiteley (2011) reviewed much of what is currently known about the physiological and ecological responses of crustaceans to ocean acidification and found that crustacean species that inhabit fluctuating environments, such as estuaries and shallow coastal regions, are likely to be more tolerant of ocean acidification than are those species inhabiting more stable environments, such as deep sea regions. According to Whiteley (2011) crustacean species capable of good iono- and osmoregulation tend to be less vulnerable to the effects of changing pH and pCO_2.

Most crustaceans have an exoskeleton, composed partially of calcium carbonate. The polymorphs of calcium carbonate used in the carapace (the dorsal section of the exoskeleton) are the most soluble forms of the crystal (high magnesium calcite and amorphous calcium carbonate). Research to date shows that calcification of crustacean carapaces does not change or increases in response to exposure to high pCO_2 levels (reviewed in Whiteley, 2011). Scientists postulate that maintaining carapace calcification in high CO_2/low pH environments may be energetically costly (Whiteley, 2011).

A variety of other effects of acidification on crustaceans have been explored. Acidification seems to affect development in the crustacean zooplankton species that have been studied to date (see Chapter 5, Section 2.4). In addition, exposure to pCO_2 levels projected for 2100 narrows the window of thermal tolerance among Atlantic spider crabs (*Hyas araneus*) at both larval and adult stages (Walther et al., 2009, 2010), suggesting that the effects of acidification on crustaceans should be considered in the context of changing ocean temperature.

A number of studies currently are underway in Washington and Alaska to explore the response of commercial crab species, including Dungeness and king crabs, to elevated pCO_2.

5.2.7 Echinoderms

Echinoderms, including sea urchins, sand dollars, seastars, sea cucumbers, and brittlestars, build calcified structures for support and protection. Among larval stages, skeletons primarily are made of amorphous calcium carbonate (a polymorph of calcium carbonate, also found in the carapaces of crustaceans). The spines and tests (shells) of adult echinoderms are made of calcite. Across many studies of sea urchins, exposure to elevated pCO_2 reduces survival and growth (Hendriks et al., 2010), and the mean effect on growth appears to be more pronounced for juveniles than for larvae (Kroeker et al., 2011). Sea urchins have been used in fertilization studies for decades because of relatively large egg size and ease of external fertilization, and this use has extended to tests of fertilization under elevated pCO_2. Effects on fertilization are more likely caused by changes in pH than by reductions in carbonate ion concentrations. One local example illustrates how acidification could affect fertilization of red sea urchins, and suggests potential problems for broadcast spawners in general (**Box 5.8**).

On the outer coast of Washington, seastars (*Pisaster ochraceus*) act as keystone species promoting coexistence and therefore biodiversity among intertidal communities on rocky shores (Paine, 1966). Similarly, sea urchins can also have a strong influence on benthic marine communities, for instance by consuming kelp species that would otherwise form structured habitats and provide primary production for food webs (Paine and Vadas, 1969; Duggins et al., 1989), although it is important to point out that urchins do not appear to limit kelps in all systems (Carter et al., 2007). Acidification-driven changes in the population dynamics of echinoderms could have strong domino effects on ecosystems, even though echinoderms have relatively small direct value to Washington from commercial fisheries (Pfister and Bradbury, 1996).

5.2.8 Fish

Fish have a strong ability to control their internal physiology, including acid-base equilibrium, and have only one small body part made of calcium carbonate (an ear bone called the otolith). For these reasons, some question whether ocean acidification will directly affect fish. However, the early life history stages of fish lack the physiological control mechanisms present in adults. For example, gills are an important organ for maintaining acid-base balance in fish, and early larval stages of fish lack gills. Fish appear to have different sensitivities to high pCO_2 conditions at different points in their life cycle: while Atlantic cod (*Gadus morhua*), an important commercial fish species, are sensitive to high pCO_2 later in the larval stage, they are relatively insensitive at egg and early larval stage and as adults (Melzner et al., 2009; Frommel et al., 2012a,b). At the sensitive later larval stage, Atlantic cod experience tissue damage in vital organs (liver, pancreas, kidney, gut) when reared at pCO_2 levels expected in Washington State in the near future (1800 µatm; Frommel et al., 2012a).

Forage fish, such as herring and smelt, play an important role in marine food webs. When exposed to pCO_2 levels projected for the next century (up to 1000 ppm CO_2), a forage fish species native to the Atlantic experienced declines in growth and survivorship and increases in abnormal development (Baumann et al., 2012). Conversely, limited evidence suggests that Atlantic herring may be resistant to changes in carbonate chemistry as eggs and larvae (Franke and Clemmesen, 2011). Studies on the response of forage fish common in Washington State to acidification are underway (J. Reum, S. Busch, P. McElhany, *personal communication*).

Among tropical fish from Australia's Great Barrier Reef, ocean acidification has been demonstrated to cause significant and varied effects on the nervous system of developing and adult fish, such as the following:

- Inability to learn from visual or odor cues (Ferrari et al., 2012a)
- Reduced homing behavior of adults and juveniles (Munday et al., 2009b; Devine et al., 2012)
- Impaired ability of a predator to detect its prey and attraction of a prey to its predators (Dixson et al., 2010; Munday et al., 2010; Cripps et al., 2011)
- Diminished and unusual response to the sight of a predator (Ferrari et al., 2012b)
- Decreased anti-predator behavior (Munday et al., 2010; Ferrari et al., 2011a, b; Melzner et al., 2011)
- Reduced ability to respond properly to auditory cues (Simpson et al., 2011)
- Altered brain function (Domenici et al., 2012), including neurotransmitter function (Nilsson et al., 2012)

These effects of acidification on the nervous system of fish have consequences for the condition of individuals and have led to higher than normal mortality due to predation when study subjects were examined in wild settings. Moreover, Australian researchers have demonstrated that acidification can cause a decline in aerobic capacity and an increase in mortality (Munday et al., 2009a). By studying a number of species, these investigators have found that species exhibit different sensitivities to changes in carbonate chemistry (Ferrari et al., 2011a) and that individuals of the same species vary in sensitivity to acidification (Munday et al., 2010). Researchers are starting to explore the impacts of ocean acidification on the nervous system of temperate fishes such as those found in Washington State.

If the sensitivities observed in tropical fish (impaired homing behavior, odor detection, and learning) are found to be general among fish species, salmon species native to Washington could be affected via their ability to return to spawning sites. The direct impacts of acidification on salmon species remain uncertain, especially because these species spend their early life stages in fresh waters of relatively low pH. One study has tested the response of Atlantic salmon, *Salmo salar*, at its first marine life stage to large changes in carbonate chemistry (pH 7.0), and detected no change in mortality, growth, condition, metabolism, or blood chemistry (Fivelstad et al., 1998).

5.3 Multiple Stressors

Ocean acidification will co-occur with changes in other environmental factors (e.g., temperature, dissolved oxygen, nitrogen) and human impacts (e.g., pollution, fisheries, habitat modification and loss; Harley et al., 2006; Whitney et al., 2007; Doney et al., 2012). To understand how ocean acidification will influence marine species and communities, we must understand the response to acidification in the context of other co-occurring stressors. In general, literature from the disciplines of physiology and ecology suggest that the response to multiple simultaneous stressors is often larger and potentially of a different nature than the additive response to each stressor considered in isolation (Paine et al., 1998; Pörtner et al., 2005). Consistent with this are findings from ecosystem models used to explore how marine food webs will respond to ocean acidification in combination with simultaneous stressors ranging from ocean warming to de-oxygenation to changes in species abundance (Ainsworth et al., 2011; Cheung et al., 2011; Griffith et al., 2011).

A handful of studies have explored how marine species will respond to simultaneous exposure to acidification and other stressors. These studies are important for evaluating which stressors cause the strongest responses, and for characterizing unexpected physiological changes that appear with synergisms. Theory predicts that the effects of simultaneous exposure to elevated temperature, elevated pCO_2, and low dissolved oxygen, reduce an organism's ability to regulate acid-base equilibrium, metabolism, and protein synthesis (Pörtner et al., 2005). Data from recent experiments and field observations on species ranging from squid to corals to pteropods are consistent with this finding (Pane and Barry, 2007; Anthony et al., 2008; Rosa and Seibel, 2008; Comeau et al., 2010b; Rodolfo-Metalpa et al., 2011). Limited research on ocean acidification in combination with stressors other than dissolved oxygen and temperature indicates that increased seawater acidity affects the uptake of metals in developing squid (Lacoue-Labarthe et al., 2009, 2011), sensitivity to UV-B radiation in some primary producers (Beardall et al., 2009), and the toxicity of the pharmaceutical clotrimazole but not triclosan in a brittlestar (Röös, 2011).

5.4 Observing and Research Needs

1. Characterize the response to ocean acidification of species that are ecologically, economically, or culturally important, or of conservation concern.
2. Elucidate *direct effects* of ocean acidification on species of concern, including shellfish.
3. Elucidate *indirect effects* of ocean acidification on species of concern, including those for which direct effects are not evident.
4. Conduct field studies in natural environments to contextualize laboratory results.
5. Deploy high resolution monitoring capabilities yielding real-time estimates of carbonate saturation state at hatcheries throughout Washington.
6. Couple biological monitoring with physical and chemical measurements.
7. Use numerical models to predict biological responses to ocean acidification, and use results from manipulative studies to parameterize and tune models.

6

Ecosystem Response to Ocean Acidification

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6.0 Key Points

6.0.1 What we know about ecosystem response to ocean acidification

- Biological processes influence seawater chemistry: for example photosynthesis and respiration can influence pH on a day/night basis and over longer periods.
- Biological processes contribute to carbon cycling in the ocean.
- Conditions in sediment habitats could differ from those in the overlying water column.
- Food webs and species interactions could change under conditions of ocean acidification.
- Biological adaptation to ocean acidification conditions has been demonstrated for some species.
- The current rate of acidification is unprecedented over the past 300 million years; similar past events have been accompanied by major marine extinctions.
- Organisms in different habitats will be exposed to different conditions: upwelling systems, deep fjords, semi-isolated bays will differ in the expression of acidification.

6.0.2 What we need to know about ecosystem response to ocean acidification

- Do system-level responses differ from those of individual organisms? If so, how?
- How might marine food webs be altered?
- How might marine diseases respond?
- What is the scope for genetic adaptation to ocean acidification?
- Which habitats or systems are at greatest risk of change due to ocean acidification?

Chapter 6 moves beyond species-specific responses to acidification to consider acidification in the context of food webs and ecosystems. We consider biological and ecological responses at a range of spatial and temporal scales. Our intent in this chapter is to begin to create a picture of how biological and ecological systems and processes in Washington state waters might change in response to ocean acidification. In this context is important to recognize that waters of the California Current System (including waters in Washington State) already express low pH and carbonate saturation state. While projections of future ocean acidification in this system can be made with some confidence (Gruber et al., 2012), the effects of changing seawater chemistry on organisms and ecosystems remains far less certain, and the potential for adaptation is not known. Despite uncertainties in biological and ecological response to acidification, simulation models indicate that the California Current System is rapidly evolving towards conditions that exceed the natural range of variation in carbonate chemistry, and away from conditions to which the native organisms have become adapted (Gruber et al., 2012).

6.1 Biological Influences on Seawater Chemistry

6.1.1 Photosynthesis and respiration

In photosynthesis, primary producers use light as an energy source to transform simple inorganic carbon molecules, such as CO_2, into larger organic carbon molecules (sugars). Sugars, and the still more complex carbohydrates that they can be linked together to form, contain chemical energy. When these molecules are broken down during respiration, CO_2 is once again released along with the energy to fuel metabolic life processes. Although we use CO_2 as shorthand here for an inorganic carbon source, recall from Chapter 5 that some aquatic primary producers utilize bicarbonate ion (HCO_3^-) as a substrate for photosynthesis. The reciprocal chemical reactions of photosynthesis (equation 6) and respiration (equation 7) can be more apparent when written as equations:

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2 \quad \text{(photosynthesis)} \qquad (6);$$

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \quad \text{(respiration)} \qquad (7).$$

These equations illustrate that, for every molecule of CO_2 used in photosynthesis, a molecule of oxygen (O_2) is released, and for every molecule of O_2 used during respiration, a molecule of CO_2 is released (the actual ratios for photosynthetic quotient and respiratory quotient can deviate slightly from 1 due to the synthesis and breakdown of molecules other than glucose (Schmidt-Nielsen, 1997; Larkum et al., 2006)). Consequently, the relative rates of photosynthesis and respiration will influence seawater chemistry. An aquatic system is net autotrophic when photosynthesis exceeds respiration and net heterotrophic when respiration exceeds photosynthesis. Net autotrophic systems often occur where nutrients are high and light is available, whereas net heterotrophic systems are frequently light-limited (e.g., below the photic zone in deep water, or where turbid water interferes with light penetration). Nighttime low light also produces net heterotrophy, which explains the strong day-night variation in pH observed in many field studies, particularly in nearshore systems where biomass is high (**Box 6.1**).

6.1.2 Carbon cycling through fish, invertebrates, and shells

Organisms can affect the global carbon cycle through the production of new biomass or respiration of existing biomass, resulting in the uptake or release of CO_2 as described above. However, in marine settings, organisms can also alter the marine carbon cycle through the formation or dissolution of calcium carbonate minerals. When organisms form calcium carbonate minerals they

BOX 6.1 STRONG DAY-NIGHT pH VARIATION INDICATING THE SHIFT BETWEEN NET AUTOTROPHY AND NET HETEROTROPHY (Wootton et al., 2008)

In the plot below, each point is a measurement of pH from a nearshore station on Tatoosh Island, with colors distinguishing measurements from different summer months, e.g. black in May, purple in August, yellow in September. The pH is generally lowest just before dawn, most likely due to build-up of dissolved inorganic carbon (DIC; the sum of CO_{2aq}, HCO_3^-, and CO_3^{2-}) in the water as organisms respire overnight. During daylight hours, photosynthesizers draw down DIC, and the pH rises through most of the day.

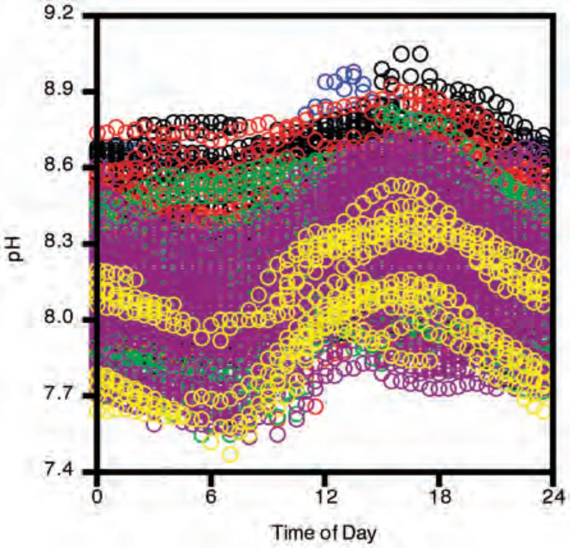

Figure 6.1: Diurnal variation in nearshore pH at a station on Tatoosh Island, from Wootton et al. (2008).

remove dissolved inorganic carbon and alkalinity from the seawater medium in which they are forming their shells. Very generally the simplified carbonate chemistry of shell formation is:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad \text{(biocalcification)} \qquad (8).$$

In short, calcium carbonate shell formation results in CO_2 production, reduction in total dissolved inorganic carbon, and a decline in alkalinity. The dissolution of calcium carbonate results in the inverse. These dynamics often are utilized in experimental settings to measure calcification using a method called the alkalinity anomaly method (Smith and Key, 1975). Coral reef ecologists can detect measureable changes in seawater chemistry as a result of coral calcium carbonate formation, and they use these values to estimate entire reef ecosystem calcification and growth (Kinsey, 1978; Shamberger et al., 2011).

Three examples of biological effects on (rather than responses to) marine and estuarine carbonate chemistry are: 1) dense shell aggregates, such as oyster reefs, 2) dense populations of shell-forming organisms, and 3) gut passage or osmoregulation in organisms. In temperate estuaries and nearshore environments shellfish often are found in aggregations. This sort of aggregation has been previously articulated by Kidwell and Jablonski (1983) as the "taphonomic feedback" hypothesis. This hypothesis proposes that upon death, shell-forming organisms leave behind their hard parts, which attract and provide substrate for other shell-forming organisms, thus providing a feedback loop in which shell begets shell. This is not only the case for oysters in reef settings, but appears also to be true for sediment-dwelling bivalves such as clams (Carriker, 1961), in which shells from dead clams help buffer CO_2 produced by respiration in sediments rich in particulate organic matter. In an oyster reef, the formation of shell material is coupled to production of biological deposits of excreted solids, which ultimately provides CO_2 to re-dissolve shells. If shells are removed from the system and not replaced, the production of carbon dioxide from respiration is decoupled from the potential buffering effect of shells (Waldbusser et al., *in press*). Oyster shells and other biologically produced calcium carbonates are not inert, but instead degrade over time due to dissolution and bioerosion by other organisms (Green et al., 2009; Carver et al., 2010). Estimated rates of shell degradation in one recent study of Delaware Bay were found to result in shell half-lives of 3-10 years (Powell et al., 2006), and were corroborated recently in a laboratory study by Waldbusser et al. (2011). The potential magnitude of this formation and dissolution on system-wide carbonate chemistry recently was conservatively estimated by Waldbusser et al. (*in press*), who found that the buffering capacity of oyster shell contributed nearly 90% of the total dissolved alkalinity in Chesapeake Bay prior to oyster harvesting. These historic reconstructions are difficult to perform without adequate data prior to significant impacts. However in a current study of echinoderm (e.g., sea urchin) impacts on the global carbon cycle, Lebrato et al. (2010) recently estimated that echinoderm shell production on the seafloor might account for 5–25% of all the calcium carbonate produced in the ocean's overlying waters. Finally, gut passage by organisms, or the release of calcium carbonate from the guts of fish regulating the "saltiness" of their blood, could also contribute significantly to carbonate cycling. Sediment feeding organisms increase rates of calcium carbonate dissolution by passing this material through guts that are more acidic, possibly contributing to 5% of the total ocean seafloor calcite dissolution (Jansen and Ahrens, 2004). The opposite effect is generated by marine fish that must remove extra salts and minerals from their body fluids by excretion of solid calcium carbonate, with estimates of fish contributing between 3 and 15% of the total ocean calcium carbonate production (Wilson et al., 2009). It is becoming increasingly apparent that organisms may have significant effects on carbonate cycling in the world's oceans; however, our understanding of the extent and impact of species loss on carbonate cycling is poorly described.

6.2 Responses in Sediment Habitats

Ocean acidification research generally has focused on the chemistry of the water column at varying depths. However, in many sediment habitats pCO_2 is elevated within the upper layers of the sediment due to the respiration of organic matter within these habitats. The role of this metabolic CO_2 in dissolving calcium carbonate in deeper habitats has been long recognized (Emerson and Bender, 1981), and more recently attention has shifted to habitats closer to shore (McNichol et al., 1988; Rude and Aller, 1991; Green and Aller, 2001) and impacts on infaunal organisms (those that live within the sediments) inhabiting these environments (Green et al., 2009; Widdicombe et al., 2009). It is important to note that multiple factors will ultimately affect the conditions experienced by organisms in nearshore marine sediments with respect to changes in carbonate chemistry. Among these influential factors are changes in temperature, deposition of organic matter, and changes in pCO_2 levels in the overlying waters. However, increasing atmospheric CO_2 will likely cause unfavorable conditions to become more frequent and longer in duration.

Recent experimental evidence from sediment environments shows negative responses by several organisms to elevated pCO_2 including changes in crab behavior (de la Haye et al., 2012), mild impacts on burrowing shrimp (Donohue et al., 2012), and on clams (Green et al., 2009; Waldbusser et al., 2010). Because bivalves have received considerable attention it is worthwhile further exploring sediment dwelling bivalves. In field and laboratory experiments, hard clams, *Mercenaria mercenaria*, have responded positively to increases in aragonite saturation state (Green et al., 2009, 2012; Waldbusser and Green, 2011). Utilizing pulverized clamshell in experimental plots, Green et al. (2009) found that shell material had a positive effect on recruitment of settling clams to experimental cores with elevated carbonate saturation states. In laboratory experiments, Green et al. (2012) confirmed these findings by studying the burrowing behavior of juvenile clams. They observed an increasing proportion of clams burrowed when saturation state for aragonite was closer to 1.0, however some clams burrowed under corrosive conditions. Putting survival, growth, and behavior of burrowing clams together in a population model of the early post-larval stages, Waldbusser and Green (2011) found that increasing saturation state increased the survival of hard clams to larger, more tolerant sizes. Altering individual growth rate in the model (to assess possible effects due to natural differences in growth among populations) also provided an advantage to juveniles, in that it allowed them to reach an "escape" size (a size at which they can overcome acidification effects) more quickly, thus increasing survival.

6.3 Food Web Responses to Acidification

6.3.1 Food web interactions

A food web is a diagram of the feeding interactions of organisms within a community. In a food web, different organisms or groups are represented as nodes in the web, and the links between nodes show who eats whom. Organisms also interact in ways that do not simply involve consumption; for instance seagrasses and bivalves can compete for space (Tallis et al., 2009), but such interactions are not described in food webs. Evidence from laboratory experiments suggests that the demographics, size, and nutritional content of some species may change in response to changing carbonate chemistry, and these effects are likely to influence food webs (Rossoll et al., 2012). The importance of the food web concept lies in the expectation that the organisms present in a community can change in abundance because of their interactions with other species, not simply because of their physiological performance under changing environmental conditions.

Competitive interactions, in addition to predator-prey interactions, could change under conditions of acidification. As an example, the balance between kelp forests and turf algae in southern Australia is unaffected under increased nutrient loads and projected future CO_2 levels (Falkenberg et al., 2012). However, if openings are created in kelp forests, turf algae outcompete kelp

BOX 6.2 RESPONSE OF A ROCKY INTERTIDAL COMMUNITY ON TATOOSH ISLAND, WASHINGTON TO DECREASING SEAWATER pH (Wootton et al., 2008)

Local research has demonstrated a response of the intertidal biological community to changes in ocean pH. On Tatoosh Island, at the mouth of the Strait of Juan de Fuca, the organisms making up the rocky intertidal assemblage can vary over time. In years of higher pH, these transitions tend to involve the replacement of non-calcified species by calcified species, or the persistence of calcified species. In contrast, in years of lower pH, calcified species are more likely to be replaced by non-calcified species. When these patterns were incorporated into a model of community change over time, dominant calcifying animals were predicted to decline due to acidification, calcareous coralline algae were predicted to show little change, and non-calcified algae and subdominant calcifying animals were predicted to increase. These changes are thought to be due to pH responses mediated through the hierarchy of competition for space.

under high nutrient and pCO_2 levels. This result has implications for maintenance of the kelp forest ecosystem under disturbance events in future ocean conditions (Falkenberg et al., 2012). A local example describes changing competitive interactions among both invertebrates and seaweeds (**Box 6.2**; Wootton et al., 2008). Generally, it is difficult to predict exactly how a perturbation to one part of the food web will affect other species (Russell et al., 2011).

6.3.2 Wild fisheries and food webs

Wild fisheries (e.g., geoduck clams, Dungeness crab, salmon, halibut, and others) are of great economic value to Washington State. These species are embedded in marine food webs that are sensitive to changes in environmental conditions. Evidence from laboratory experiments on species response to acidification suggests that the demographics, size, and nutritional content of some species can change in response to changing carbonate chemistry (see Chapter 5); these effects are likely to influence food web structure and function. The abundance of fished species can vary as the food web changes. At this time, we have insufficient information to determine the response of marine food webs in Washington State to acidification. New research on phytoplankton, the dominant zooplankton species, and other ecologically important species in food webs will be crucial for defining the direction and magnitude of these effects.

Ecological models provide a tool to explore how foods webs and fisheries could change as their component species vary in response to acidification. Three recent papers have used numerical models to explore the ecological impacts of acidification and other aspects of climate change. Ainsworth et al. (2011) found that acidification in isolation causes small reductions in the catch of fished species in five northeast Pacific food webs. However, imposing acidification scenarios on these foods webs in combination with scenarios of four other impacts of global change (primary production, species range shifts, zooplankton community size structure, and ocean deoxygenation) reduced fisheries landings by 20% relative to harvest under unchanged environmental conditions. Numerical modeling exercises for other ecosystems can give indications about the types of perturbations that acidification can cause in ecosystems. An ecosystem model used to explore changes in marine systems of southeast Australia indicated that simultaneous exposure to acidification and fisheries exploitation is likely to cause unexpected changes in the structure of food webs (Griffith et al., 2011). Scenarios of acidification and ocean deoxygenation imposed on harvested species from the northeast Atlantic reduced projected future harvest by 20–30% (Cheung et al., 2011). New work on the response to acidification of food webs in Puget Sound is nearing completion, and suggests that food web interactions can yield directional changes in species biomass that are different than those based on extrapolations from single species laboratory experiments (Busch et al., *submitted*). A project linking spatially and temporally explicit ocean chemistry forecasts from regional ocean models with scenarios of the response of species in the

California Current ecosystem to acidification will start in September 2012 (I. Kaplan, *personal communication*).

6.4 Biological Adaptation and Acclimatization

6.4.1 Evolutionary potential of calcifying species

For many species, persistence under changing ocean conditions will require genetic adaptation. Genetic adaptation refers to the process of populations of individuals acquiring advantageous traits through natural selection (Kawecki and Ebert, 2004). The *adaptive potential* of a population—its ability to respond to environmental change through genetic adaptation—depends on the presence of sufficient genetic variation for selection to act upon. Adaptation occurs over generations and must be distinguished from phenotypic plasticity, which refers to an individual's ability to tolerate or become accustomed to new environmental conditions. Evidence for genetic adaptation to ocean acidification conditions is beginning to emerge for some taxa. For example, populations of the calcified coccolithophorid *Emiliania huxleyi* maintained under elevated pCO_2 conditions for about 500 generations showed enhanced growth rates compared with control populations, and also demonstrated some recovery of calcification potential (Lohbeck et al., 2012). The presence of genotypes tolerant of high temperature and low pH has been demonstrated in populations of the urchin *Centrostephanus rodgersii*, indicating that the capacity for genetic adaptation to ocean acidification conditions exists in this species (Foo et al., 2012). More generally, spatially-varying selection helps to maintain the intraspecific genetic variation that allows adaptation to changing environmental conditions (Kelly and Hofmann, 2012). It follows that genetic variation and evolutionary potential could be greater in regions characterized by naturally high spatial and temporal variation in pH and pCO_2 (such as Washington's coastal waters) than in regions lower levels of natural variation (such as open ocean environments).

Shellfish hatcheries can influence adaptation of farmed populations through selective breeding programs in which animals with certain performance traits are used as broodstock (parents) for the next generation (Parker et al., 2011, 2012). Such methods are commonly-used farming practices and can facilitate or hinder the adaptive potential of farmed shellfish. In the natural environment the number of parents that contribute offspring to the next generation can vary greatly in oysters (Hedgecock, 1982, 1986, 1994; Hedgecock et al., 2006; Karlen et al., 2010; Hedgecock and Pudovkin, 2011), urchins (Palumbi and Wilson, 1990), and geoducks (Straus, 2010). Selective breeding in farmed populations can have unintended consequences for wild populations if outcrossing between farmed and wild conspecifics occurs. For example, local adaptation among wild populations (as seen in the mussel Mytilus; Riginos and Cunningham, 2005) could be disrupted or lost by outcrossing with artificially selected or genetically uniform hatchery populations, thereby reducing fitness in the wild population (Camara and Vadopalas, 2009).

Acidification could become a strong selective force among shellfish populations. The sensitivity of larval and, to a lesser extent, later life stages to acidification has been demonstrated, but empirical studies assessing the effects of exposure of gametes or larvae to acidification on later life stages and the potential for genetic-level adaptive responses at the population level are rare. Several recent studies illustrate the potential for selection and adaptation of marine species to acidification. Fertilization success and early larval performance of intertidal sea urchins reflected that of the tide pools of origin; those that experienced low pH in nature were better able to withstand experimentally acidified waters (Moulin et al., 2011). Similarly, variation in spider crab larval development under varying climatic conditions (temperature and pH) suggested evolutionary adaptation (Walther et al., 2010). The observation of variations in individual response within and among populations suggests the potential for adaptation. Investigators have observed varying responses among marine species (e.g., Kroeker et al., 2010; Dupont et al., 2010 reviews). For example, Waldbusser et al. (2010) suggested that differences in genotypes may explain observed differences in shell deposition in response to increased CO_2 conditions between populations of hard clams, *Mercenaria* spp.

The degree of variation and heritability of the responses to acidification will vary within and among species. Red urchins, *Strongylocentrotus franciscanus*, exhibited wider phenotypic variation and higher sire-based heritability of measured responses to acidification than did *Mytilus trossulus*, mussels native to the northeast Pacific (Sunday et al., 2011). These data suggest that rates of evolution in response to acidification could be faster for *S. franciscanus* than for *M. trossulus* (Sunday et al., 2011). Recently, Parker et al. (2012) illustrated effects of elevated CO_2 conditions on *Saccostrea glomerata*, the Sydney Rock oyster, in a selection and adaptation study. Larvae of parent oysters conditioned under high CO_2 conditions grew faster, were larger, and more likely to survive to the eyed larval stage compared to those of parents held under ambient conditions. This effect was elevated in hatchery-selected oyster populations compared with wild-type populations (Parker et al., 2012). Thus, the potential for adaptation to acidification is present in marine populations and can vary within and among species, including parasites and pathogens.

6.4.2 Evidence from contemporary systems

Biological communities surrounding submarine volcanic vents that release CO_2 serve as natural laboratories for studying the impacts of ocean acidification on entire biological communities. Observations from these systems indicate that exposure to pCO_2 levels considered likely in the open ocean by 2100, when the pH is projected to drop to 7.8, can substantially alter both temperate and tropical marine communities, decreasing the diversity and recruitment of calcifiers and some non-calcifying species, and shifting the community to non-calcifying macroalgae and seagrasses (Hall-Spencer et al., 2008; Karlen et al., 2010; Fabricius et al., 2011; Kerrison et al., 2011; Kroeker et al., 2011; Porzio et al., 2011).

6.4.3 Evidence from the paleontological record

Oceanic CO_2 concentrations have been high in the geological past. Knowing how quickly these high CO_2 states developed is important for understanding the ocean chemistry conditions during these periods (Hönisch et al., 2012). When high CO_2 states develop slowly (e.g., over periods greater than ten thousand years), the natural processes of rock weathering and carbonate dissolution keep carbonate saturation states high, even though seawater pH is relatively low. Conversely, when high CO_2 states develop quickly (e.g., over periods less than tens of thousands of years), as is happening currently and occurred historically in response to major volcanic events, pH and carbonate saturation state decline in concert. The rate at which carbon dioxide states develop also has implications for the response of biological communities. Low calcium carbonate saturation states are challenging for organisms that make calcium carbonate structures. In addition, rapid rates of change in environmental conditions are more difficult for organisms to adapt to, especially if they are long lived. The rate of CO_2 change that the oceans are experiencing now is likely unprecedented over the past 300 million years (Kump et al., 2009; Hönisch et al., 2012).

A handful of events in Earth's geologic past can be used as analogs of the current ocean acidification and global change events, and indicate how biological communities responded to change in the past (Kump et al., 2009). The events that occurred during the Paleocene-Eocene Thermal Maximum (about 55 million years ago) are thought to be the closest analog to current times (Widdicombe and Spicer, 2008; Doney et al., 2009). During this period, the earth experienced a rapid increase in CO_2, which caused the calcite saturation horizon to shoal by 2 km and also caused an increase in global temperature (reviewed in Zachos et al. (2005) and Pelejero et al. (2010)). In response, deep-sea benthic foraminifera experienced a major extinction event, the collapse of coral reefs neared completion, coastal and benthic biological communities experienced high species turn over, and the incidence of deformities in plankton was relatively high (Zachos et al., 2005; Gibbs et al., 2006; Ridgwell and Schmidt, 2010; Hönisch et al., 2012). The transition between the Permian and Triassic periods (251 million years ago) is another analog for the conditions that we expect to face in the near future. This period is characterized by ocean acidification, hypoxia, and warming, and, during it, marine communities experienced a major extinction event in which 54% of marine families, 68% of marine genera, 92% of marine species disappeared (Knoll et al., 2007). This extinction event was selective on physiological traits: those species with calcium carbonate structures and limited ability to buffer internal physiology were more likely to go extinct than other species (Schmidt-

Nielsen, 1997; Knoll et al., 2007; Clapham and Payne, 2011). For example, all calcified coral species disappeared at the end of the Permian period (Knoll et al., 2007) (uncalcified corals evolved the ability to calcify in the Triassic). Events during these two time periods suggest that marine species and communities responded to changes in ocean chemistry that were similar to those we are currently experiencing. While it is extremely challenging to predict exactly how marine communities will respond to future changes in ocean chemistry, Earth's history suggests that we can expect marine communities to differ in structure in the future.

6.5 Disease Expression in Changing Environments

Parasites and pathogens are normal and essential components of every ecosystem. Host species co-exist with their parasites and pathogens under favorable environmental conditions. Shifts in the environment, including increasing temperature and acidification, have been linked to enhanced disease expression (see reviews by Harvell et al., 2002; Kuchel et al., 2011). Such shifts in climate can impair the immune response of the host species and increase the frequency of disease. This is especially true for ectothermic (cold-blooded) animals such as shellfish (Travers et al., 2008), corals (Harvell et al., 2002; Reed et al., 2010) and fish (see review by Bowden, 2008). In Washington State, the re-emergence of *Vibrio tubiashii*, a bacterial pathogen of larval Pacific oysters, was linked to changes in climate including thermal shifts and upwelling of low pH waters (Elston et al., 2008). Changes in the host species can also increase the frequency of disease. For example, inbreeding or disruption of local adaptation in the host species could favor the parasite over the host (e.g., Dionne et al., 2007). Alternatively, changes in the parasite can result in increased *virulence* (causing the parasite to be better able to infect and overcome the host immune response) or increased *pathogenicity* (allowing the pathogen to cause more disease; e.g., Martenot et al. (2011)). The converse can also occur whereby changes in the environment, host, or pathogen favor the host, thereby reducing or eliminating a particular pathogen or disease from the population. For example, Pacific oysters selected for resistance to summer mortality showed evidence of enhanced resistance to a herpesvirus infection (Dégremont, 2011). Similarly, early life stages of selected farmed lines of Sydney Rock oysters were more resistant to the effects of acidification than were non-selected lines (Parker et al., 2011). Thus, host-parasite relationships are predicted to change with changing ocean conditions and variations in these relationships will also vary among taxa.

6.6 Marine Ecosystems of Washington

Below we offer brief characterizations of marine ecosystems of Washington State. Oceanographic attributes of these systems are summarized in Chapters 2–4.

6.6.1 Washington's outer coast ecosystem

Intertidal and shallow subtidal systems of the outer coast are characterized by bedrock and cobble habitats in the north and sandy habitats in the south. Rocky habitats in the north support a diverse flora and fauna typical of the region consisting of calcified and uncalcified seaweeds, invertebrates and their predators, including fish, seabirds, and marine mammals (Wootton, 1997). Sandy habitats in the south support a less conspicuous fauna that includes important resources such as razor clams (LeClair and Phelps, 1994) and other infaunal species (e.g., polychaetes, crustaceans, sand dollars).

Along Washington's outer coast, seasonal phytoplankton blooms fuel the development of productive food webs (Landry and Hickey, 1989). These food webs support populations of seabirds and marine mammals, and also provide the basis for tribal, commercial, and recreational fisheries (most notably, for razor clams, salmon and Dungeness crab). Occasionally, conditions favor the formation of harmful algal blooms (HABS) comprised of dinoflagellate or diatom species. Some of these HABS can be toxic to humans; others can have negative impacts on fish and wildlife species (Hallegraeff, 1993; Horner et al., 1997; Van Dolah, 2000; Gilbert et al., 2005).

Deep subtidal areas of the outer coastal region are typified by soft sediment habitats. These habitats support populations of infaunal and epibenthic (on-bottom) species that include bivalves, crabs, and cold-water corals. Commercially important and protected fish species are associated with these deep benthic habitats.

6.6.2 Puget Sound and the Strait of Juan de Fuca ecosystem

Intertidal communities exist as a narrow fringe along the steep shores of the estuarine fjord of Puget Sound (Dethier and Schoch, 2005). Substrate type generally reflects hydrodynamic energy, with soft sediments (mud or sand) on calmer beaches and larger-sized particles such as bedrock or cobble occurring primarily where wave energy is relatively high. Intertidal community structure is strongly associated with sediment grain size (Dethier and Schoch, 2005). On cobble beaches, the diversity and biomass of species living both on and in sediment declines from northern to southern Puget Sound (Dethier et al., 2010), however, growth rates of some species can be high in southern Puget Sound, as evidenced by use of that area for shellfish aquaculture. Intertidal temperatures increase from the outer coast eastward along the Strait of Juan de Fuca, and this shift in environmental conditions influences vertical ranges of intertidal organisms (Harley and Helmuth, 2003).

Eelgrass occurs in shallow soft sediment habitats throughout much of Puget Sound, covering more than 20,000 ha (Gaeckle et al., 2011). Eelgrass is evenly distributed between flat shallow habitats of bays and river mouths, and narrow linear beds that follow the shoreline (Essington et al., 2011). Eelgrass beds are more plentiful in the North Sound than the South Sound (Gaeckle et al., 2009). Ecosystem services provided in general by seagrasses include primary production (Mateo et al., 2006), amelioration of wave energy and substrate stabilization (Koch et al., 2006), habitat provision for higher trophic level species (Duffy, 2006; Gillanders, 2006) and carbon sequestration (Fourqurean et al., 2012).

Water column habitats of the Puget Sound ecosystem include phytoplankton, zooplankton, fish, marine birds, and mammals. In the central basin, biomass is dominated by (in order of contribution): infaunal bivalves including geoducks (which constitute the greatest single-species biomass in Puget Sound), soft infauna (worms, etc.), phytoplankton, small crustaceans, ratfish, and copepods, each of which represents more than 20 metric tons per square kilometer (Harvey et al., 2012). Juvenile and sub-adult wild salmon depend on nearshore habitats of Puget Sound for food and shelter, and return as adults to spawn (Essington et al., 2011). Forage fish, such as Pacific herring, surf smelt, and Pacific sand lance, are ubiquitous in this environment (Essington et al., 2011).

Around Puget Sound, 190,000 acres are classified as commercial and recreational shellfish beds (though ~19% of these are currently closed due to pollution) (Washington Department of Health, 2011).

The ecosystem of Puget Sound and its surrounding watershed is considered highly altered from its natural state (Harvey et al., 2012). The 2006 National Land Cover Database classifies 20% of the watershed as active or fallow agricultural land (grass/shrub/cultivated/pasture), and 10% as developed or urban (Fry et al., 2011); more recent estimates for central Puget Sound report 23% of the land as developed (Alberti et al., 2004; Hepinstall et al., 2008). Fifty-three percent of the watershed is still considered forested, though this value includes land managed for timber (Alberti, 2009). Shorelines in this region have been substantially altered by human activities; for example, 25% of the 2500 km of shoreline has been armored (Bouta, 2010). Wetlands, which provide important ecosystem services with respect to habitat provision and water quality, have been displaced by development; Collins and Sheikh (2005) estimate the current area of tidal wetlands to be 17 to 19% of their historical extent (29,500 acres).

Organisms in Hood Canal are periodically affected by low-oxygen conditions (hypoxia), which can cause mortality of bottom-dwelling species (Essington and Paulsen, 2010). Hypoxic events in Hood Canal and some areas of South Puget Sound have been reported since the mid 1900s, but have recently increased in frequency and intensity (Albertson et al., 2002; 2007; Newton, 2007). Anthropogenic nitrogen inputs are thought to be contributing to this trend (Diaz and Rosenberg, 2008).

6.6.3 Estuarine ecosystems

Three major estuaries occur on the outer coast of Washington: Willapa Bay, Grays Harbor, and the Columbia River Estuary. Estuarine organisms are characterized by their capacity to tolerate substantial variation in salinity on a tidal and seasonal basis. In Willapa Bay and Grays Harbor, vast intertidal flats make up about half of the area. These flats are occupied by infaunal clams, burrowing shrimp, and seagrass, and are the site of native and commercial shellfish beds (Feldman et al., 2000; Dumbauld et al., 2011). Willapa Bay alone produces about 10% of the cultured oysters in the U.S., and Manila clam production has increased by an order of magnitude over the past two decades (Ruesink et al., 2006). Shellfish aquaculture also occurs in Grays Harbor. Subtidal habitats in these estuaries support populations of juvenile and adult fish species (including the Environmental Species Act-listed green sturgeon, and commercially valuable salmon), Dungeness crab, and marine mammals (Hosack et al., 2006; Dumbauld et al., 2008). Birds are abundant in Willapa Bay, with seasonal use particularly high during migration (e.g., Patten and O'Casey, 2007). Estuarine ecosystems contain relatively high proportions of non-native species, for instance 45 in Willapa Bay (Wonham and Carlton, 2005), whereas species invasions are rare in Washington's outer coast ecosystem. A major tideflat invader was *Spartina alterniflora* (smooth cordgrass), which reached 4% cover (25% of Dungeness crab foraging habitat) in Willapa Bay prior to effective control starting in 2005 (Ruesink et al., 2006; Holsman et al., 2010).

Notable species that use the Columbia River estuary include five species of Pacific salmon, which are typically managed according to evolutionarily significant units (ESU), that is, distinct populations that are reproductively isolated: 1 Chum ESU (*Oncorhynchus keta*, threatened), 1 Coho ESU (*O. kisutch*, threatened), 4 Sockeye ESUs (*O. nerka*, including Snake River endangered), 8 Chinook ESUs (*O. tschawytscha*, 1 endangered, 4 threatened), and 5 Steelhead ESUs (*O. mykiss*, all threatened) (**http://www.nwr.noaa.gov/ESA-Salmon-Listings/Salmon-Populations/**). These species move through the estuary during their life-history transitions from freshwater to marine as juveniles, and on the return trip to spawn as adults. Chinook salmon, in particular, use shallow-water marsh habitats for feeding during their outmigration, and salmon have been collected from these shallow habitats during all months of the year, with peaks in late spring to early summer (Bottom et al., 2008). Birds, especially Caspian terns, cormorants, and seagulls, nest on islands within the Columbia River estuary and are actively being managed to reduce their consumption of salmon smolts (Roby et al., 2002; Maranto et al., 2010).

Several studies employing stable isotope techniques have demonstrated that intertidal organisms (barnacles, oysters) near rivers use terrestrially derived carbon as an energy source, possibly by filtering particulate matter directly or filtering microorganisms (phytoplankton that have fixed terrestrially sourced DIC, or heterotrophs that have consumed particulate organic matter). These studies come from shallow estuaries such as Willapa Bay (Ruesink et al., 2003) and

Totten Inlet (Ruesink et al., *unpublished data*), as well as small coastal river mouths (Tallis, 2009). Along the outer coast and Strait of Juan de Fuca, barnacles living near streams that drain logged watersheds use more terrestrially derived carbon than do those living near streams draining unlogged watersheds (Tallis, 2009).

In Puget Sound, thousands of streams create pocket estuaries where fresh and saltwater mix. Shellfish aquaculture operations in Puget Sound and Hood Canal often occur near river mouths or where the salinity is below 30. The impact of land-based inputs is clear from the Department of Health closures of shellfish harvesting areas due to fecal coliform bacteria. River mouths in this region have been dramatically altered due to a history of diking to create agricultural farmland or industrial and domestic space, and dike removal has been considered in the context of restoration in Puget Sound (PSP Vital Signs dashboard **http://www.psp.wa.gov/vitalsigns/estuaries.php**).

6.7 Observing and Research Needs

- Determine vulnerability of key habitats and systems.
- Develop strategies to build and preserve resilience and mitigation potential, especially in vulnerable habitats.
- Develop and test new adaptation and mitigation strategies.
- Establish sites for long-term observation.

7

Recommendations for Ocean Acidification Research and Monitoring

Washington State Blue Ribbon Panel on Ocean Acidification
Panel Scientists

WE RECOMMEND FOUR strategies for ocean acidification research and monitoring. These strategies are based on and are consistent with the research and monitoring needs described in Chapters 1 through 6 of this scientific summary. The recommendations as presented below also appear in Chapter 7 of the Full Report of the Washington State Blue Ribbon Panel on Ocean Acidification. That report includes recommendations for other topics, such as source reduction, adaptation, and education, in addition to these. For consistency, the numerical identifiers used for the research and monitoring strategies and actions are identical in both documents.

Scientifically based actions are required to reduce the risk of ocean acidification to Washington's shellfish, other organisms, and marine ecosystem, and to sustain the ecological, economic, and cultural benefits they provide. Investing in Washington's ability to monitor and investigate the effects of ocean acidification is central to providing—and building on—that necessary scientific foundation. Some of the seminal research on ocean acidification has been conducted in the North Pacific Ocean and in Washington's shelf and estuarine waters. We now need to develop a better understanding of how local water chemistry—already known to be highly variable—changes through time. We also must understand the responses that are likely among local marine species and ecosystems. This will allow us to develop predictive capability with regard to ecosystem responses to large-scale chemical and physical changes associated with ocean acidification. Critical information needs are to:

- Understand the status and trends of ocean acidification in Washington's marine waters. At present the general chemical processes of ocean acidification are well understood. However, the status of ocean acidification in local waters, including estuaries, is not well characterized, nor are many of the complex physical, chemical, and biological interactions that influence the progression and extent of ocean acidification in Washington's marine waters.
- Quantify the various natural and human-caused acidifying influences so we can understand the relative significance of these different influences at different locations and time scales. A combination of global and local factors contributes to ocean acidification, but the degree to which each factor contributes to the problem will vary by location and season. Quantification of the various acidifying influences will help managers identify where particular response strategies are likely to be most effective. Some locations may respond well to efforts to scale back the supply of acidifying inputs, while other sites may be best

suited for adaptation to the inevitable effects of ocean acidification.

- Understand the biological responses of local species to ocean acidification and associated stressors. We need to know more about the organisms that live within our marine environments. Biological responses to ocean acidification are highly variable and cannot be reliably predicted from first principles; experimental studies are required. Life scientists worldwide are compiling a rapidly growing database of experimental observations, but studies performed on Washington's species are relatively few. Laboratory and field investigations of our local marine species will be needed to build scientific understanding and guide effective responses to changing water chemistry.
- Understand system dynamics of Washington's marine environment well enough to make short-term forecasts and long-term predictions of global and local acidification effects. Real-time data and short-term forecasts can, for example, alert hatchery managers to the approach of threatening waters. While we recognize the importance of shellfish in Washington, we emphasize that the science must extend beyond shellfish resources to the broader marine ecosystem. The ability to model ocean chemistry, species and ecosystem responses, and socioeconomic impacts will serve a variety of functions, from helping guide the effective management, restoration and protection of natural resources to estimating the costs and benefits of response vis a vis economic, cultural and ecological values. The ultimate goal is to provide sound guidance for important human choices.

We note that all strategies described below are of **equal priority**. Specific actions listed under each strategy are **prioritized in order of importance**. The Implementation Leads proposed under each action are *provisional* and may change. Identification as Implementation Lead implies the necessary expertise to perform the specified function, but *does not* imply that funding for the activity exists. In most cases, new funding will be required to implement the recommended actions.

Of paramount importance, the Panel scientists recommend an overarching action to:

Create an ocean acidification science coordination team to promote scientific collaboration across agencies and organizations and connect ocean acidification science to adaptation and policy needs.

The Panel strongly encourages the establishment of a science coordination team for ocean acidification-related research in Washington State. Such a team would promote collaboration across agencies and organizations, reduce redundancies, and improve efficiencies in implementation of the recommended actions while also helping to connect science to adaptation and policy needs, including evaluating and field testing new management approaches. The team should consist of diverse entities, including representatives from federal, state, tribal and local governments, universities, industries, non-governmental organizations, and others.

The recent Pacific Northwest oyster seed crisis and the subsequent hatchery production gains offer a good illustration of a well-coordinated collaboration among scientists, managers, and shellfish growers. This collaboration has produced significant scientific discoveries and has helped to guide adaptation in the oyster industry. It provides a model of collaboration that can be replicated and enlarged to effectively address problems of ocean acidification in Washington State.

Strategy 7.1:
Understand the status and trends of ocean acidification in Washington's marine waters.

Washington's coast encompasses a great variety of environments, including high-energy sandy shores, rocky bluffs and sea stacks, deep, dark fjords, and sunlit, shallow bays. Some sites are relatively remote from human influence, while others support intensive use by humans. Strategic surveys of these diverse waters and selection of a few sites for a sustained closer look will help to elucidate controlling processes and important linkages, which will differ from place to place and season to season.

Action 7.1.1:
Establish an expanded and sustained ocean acidification monitoring network to measure trends in local ocean acidification conditions and related biological responses.

We need sustained, expanded monitoring to provide data at a spatial and temporal resolution sufficient to understand the current status of ocean acidification in Washington waters and to discern trends across space and over time. Failure to measure these effects through appropriate monitoring would effectively "blindfold" Washington's marine-based industries, coastal communities, and resource managers. Establishing an acidification monitoring network will improve the options for adaptation in business and industry. Moreover, sustained and expanded monitoring of acidification conditions will provide information essential to adaptive management of marine ecosystems and the living resources they support.

Despite this need, no sustained ocean acidification monitoring network for Washington's coastal waters currently exists. The elements and assets that now exist need to be enhanced and sustained. It is essential that the network provide data at high enough resolution to reveal the current status of acidification in Washington waters and to discern trends across space and over time. Additionally, a subset of monitoring stations must be established to simultaneously collect the physical, chemical, and biological data required to evaluate the relationships between changing chemical conditions and biological responses among organisms living in the water and on the sea-bed. The stations should be chosen strategically to include existing sites at shellfish hatcheries and other shellfish growing areas, sites with existing biological time series, and areas representative of ecological and oceanographic processes within Washington waters.

Shellfish growers, under the aegis of the Pacific Coast Shellfish Growers Association, have established several sites for collecting such data. These sites need to be sustained and expanded. The scientific information obtained at these sites is essential not only for shellfish growing operations, but also to increase our scientific understanding of biological responses to marine chemistry.

Data collection. The expanded network proposed here would allow for collecting measurements at appropriately high spatial and temporal resolution to detect trends in local conditions and to characterize:

- The pH and carbon chemistry of marine waters in Washington;
- The variation in chemistry over space and time;
- How the watershed, ocean, and atmosphere affect status and trends;
- How biological processes affect chemical conditions; and
- How biological responses to water chemistry vary over space and time.

The expanded network should use a variety of platforms, including ship surveys, moorings, fixed stations, and gliders that build upon existing assets and capabilities. Maps of existing assets and potential sites are shown in **Figures 7.1** through **7.4**. These assets include:

- Cruises, moorings, fixed stations, and gliders on the Washington coast;
- Cruises, moorings, and fixed stations in Puget Sound and the Strait of Juan de Fuca;
- Cruises and fixed stations in the Columbia River Estuary; and
- Cruises, moorings, and fixed stations in shallow estuaries.

Data quality provisions and training. Ensuring reliable data quality is critical. All chemical monitoring should be conducted according to the *European Program on Ocean Acidification (EPOCA) Guide to Best Practices for Ocean Acidification Research and Data Reporting* (Riebesell et al., 2010) and *Guide to Best Practices for Ocean CO_2 Measurements* (Dickson et al., 2007). New best-practice standards should be developed as needed for specific applications. Training programs for accuracy and repeatability in data collection will need to be developed and implemented for scientific and technical personnel participating in the monitoring network.

Preserving data and public access to data. Once obtained, data must be archived and made accessible to the public, and the quality of the data must be defined. This need can be met in part by leveraging the existing data delivery system of NANOOS (Northwest

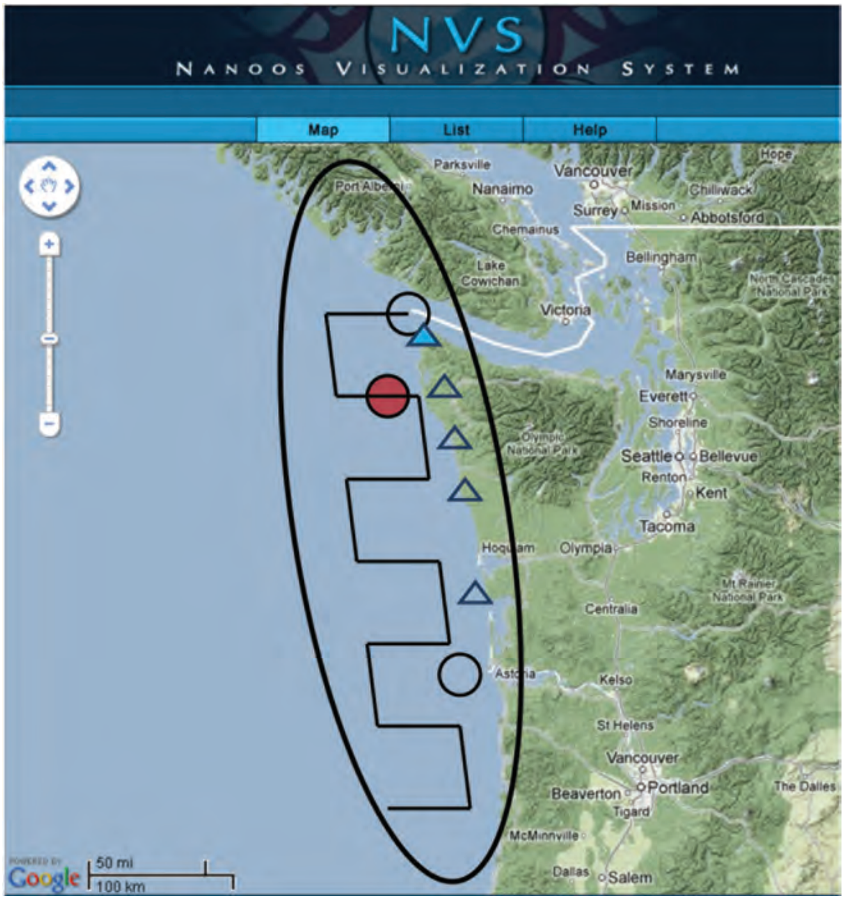

Figure 7.1: Schematic of elements required for an outer-Washington coastal ocean acidification observing system, over the approximate area denoted by the open oval. Red circle indicates the existing ocean acidification buoy at La Push, operated by UW and NOAA with support from both NANOOS and NOAA's Ocean Acidification Program. Open circles denote need for critical buoys off the Strait of Juan de Fuca and the Columbia River. Filled blue triangle denotes nearshore monitoring at Tatoosh Island. Open blue triangles denote other possible nearshore observation sites. Lines indicate need for surveys along coast, which could be served by cruises, or possibly more cost effectively, with glider/s.

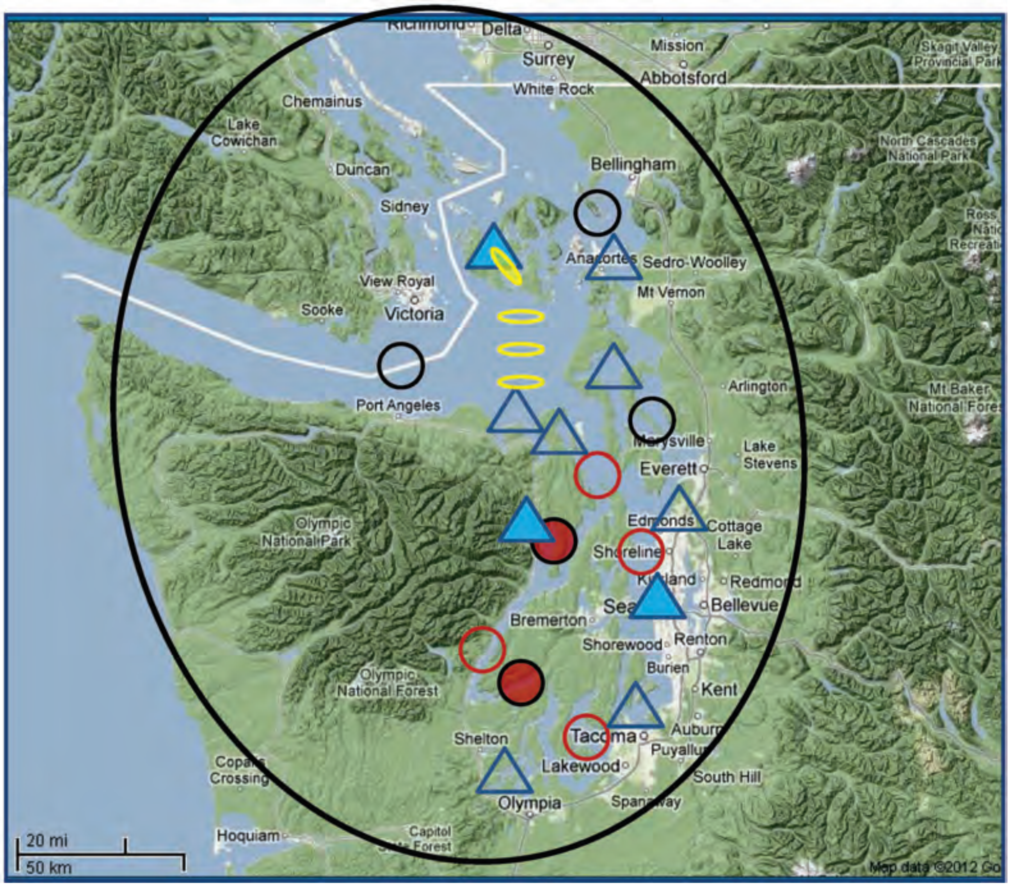

Figure 7.2: Schematic of elements required for an ocean acidification observing system for Puget Sound and the Strait of Juan de Fuca, over the approximate area denoted by the open oval. Red circles are existing buoys with ocean acidification-relevant sensors at Twanoh and Dabob bays, maintained by UW and NOAA with partial support from NANOOS and National Estuary Program funds. Open circles denote need for such measurements in other basins of Puget Sound and the Strait (e.g., South Sound, Whidbey, Main Basin, Admiralty Inlet, Northern Straits). Red open circles indicate existing buoys that do not have ocean acidification sensors. Filled blue triangles denote nearshore ocean acidification monitoring at the Seattle Aquarium (NOAA and King County), Dabob Bay (Taylor Shellfish Hatchery), and the UW Friday Harbor Laboratories. Open blue triangles denote other possible nearshore ocean acidification monitoring sites or land-based index stations. The diagonal yellow oval indicates an ocean acidification time series in San Juan Channel (partially funded through the UW) and the three open yellow ovals indicate Joint Effort to Monitor the Strait (JEMS) time series (Washington Department of Ecology and UW) where ocean acidification sampling could be added. Efforts in this domain should be coordinated with Canada.

Figure 7.3: Schematic of elements required for an ocean acidification observing system for the Columbia River estuary, over the approximate area denoted by the open oval. Green circles are existing moorings with ocean acidification-relevant sensors, supported by the Oregon Health and Sciences University-Center for Coastal Margin Observations and Predictions (CMOP), funded through the National Science Foundation.

Association of Networked Ocean Observing Systems; **http://www.nanoos.org**), which currently delivers ocean acidification data streams from NOAA, the University of Washington, the Pacific Coast Shellfish Growers Association, tribes, and others. Further investment is required to provide all of the capabilities listed above.

Implementation time frame: Monitoring can proceed immediately, pending funding, leveraging existing fixed sensors, buoys, ships, and gliders. Many parts of this action can be operational within one year; some parts are operational currently, but need sustained support; other parts can be enhanced to include ocean acidification monitoring.

Estimated cost: See **Table 7.1** for unit costs for specific activities. Total cost depends on scale and is modular and scalable. The Ocean Acidification Science Coordination Team will require sustained funding to carry out activities related to this action, including technical training, data archival, and data delivery. Existing resources and capacity from NANOOS can be leveraged for data archival and data delivery.

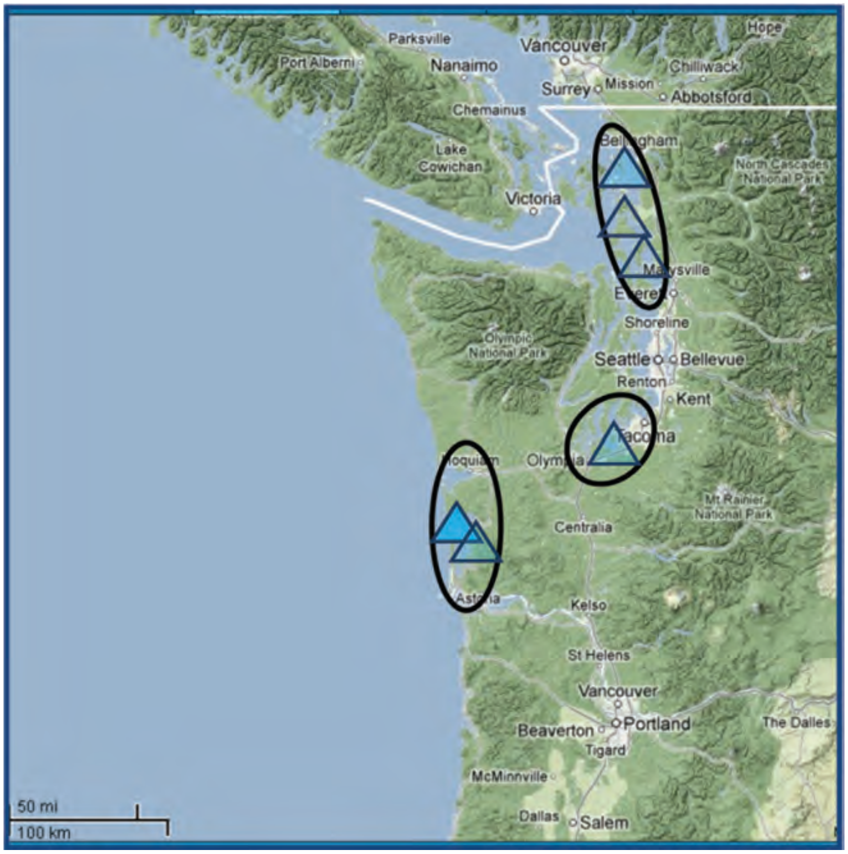

Figure 7.4: Schematic of elements required for an ocean acidification observing system for the shallow estuaries of Puget Sound and the outer Washington coast, over the approximate areas denoted by the open ovals. The solid filled blue triangle denotes nearshore chemistry/biology monitoring in Willapa Bay (Pacific Shellfish Institute) and semi-transparent blue triangles denote locations of recent nearshore chemistry/biology time series index stations in Willapa Bay (Washington Sea Grant), Totten Inlet (Puget Sound Partnership), and Bellingham Bay (Lummi Indian Hatchery and Pacific Coast Shellfish Growers Association) that could be continued. Open blue triangles denote other possible nearshore observation sites in shallow estuaries within the North Puget Sound and Whidbey basins, and the Eastern Strait.

Table 7.1: Estimated costs for ocean acidification monitoring in Washington marine waters

Activity	Startup Costs/unit	Maintenance Costs /unit \$K yr^{-1}
Survey Cruises		
Dedicated Cruise		400
Piggyback Cruise		200
Small Boat Cruise		50
Moorings		
Build New Mooring	200	50
Enhance Existing Mooring	100	50
Shore-based Sites		
Develop New Site	100	60
Enhance Existing Site	80	60
Profiling Glider		
Start New Glider	100	60
Wave Glider		
Start New Glider	160	60

Implementation Co-Leads: University of Washington, in collaboration with NOAA.

Implementation Partners: NANOOS, Washington Department of Ecology, tribes, Pacific Coast Shellfish Growers Association, Taylor Shellfish Farms, Lummi Hatchery, Puget Sound Ecosystem Monitoring Program (PSEMP), California Current Ocean Acidification Network (C-CAN), Inter-governmental Policy Council, Center for Coastal Margin Observation and Prediction, Olympic Coast National Marine Sanctuary, Washington Sea Grant, Puget Sound Partnership, Marine Science Centers (including Seattle Aquarium), Olympic Regional Harmful Algal Blooms Partnership, and others.

Action 7.1.2: Develop predictive relationships for indicators of ocean acidification (pH and aragonite saturation state).

Carbon system parameters (dissolved inorganic carbon or DIC; total alkalinity or TA; CO_2 partial pressure or pCO_2) and pH in estuarine and coastal waters are influenced by water properties such as temperature, salinity, and dissolved oxygen. These latter parameters are relatively easy to measure, whereas carbon system parameters and pH are relatively difficult and expensive to measure. Developing and refining predictive relationships between these parameters will allow us to use mooring and glider data to provide high-resolution time series data on carbon system parameters, pH, and aragonite saturation state. These will also provide an independent test of the accuracy of the pCO_2 and pH sensors.

Implementation time frame: Can proceed immediately if additional resources are available, leveraging existing data and NOAA efforts from the outer coast.

Estimated cost: $80,000 per year.

Implementation Co-Leads: University of Washington and NOAA.

Implementation Partners: Pacific Coast Shellfish Growers Association, Pacific Shellfish Institute, Washington Department of Ecology, tribes, and others.

Action 7.1.3:
Support development of new technologies for monitoring ocean acidification.

Advances are needed in the monitoring of both ocean acidification and biological response. Current technologies for monitoring acidification are limited and best used when large volumes of seawater are available for immediate analysis. Sensors with high precision and accuracy are available for only two carbon parameters, pCO_2 and pH, and are expensive. Development of new or improved technologies for measuring pH, dissolved inorganic carbon, total alkalinity, and pCO_2 will improve capability to monitor ocean acidification.

For example, development of a new technique for carbon system parameter analysis that can use small volumes of seawater would allow the Washington Department of Ecology's seaplane sampling protocol to include monitoring for ocean acidification, and development of an improved pH sensor with better accuracy and precision would improve data collection from moorings and gliders.

The need to develop new technologies has been highlighted recently. The X Prize Foundation is sponsoring an Ocean Health X Prize. The winners must build and demonstrate the most accurate and reliable deep-ocean pH sensors to help measure the global effects of carbon dioxide on the world's oceans. The prize is seeking improvements in the speed, depth tolerance, and lifetime of autonomous pH sensors.

Monitoring plankton in conjunction with chemical parameters can reveal correlations between changing ocean chemistry and changes in plankton communities—a primary impact of ocean acidification. The current biological monitoring method, collecting plankton with nets for manual identification, is costly, inefficient, and unsuitable for continuous biological monitoring. Computer image-recognition systems have already been developed for facial recognition and medical research and could be applied to biological monitoring of plankton.

Implementation time frame: Near term (less than 5 years).

Estimated cost: $150,000 to $200,000 per year.

Implementation Co-Leads: University of Washington and NOAA.

Implementation Partners: Washington Department of Ecology, Scripps Institution of Oceanography, X-Prize Foundation, Suquamish Tribe, and others.

Strategy 7.2:
Identify factors that contribute to ocean acidification in Washington's marine waters, and estimate the relative contribution of each.

In addition to atmospheric carbon dioxide, other processes that generate carbon dioxide in the water column can contribute significantly to acidification in coastal waters. The combined effects of various processes (nutrient inputs, respiration, nitrogen oxide and sulfur oxide inputs, local atmospheric sources of carbon dioxide, and dissolved and particulate carbon loadings) are now acknowledged to be important drivers of ocean acidification, particularly when the land nearby is highly populated or agriculturally developed. We need to develop quantitative estimates of how much these individual processes contribute to ocean acidification in Washington waters.

Action 7.2.1:
Quantify key natural and human-influenced processes that contribute to acidification based on estimates of sources, sinks, and transfer rates for carbon and nitrogen.

Inorganic dissolved and particulate forms of carbon can directly affect the pH and carbonate chemistry of marine waters. Nitrogen can indirectly affect pH through enhancement of primary production followed by sinking, decomposition, and respiration of organic material. We need to develop a quantitative understanding of how the various forms of carbon and nitrogen enter and flow through the marine system (i.e., a budget) in order to describe and rank regional acidification drivers and develop strategies for mitigation.

To accomplish this, data from observations and numerical models should first be used to construct budgets for carbon and nitrogen in coastal and inland waters that capture physical and biological processes significant to the area of application. Second, we need to quantify key processes, including the human contribution, to acidification in Washington waters. Specific focus should be given to quantifying the role of nutrient loading from human sources, nitrogen oxides and sulfur oxides inputs from atmospheric and riverine sources, local atmospheric sources of carbon dioxide, and dissolved and particulate carbon loadings. These processes should be investigated on a spatial scale that is relevant to regulation and should cover seasonal variation.

Implementation time frame: This is a major undertaking that will benefit from sequencing of activities. Data are needed to construct budgets for carbon and nitrogen. Some data already exist, but new data will be required for input to models. Existing models will require further development and refinement, and new models may need to be constructed, as noted in Action 7.2.2. Funding will be required to fully implement this research, and the time frame for implementation depends on the level of funding. In the best scenario, this may likely take 5 years.

Estimated cost: $500,000 to $1M.

Implementation Co-Leads: Washington Department of Ecology and University of Washington.

Implementation Partners: EPA, NOAA, Joint Institute for the Study of the Atmosphere and Ocean (JISAO), and Pacific Northwest National Laboratory (PNNL).

Action 7.2.2:
Develop new models or refine existing models to include biogeochemical processes of importance to ocean acidification.

Modeling is a powerful tool that can be used to understand areas of sensitivity and to evaluate the strength of underlying mechanisms. Regionally, existing modeling capacity exists for circulation, conventional water quality, and plankton processes. None of these models incorporates carbon chemistry parameters and pH, limiting their utility for evaluating ocean acidification impacts.

Implementation time frame: Near term (less than 5 years).

Estimated cost: Dependent on need, likely $500,000 per year.

Implementation Co-Leads: University of Washington and Washington Department of Ecology.

Implementation Partners: NOAA, Joint Institute for the Study of the Atmosphere and Ocean (JISAO), EPA, and Pacific Northwest National Laboratory (PNNL),

Strategy 7.3: Characterize biological responses of local species to ocean acidification and associated stressors.

Shellfish species are vulnerable to the effects of ocean acidification, as has been repeatedly demonstrated through experimental and observational studies. Consequently, Washington's shellfish resources, both wild and commercial, are at risk. Shellfish of ecological and economic importance include but are not limited to oysters, mussels (native and Mediterranean), clams (e.g., geoduck, razor, littleneck, Manila), scallops, Dungeness crab, shrimp (e.g., spot prawns, pink shrimp), pinto abalone, and urchins.

Washington's shellfish resources rely on and are embedded in productive marine ecosystems. To sustain shellfish resources and the aggregate services and values provided by Washington's marine ecosystems, diverse elements of the ecosystem must be investigated for their response to ocean acidification. These include groups such as zooplankton and forage fish that maintain critical linkages in marine food webs, benthic species that create important structural habitat, and seagrasses and seaweeds that provide both structural habitat and potential mitigating effects.

Action 7.3.1:

Determine the associations between water and sediment chemistry and shellfish production in hatcheries and in the natural environment.

A more complete understanding of the effects of seawater chemistry on the survival and growth of shellfish in hatcheries will assist growers in making modifications to culture practices to sustain productivity. Outside of hatcheries, on shellfish farms and in natural settings, both seawater chemistry and sediment chemistry will influence shellfish viability, and the effects of both need investigation. Field studies that document the status and trends in farmed and natural shellfish populations and pair these data with chemistry measurements are required to detect changes in productivity, population size, and status over time. Determining species- and strain-specific responses to ocean acidification will help guide management strategies for wild populations and culture practices in hatcheries and on farms. Identification of robust populations, stocks, or strains and favorable local environments can guide efforts to promote sustainability.

Implementation time frame: Near term (less than 5 years).

Estimated cost: Will scale with the number of species and environments studied.

Implementation Co-Leads: Washington Department of Natural Resources, in collaboration with the University of Washington and Washington Department of Ecology.

Implementation Partners: Pacific Shellfish Institute, Taylor Shellfish Farms, Lummi Nation Shellfish Hatchery, Whiskey Creek Shellfish Hatchery, Puget Sound Restoration Fund, tribes, Intergovernmental Policy Council, Puget Sound Ecosystem Monitoring (PSEMP), Washington Department of Fish and Wildlife, NOAA Ocean Acidification Program, and Washington Sea Grant.

Action 7.3.2:

Conduct laboratory studies to assess the direct effects of ocean acidification, alone and in combination with other stressors, on local species and ecosystems.

Better understanding of the effects of ocean acidification on species of local importance, and their capacity to adapt to ocean acidification, will help guide management strategies, policy actions, and human adaptation. Laboratory studies to assess the direct effects of pH and carbon system variables on survival, growth, and reproduction of species living in Washington waters will improve our understanding of species-specific responses to ocean acidification.

Acidification co-occurs with other environmental changes, and organisms will respond to the full suite of stressors to which they are exposed. Laboratory studies can be used to determine biological responses of multiple species to ocean acidification in combination with other factors, such as temperature, nutritional status, and oxygen stress. Research priorities include species of ecological, economic, or cultural significance, species of conservation concern, and species that can influence human health and well-being (e.g., species that cause harmful algal blooms). Variation in response to ocean acidification within species will help estimate the genetic potential of that species to adapt to ocean acidification.

Implementation time frame: Near term (less than 5 years).

Estimated cost: Will scale with the number of species tested.

Implementation Lead: University of Washington.

Implementation Partners: NOAA, Pacific Coast Shellfish Growers Association, tribes, Inter-governmental Policy Council, Washington Department of Fish and Wildlife, and others.

Action 7.3.3:
Conduct field studies to characterize the effects of ocean acidification, alone and in combination with other stressors, on local species.

Field studies conducted in natural environments allow organisms to be studied in the context of their natural habitats, building on and refining insights gained from laboratory studies. A practical approach to field studies could initially focus on species that, based on laboratory studies, are sensitive to pH, those that are expected to be affected strongly via indirect effects of ocean acidification, and those (such as zooplankton) that form critical linkages in trophic webs.

Experimental and observational field studies can identify ecological processes affected by pH and carbon chemistry, including indirect effects of ocean acidification that are mediated through food-web interactions, other ecological interactions, or habitat transformation. Field-based research conducted across the diversity of Washington's marine habitat types will help determine habitat-specific responses and estimate habitat-specific risk and vulnerability.

Implementation time frame: Near term (less than 5 years).

Estimated cost: Will scale with the number of species and environments studied.

Implementation Lead: University of Washington.

Implementation Partners: NOAA, Pacific Coast Shellfish Growers Association, Washington Department of Fish and Wildlife, tribes, and others.

Strategy 7.4: Build capabilities for short-term forecasting and long-term prediction of ocean acidification.

Operational models are required to understand hourly, weekly, and seasonal changes in seawater chemistry and will provide information on timescales that are useful to hatchery managers for directing operations and to scientists for determining longer-term trends. The long-term prediction of ocean acidification status and biological response will help guide planning, restoration decisions, and adaptation strategies.

Action 7.4.1:
Establish the ability to make short-term forecasts of corrosive conditions for application to shellfish hatcheries, growing areas, and other areas of concern.

Better forecasting of corrosive conditions on the scale of days to weeks will help hatcheries and growers minimize the effects of ocean acidification on shellfish production. Forecasts could also be of use to managers of wild shellfish populations. A first step to improve forecasting capability is to develop and use real-time monitoring and model-based values of atmospheric and oceanographic variables to forecast risk of corrosive conditions. A second step is to provide online access to a suite of variables that forecast corrosive conditions, so that shellfish growers and managers can track conditions in real time.

Implementation time frame: Near term (2 years).

Estimated cost: $500,000 to $1M.

Implementation Lead: University of Washington.

Implementation Partners: Washington Department of Ecology, Pacific Northwest National Laboratory, shellfish growers, Pacific Coast Shellfish Growers Association, tribes, and Joint Institute for the Study of the Atmosphere (JISAO), and NOAA.

Action 7.4.2:
Enhance the ability to predict the long-term future status of carbon chemistry and pH in Washington waters and create models to project ecological responses to predicted ocean acidification conditions.

Numerical modeling allows for the development of future scenarios over time-scales of decades to centuries, which will help inform human response and adaptation to ocean acidification, including decisions regarding protection and restoration of resources and habitats. Numerical models can be developed to predict long-term changes in carbon chemistry and pH in Washington's marine waters. These models can be refined, and predictive skill can be improved as new data become available. A longer-term goal is to apply our understanding of biological responses to ocean acidification to coupled physical-biological models to project ecological responses to future ocean conditions.

Implementation time frame: Near term (less than 5 years).

Estimated cost: $300,000 to $500,000 initially.

Implementation Lead: University of Washington and NOAA.

Implementation Partners: Joint Institute for the Study of the Atmosphere (JISAO), Washington Department of Ecology, Pacific Northwest National Laboratory, shellfish growers, Pacific Shellfish Institute, tribes Washington Sea Grant, and others.

Action 7.4.3:

Enhance the ability to model the response of organisms and populations to ocean acidification to improve our understanding of biological responses.

It is not feasible to perform empirical studies on all species, life stages, and biological processes. Models allow scientists to better understand and characterize the mechanisms that determine how species and populations respond to carbon chemistry and pH, thereby improving the ability to generalize across species, life history stages, and processes. Model outputs can save time and expense by informing the design of second-generation manipulative experiments and field studies.

A first step is to build models that characterize the mechanisms behind biological responses to ocean acidification at the individual- and population-levels. These models then can be refined as new data from experimental studies become available. Ultimately, model outputs can be used to inform the design of laboratory and field studies, detect critically vulnerable biological processes and organisms, and guide human response and adaptation.

Implementation time frame: Near term (less than 5 years).

Estimated cost: $300,000 to $500,000 initially.

Implementation Co-Leads: University of Washington and NOAA.

Implementation Partners: Washington Department of Ecology, Pacific Northwest National Laboratory, tribes, and Washington Sea Grant.

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Glossary

Glossary of Terms

(terms in italics are included in this glossary)

Adaptive potential	The ability of a population to respond to environmental change through genetic adaptation.
Alkalinity	A measure of the maximum capacity of an aqueous solution to neutralize acids.
Amorphous calcium carbonate	The least stable *polymorph* of *calcium carbonate*.
Anthropogenic	Resulting from human activity.
Aqueous CO_2	CO_2 that is dissolved in water.
Aragonite	A *polymorph* of the mineral *calcium carbonate*, found in mollusc shells (particularly the larval and juvenile forms) and coral skeletons. It dissolves more readily than *calcite*.
Assemblage	A collection of species within a community.
Autotroph	Autotroph (from the Greek meaning "self-feeder") is an organism that fixes inorganic carbon into complex organic compounds (such as carbohydrates, fats, and proteins) using energy from light (*photosynthesis*) or inorganic chemical reactions (chemosynthesis).
Biocalcification	The production of *calcium carbonate* by living organisms to form shells, skeletons, *carapaces*, and other stiff structures.
Biomass	Biological material from living, or recently living organisms.
Biomineral	A mineral produced by a living organism.
Calcifier	An organism that carries out *biocalcification*. Calcifiers include organisms such as coccolithophores, corals, *foraminifera*, *echinoderms*, *crustaceans*, and *molluscs*.
Calcite	A *polymorph* of the mineral *calcium carbonate*, found in the shells of many marine organisms, including adult oysters; it dissolves less readily than *aragonite*.

Calcium carbonate	A mineral composed of calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions. Marine *calcifiers* incorporate *polymorphs* of $CaCO_3$ into their shells, skeletons, etc.
Carapace	The dorsal section of the *crustacean exoskeleton*.
Cohort	A group of organisms that share a common characteristic or experience within a defined period.
Conspecifics	Organisms that belong to the same species.
Copepod	A term from the Greek meaning "oar-feet," applied to a group of small aquatic crustaceans, which include both *planktonic* and benthic species.
Crustaceans	A large subgroup of arthropods, which includes animals as crabs, shrimp, *copepods*, krill, and barnacles. Some crustaceans incorporate *amorphous calcium carbonate* into their *exoskeletons*.
D-hinge stage	An early developmental stage in larval oyster development, where the nascent larval shell resembles the letter *D*.
Diatom	A major group of *microalgae*, and one of the most common types of *phytoplankton* in Washington waters.
DIC	"Dissolved Inorganic Carbon"; the sum of the concentrations of inorganic carbon species in a solution. These include carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate (CO_3^{2-}).
Dinoflagellate	A large group of flagellate *protists*. Most forms are *planktonic*, many are *photosynthetic*, and some can produce toxins.
DO	"Dissolved Oxygen"; The concentration of molecular oxygen dissolved in water. Measured as a concentration using a variety of units, including mg/L and *µmol/kg*.
DOC	"Dissolved Organic Carbon"; a broad classification for organic molecules smaller than 0.45 micrometers resulting from decomposition of dead organic material, or *biomass*. DOC in marine and freshwater systems is one of the greatest cycled reservoirs of organic matter on Earth.
Echinoderms	A phylum of marine invertebrates that includes seastars and sea urchins. Echinoderms (whose name means "spiny-skin") are characterized by a mesodermal skeleton composed of calcareous plates or ossicles, and 5-point radial symmetry at some point in their development.

Ecosystem services	Resources and beneficial processes that are supplied by natural ecosystems.
Evolutionarily significant unit	An evolutionarily significant unit (ESU) is a population or group of populations that is substantially reproductively isolated from *conspecific* populations.
Epibenthic	Living on the surface of the seabed.
Eukaryote	An organism containing membrane-bound organelles such as the nucleus.
Eutrophication	The ecosystem response to the addition of nutrients, such as nitrates and phosphates, to an aquatic system. *Phytoplankton* blooms and the potential for subsequent *hypoxia* are typical responses. Estuaries tend to be naturally eutrophic because they tend to concentrate land-derived nutrients. Marine systems are typically limited by nitrogen whereas freshwater systems are typically limited by phosphorus. *Upwelling* in coastal systems also naturally promotes increased productivity by conveying deep, nutrient-rich waters to the surface. Human-sourced nutrient loads can contribute to eutrophication, particularly in estuaries where anthropogenic nitrogen loads to *stratified* surface waters, which are often nutrient-limited, can be appreciable.
Exoskeleton	An external skeleton that supports and protects an animal's body, such as a shell or *carapace*.
Fecal coliforms	Bacteria whose presence indicates contamination by fecal material.
Food web	A food web describes feeding connections in an ecological community.
Foraminifera	A large phylum of amoeboid *protists* that are among the most common marine *plankton* species. Foraminifera typically produce a test, or shell, made of *calcium carbonate*.
Gametes	Sperm and egg cells that fuse with one another during fertilization in organisms that reproduce sexually.
Genotype	The heritable instructions carried by an organism within its genes.
Heterotrophic	A heterotroph (from the Greek meaning "different-nutrition") is an organism that cannot fix carbon and therefore uses organic carbon for growth.

Hypercapnia	An excess of carbon dioxide in the blood.
Hypoxia	Depletion of dissolved oxygen (*DO*) to a point that is detrimental to aquatic organisms. Hypoxia is typically defined as 2 mg/L or 65 *µmol/kg* oxygen concentration.
Infauna	Organisms that live within the sediments.
Intertidal	The intertidal zone, sometimes referred to as the littoral zone, is the area that is above water at low tide and under water at high tide.
Macroalgae	Macroscopic, multicellular algae; commonly referred to as seaweeds.
Meta-analysis	A systematic and statistical technique for combining findings from independent studies.
µatm	"Microatmospheres"; A unit of atmospheric pressure; one millionth of 1 atmosphere (atm).
µM or µmol L^{-1}	A unit of "molarity" (concentration); describing the molar amount of a solute divided by the volume of the solution.
µmol/kg	"Micromols/kilogram"; A unit of "molality" (concentration); describing the molar amount of a solute divided by the mass of the solvent.
Microalgae	Microscopic algae; an important component of *phytoplankton* communities.
Molluscs	A large phylum of invertebrate animals, which includes shell-forming bivalves, gastropods (from the Greek meaning "stomach-foot"), and cephalopods ("head-foot").
Nitrification	The aerobic oxidation of ammonia into nitrite, and subsequently from nitrate into nitrates, by biological organisms.
NO_X/SO_X	Generic terms for nitric oxide (NO), nitrogen dioxide (NO_2), and sulfur oxides, such as SO_2. NO_X, and SO_X are produced by the processing and burning of fossil fuels, and are major contributors to acid deposition (rain).
Operational model	An operational model assimilates real-time data to continuously calculate current conditions.
Oxidation	Oxidation is the increase in the chemical oxidation state of a molecule, atom, or ion. For example, organic carbon is oxidized to CO_2.

Pathogenicity	The pathogenicity of an organism refers to its ability to cause disease in a host, as determined by the pathogen's *virulence* factors.
pCO_2	The partial pressure of CO_2. Quantitative units used to describe pCO_2 are microatmospheres (*µatm*).
pH	The term used to describe acidity; pH is the negative log of the hydrogen ion (H^+) concentration in an aqueous solution.
Phenotype	The composite of an organism's observable characteristics or traits, such as its morphology, development, and physiological properties.
Photosynthesis	The process used by plants and other organisms to capture the sun's energy to split water into hydrogen and oxygen. The hydrogen is combined with carbon dioxide (absorbed from air or water) to form sugar (glucose); oxygen is produced as a waste product.
Phytoplankton	*Photosynthesizing* microorganisms that inhabit the upper sunlit layer of the ocean. In terms of numbers, the most important groups of phytoplankton include the *diatoms*, cyanobacteria, and *dinoflagellates*.
Plankton	Organisms that drift in the ocean.
POC	"Particulate Organic Carbon"; organic material that is too large to pass through a 0.45 micrometer filter, derived from dead organic matter such as plants.
Polymorph	A specific crystalline form of a compound, such as *calcium carbonate*, that can crystallize in different forms.
ppm	"Parts per million"; often used to describe the relative abundance of dissolved chemical species or gases in water.
Primary productivity	The production of organic compounds from atmospheric or *aqueous* CO_2 though *photosynthesis*. Primary productivity sustains the *food web*. In marine ecosystems, *phytoplankton* are the major primary producers.
Process studies	An organized, systematic investigation of a particular process designed to identify all of the state variables involved and to establish the relationships among them.
Protists	A diverse group of eukaryotic (nucleus-containing) microorganisms, characterized by relatively simple organization (unicellular, or unspecialized multicellular).

Pteropod	A term from the Greek meaning “wing-foot,” applied to two separate *taxonomic* groups of free-swimming sea snails.
Recruitment	Recruitment occurs when juvenile organisms survive to be added to a population (e.g., the dispersal, settlement to the bottom, and metamorphosis of *planktonic* larvae into new adult organisms).
Remineralization	The transformation of organic molecules to inorganic forms, typically mediated by biological activity (e.g., *respiration* of organic carbon to CO_2 and H_2O).
Respiration	The metabolic conversion by organisms of nutrients into biochemical energy. Biological respiration consumes oxygen and generates CO_2 as a waste product.
Saturation horizon	The depth at which the *saturation state* (Ω) for a given mineral = 1.0.
Saturation state	The saturation state (Ω) of a mineral is a measure of the *thermodynamic* potential of that mineral to form or to dissolve; At Ω values greater than 1.0, precipitation of the mineral is thermodynamically stable. Saturation states of the *calcium carbonate* minerals *aragonite* and *calcite* in seawater are calculated as the product of the concentrations of Ca^{2+} and CO_3^{2-}, divided by the apparent (i.e., relevant to seawater conditions) *solubility product* of those minerals.
Shoreline armoring	The construction of bulkheads, seawalls, riprap, or any other structure used to harden a shoreline against erosion.
Solubility product	K_{sp}; the product of the concentration of the ions that are present in a saturated solution of an ionic compound at *thermodynamic* equilibrium.
Stratification	Stratification occurs when water masses with different densities—determined by salinity and temperature—form layers that act as barriers to water mixing. These layers are arranged according to density, with the least dense water masses sitting above the more dense layers.

TA	"Total alkalinity"; the stoichiometric sum of the basic chemical species in an aqueous solution that neutralize acids. In seawater, most of the *alkalinity* is contributed by carbonate species, but other common basic components include borate, hydroxide, phosphate silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids, and sulfide.
Taxonomy	The classification of organisms into groups based on similarities of structure, origin, etc. A *taxon* is a taxonomic group of any rank, such as a species, family, or class.
Thermodynamic	According to the laws of physical science concerned with heat and its relation to other forms of energy and work.
TMDL	"Total Maximum Daily Load" is a regulatory term in the U.S. Clean Water Act, describing a value of the maximum amount of a pollutant that a body of water can receive while still meeting water quality standards.
Upwelling	A process caused by winds that displace surface ocean waters, and result in the upward movement of deeper waters, which are typically colder, saltier, nutrient- and CO_2-rich but oxygen-poor. Along the U.S. West Coast when winds blow from north to south, which is most common during summer months, surface ocean waters are pushed away from the coast due to the rotation of the Earth, and replaced by intermediate-depth ocean water.
Virulence	Virulence describes either the ability of a pathogen to infect a host, or the severity of the disease caused by that pathogen.
xCO_2	The mole fraction of CO_2 (ppm) in dry air.
Zooplankton	*Heterotrophic plankton*, which feed on bacterioplankton, *phytoplankton*, and other zooplankton. Individual zooplankton are usually too small to be seen with the naked eye, but some, such as jellyfish, are large.

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