

PETITION FOR ADDITIONAL WATER QUALITY CRITERIA AND
GUIDANCE UNDER SECTION 304 OF THE CLEAN WATER ACT, 33
U.S.C. § 1314, TO ADDRESS OCEAN ACIDIFICATION

BEFORE THE ENVIRONMENTAL PROTECTION AGENCY



Coral reefs at natural CO₂ vents, where coral development ceases in response to high CO₂ levels.
Photos courtesy of Katharina Fabricius.

APRIL 17, 2013



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1. Notice of Petition

With this legal petition, the Center for Biological Diversity requests that the Environmental Protection Agency (“EPA”) promulgate additional water quality criteria to measure ocean acidification as well as publish guidance on ocean acidification pursuant to Section 304 of the Clean Water Act. 33 U.S.C. § 1314(a)(2).

The right of an interested party to petition a federal agency is a freedom guaranteed by the first amendment: “Congress shall make no law ... abridging the ... right of people ... to petition the Government for redress of grievances” (U.S. Const., amend I).¹

Under the Administrative Procedures Act (“APA”), all citizens have the right to petition for the “issuance, amendment, or repeal” of an agency rule (5 U.S.C. § 553(e)). A “rule” is the “whole or a part of an agency statement of general or particular applicability and future effect designed to implement, interpret, or prescribe law or policy” (5 U.S.C. § 551(4)). Thus, the petitioners have the right to petition for this rule. EPA is required to respond to this petition: “Prompt notice shall be given of the denial in whole or in part of a written application, petition, or other request of an interested person made in connection with any agency proceeding” (5 U.S.C. § 555(e)).

The petitioned action is for a non-discretionary action under the Clean Water Act and therefore EPA is required to respond and the action is enforceable. This petition is enforceable under the citizen suit provision of the Clean Water Act (33 U.S.C. § 1365). The federal district courts of the United States have jurisdiction over a claim that the Administrator of the EPA has failed to perform a non-discretionary duty (33 U.S.C. § 1365(a)(2)). The subject of this petition, promulgation of water quality criteria and guidelines under Section 304, is a non-discretionary duty because the current criteria and guidelines do not reflect the latest scientific knowledge and fail to protect marine water quality, as required by the Clean Water Act.

Further, the APA provides for judicial review of a final agency action (5 U.S.C. § 704). The scope of review by the courts is determined by Section 706 of the APA (5 U.S.C. § 706). The APA also permits courts to compel agency action unlawfully withheld or unreasonably delayed (Id.).

2. Petitioner

The Center for Biological Diversity is a nonprofit environmental organization dedicated to the protection of imperiled species and their habitats through science, education, policy, and environmental law. The Center’s Oceans Program aims to protect

¹ See also *United Mine Workers v. Illinois State Bar Ass’n*, 389 U.S. 217, 222 (1967) (right to petition for redress of grievances is among most precious of liberties without which the government could erode rights).

marine life and ocean ecosystems in United States and international waters. The Center has over 500,000 members and online activists dedicated to the conservation of endangered species and wild places. The Center submits this petition on its own behalf and on behalf of its members and staff with an interest in protecting the ocean environment.

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3. Executive Summary

The Center for Biological Diversity formally requests that pursuant to Section 304 of the Clean Water Act the United States Environmental Protection Agency promulgate additional water quality criteria for ocean acidification. We also request under Section 304 that EPA publish information on water quality in order to guide states addressing ocean acidification.

Ocean acidification is dramatically transforming the chemistry of our oceans and the health of its ecosystems. As the oceans absorb carbon dioxide emitted from the burning of fossil fuels, seawater becomes increasingly acidic. Seawater is already 30% more acidic than pre-industrial levels, and the rate of change is occurring faster than anything experienced in the last 300 million years of the earth's history. Extensive documentation in the scientific literature demonstrates that ocean acidification negatively affects a wide range of marine species by hindering the ability of calcifying marine creatures to build protective shells and skeletons and by disrupting metabolism and critical biological functions.

The Clean Water Act is the nation's strongest law protecting water quality. EPA has acknowledged the applicability of the Clean Water Act toward addressing ocean acidification. Consistent with the law's goal of "restor[ing] and maintain[ing] the chemical, physical, and biological integrity of the Nation's waters," Section 304 requires

EPA to promulgate water quality criteria. In turn, states rely upon the criteria to set water quality standards and develop pollution controls. This petition presents scientific information demonstrating that new water quality criteria, acting in concert with the existing marine pH criterion, are necessary to address the water quality threats posed by ocean acidification. This petition requests that EPA initiate a rulemaking and promulgate water quality criteria for ocean acidification, including but not limited to the following:

- 1) Aragonite saturation state (Ω_{ar}) shall not fall below 1.0, or for marine waters with tropical corals aragonite saturation state shall not fall below 3.3; and
- 2) Calcification rates for target calcifiers should not measurably decline.

In addition, Section 304 mandates that EPA publish information to provide guidance to states on ocean acidification, including the factors necessary to prevent deleterious changes in seawater chemistry due to anthropogenic carbon dioxide emissions and the factors necessary to prevent adverse impacts of ocean acidification on fish, shellfish, and wildlife. EPA has already determined that ocean acidification guidance is warranted, and new scientific information about ocean acidification must be incorporated into this guidance in order to assist state water quality protection programs.

4. Ocean Acidification Scientific Background

Ocean acidification is emerging as one of the greatest threats to marine water quality. The oceans absorb 22 million tons of carbon dioxide from the atmosphere each day (Orr et al. 2005). In turn, carbon dioxide is changing seawater chemistry and causing it to become increasingly acidic. Ocean acidity has increased 30% since the beginning of the industrial revolution, and seawater acidity could increase 150% by century's end (Feely et al. 2006). These changes are having a profound impact on ocean ecosystems and marine life. Accordingly, the time to act to address ocean acidification is now.

a. Chemistry of Ocean Acidification

There is a strong scientific consensus that ocean acidification is occurring and that it is caused by anthropogenic CO₂ (Interacademy Panel 2009). The oceans have absorbed about 30% of the CO₂ put into the atmosphere by humans by fossil fuel burning, cement production, and land-use changes (Friedrich et al. 2012). Each day about 22 million metric tons of CO₂ is taken up by the oceans (Feely et al. 2008). The ocean's absorption of anthropogenic CO₂ has already resulted in more than a 30% increase in the acidity of ocean surface waters, at a rate likely faster than anything experienced in the past 300 million years, and ocean acidity could increase by 150% to 200% by the end of the century if CO₂ emissions continue unabated (Orr et al. 2005; Feely et al. 2009; Hönisch et al. 2012). Ocean acidification negatively affects a wide range of marine species by hindering the ability of calcifying marine creatures to build protective shells and skeletons and by disrupting metabolism and critical biological function (Fabry et al. 2008; Kroeker et al. 2010; Feely et al. 2009).

Ocean acidification has accelerated in tandem with increases in anthropogenic CO₂. The atmospheric concentration of CO₂ reached ~392 parts per million (ppm) in 2011 (NOAA 2012) compared to the pre-industrial concentration of ~280 ppm. The current CO₂ concentration has not been exceeded during the past 800,000 years and likely not during the past 15 to 20 million years (Denman et al. 2007; Tripathi 2009). Atmospheric CO₂ emissions have risen particularly rapidly since the 2000s (Raupach et al. 2007; Friedlingstein et al. 2010). The global fossil fuel CO₂ emissions growth rate was 1.1% per year during 1990-1999 compared with 3.1% during 2000-2010, and since 2000 this growth rate has largely tracked or exceeded the most fossil-fuel intensive emissions scenario projected by the IPCC, the A1FI scenario (Raupach et al. 2007; Richardson et al. 2009; McMullen et al. 2009; Global Carbon Project 2010, 2011). The CO₂ emissions growth rate fell slightly in 2009 due largely to the global financial and economic crisis; however, the decrease was less than half of what was expected and was short-lived (Friedlingstein et al. 2010). Global CO₂ emissions increased by 5.9% in 2010 resulting in a record 33 billion tons of CO₂ emitted (Olivier et al. 2011; Global Carbon Project 2011), and CO₂ emissions reached another record high in 2011 (IEA 2012).

Anthropogenic ocean acidification exceeds the trend in natural variability significantly, up to 30 times in some regions (Friedrich et al. 2012). The rate of change in ocean acidity is unprecedented in the past 300 million years, a period that includes four mass extinctions (Honisch et al. 2012; Zeebe 2012). The seawater chemistry change is an order of magnitude faster than what occurred 55 million years ago during Paleocene-Eocene Thermal Maximum, which is considered to be the closest analogue to the present, and during that period 96% of marine species went extinct (Id.).

Globally, surface water pH has declined -0.1 units on average between 1750 and 1994, which corresponds to a 30% increase in acidity (Sabine et al. 2004). The lowest decreases have occurred in the tropics and subtropics, while the high latitudes have experienced the most severe acidification (Id.). Long-term monitoring has documented the impact of increasing atmospheric CO₂ on declining seawater pH in the Pacific and Atlantic Oceans (*see* Figure 1). Results from time-series stations show a decrease of about -0.02 pH per decade (Bindoff et al. 2007).

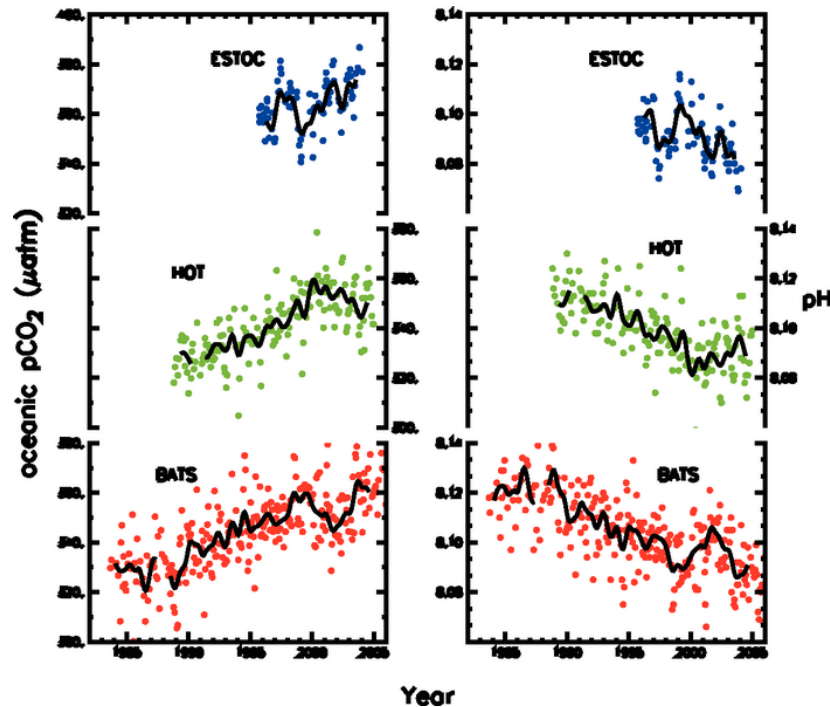


Figure 1. Changes in surface oceanic pCO₂ (left; in μatm) and pH (right) from three time series stations: Blue: European Station for Time-series in the Ocean (ESTOC, 29°N, 15°W; Gonzalez-Dávila et al., 2003); green: Hawaii Ocean Time-Series (HOT, 23°N, 158°W; Dore et al., 2003); red: Bermuda Atlantic Time-series Study (BATS, 31/32°N, 64°W; Bates et al., 2002; Gruber et al., 2002). Values of pCO₂ and pH were calculated from DIC and alkalinity at HOT and BATS; pH was directly measured at ESTOC and pCO₂ was calculated from pH and alkalinity. The mean seasonal cycle was removed from all data. The thick black line is smoothed and does not contain variability less than 0.5 years period (Bindoff et al. 2007).

In addition to affecting seawater acidity, CO₂ also reduces the availability of key chemicals, aragonite and calcite, that many marine species use to build their shells and skeletons. Waters that are supersaturated with aragonite are generally good for shell-building, while undersaturated waters ($<1.0 \Omega_{\text{ar}}$) are corrosive to some marine animals. Globally, there has been a decrease of about $-0.4 \Omega_{\text{ar}}$ (Gruber et al. 2012). The aragonite saturation state has declined 16% since the industrial revolution due, in large part, to anthropogenic CO₂ (Feely et al. 2012a; Ishii et al. 2011). Modeling of the oceans' aragonite saturation predicts that by the end of the century up to 75% of ocean volume could be undersaturated with respect to aragonite (Joos et al. 2011).

i. High Latitudes, Upwelling Systems and Coral Reef Ecosystems Are Especially Vulnerable to Acidification

Ocean chemistry is regionally variable, and some areas are especially vulnerable to the impacts of ocean acidification. This section describes some of the observations and predictions of ocean acidification in these vulnerable areas. High latitudes more readily absorb carbon dioxide because the waters are cold, areas with upwelling can make the impacts of acidification more severe, and coral reef ecosystems are highly vulnerable to ocean acidification. While the chemistry of the open ocean is rather stable, regional pH levels can be highly variable. Nonetheless, pH measurements at a variety of habitat types -- including estuary, upwelling, coastal, and coral -- revealed an average in general

agreement with the global open ocean mean pH (Hofmann et al. 2011). Many areas are already experiencing pH regimes that are not predicted to occur until the end of the century (Id.).

1. High Latitude Waters

High latitude waters, including the North Pacific and Bering Sea, are the “bellwether” of ocean acidification because these will be the first ocean regions to become persistently undersaturated with respect to aragonite as a result of greenhouse gas pollution (Fabry et al. 2009; Steinacher et al. 2009). High-latitude waters have naturally lower carbonate ion concentrations and saturation states due to a combination of cold temperatures which increase the solubility of CO₂ and ocean mixing patterns (Fabry et al. 2009; Mathis et al. 2011a). Modern-day increases in CO₂ solubility in the Arctic and North Pacific result from a combination of increasingly warmer air and water temperatures, melting ice, and increased concentration of atmospheric CO₂, all of which result in increased absorption of CO₂ by waters in northern latitudes and a hastening of the ocean acidification process (Steinacher et al. 2009). Warmer temperatures also cause a more active hydrological cycle, bringing more low-mineral CaCO₃ to the outer-shelf, and increasing the rate of undersaturation (Mathis et al. 2011a).

Because of the natural high solubility of CO₂ at northern latitudes, aragonite and calcite saturation thresholds are already very shallow in the North Pacific and Arctic oceans compared to other more temperate ocean areas, and are progressively moving higher as the concentration of anthropogenic CO₂ in the atmosphere continues to rise (Guinotte et al. 2006). In the North Pacific, the aragonite saturation horizon is only 150-200 m, compared to 2,000 m in the North Atlantic Ocean (Feely et al. 2004; Guinotte et al. 2006). In the Aleutians the aragonite saturation horizon currently stands at less than 150 m (Guinotte et al. 2006), and the calcite saturation horizon is at just 260 to 440 m (Orr et al. 2005).

Recent observations of calcium carbonate saturation states in the North Pacific and Bering Sea have found that full water column undersaturation of calcium carbonate due to ocean acidification is already prevalent. Mathis et al. (2011a) reported that extensive areas of bottom waters over the Bering Sea shelf are becoming undersaturated with respect to aragonite for at least several months (July to September), and some areas of bottom water were already observed to be undersaturated with respect to calcite (Fabry et al. 2009, Mathis et al. 2011a). Re-mineralization of organic matter exported from surface waters appears to increase bottom water CO₂ concentrations over the shelf in summer and fall, suppressing the calcite and aragonite saturation state (Ω) values. In the surface waters, removal of CO₂ by high rates of phytoplankton primary production increases saturation state values between spring and summer, but these increases are partly counteracted by sea ice melt water and terrestrial river runoff that have low saturation state values and that are increasing with climate warming.

Mathis et al. (2011a) predict that ocean acidification will likely have profound impacts on benthic and pelagic calcifying species across the Bering Sea shelf in the near future. The researchers concluded that

the observed suppression and undersaturation of Ω_{calcite} and $\Omega_{\text{aragonite}}$ in the eastern Bering Sea are correlated with anthropogenic carbon dioxide uptake into the ocean and will likely be exacerbated under business-as-usual emission scenarios. Therefore, ocean acidification could threaten some benthic and pelagic calcifying organisms across the Bering Sea shelf in the coming decades.

(Mathis et al. 2011a). Mathis et al. (2011a) found that while natural environmental processes contribute to low saturation states, anthropogenic CO_2 has driven seasonal undersaturation of aragonite in broad regions across the shelf. The researchers predict that anthropogenic CO_2 combined with natural remineralization processes will cause undersaturation conditions to persist for longer periods. This also could mean that deep winter mixing could cause the entire water column to drop below the saturation horizon, leaving the springtime water column under the ice undersaturated in respect to aragonite. Mathis et al. (2011a) show that by mid-century the Bering Sea will be persistently undersaturated with respect to aragonite on the current trajectory and subsequently calcite will become seasonally undersaturated. The study concluded that “the reduction in CaCO_3 mineral saturation states could have profound implications for several keystone calcifying species in the Bering Sea.”

Under existing CO_2 emission rates, models predict that the surface waters of the Arctic Ocean and parts of the North Pacific will be undersaturated with respect to aragonite in the next 50 years, starting as early as 2016 (Orr et al. 2005). The surface waters of the Bering Sea are predicted to be persistently undersaturated with respect to aragonite by 2050, and most of the Arctic, including broad regions of the Bering Sea, will be undersaturated with respect to calcite by the end of the century (Fabry et al. 2009, Feely et al. 2009, Mathis et al. 2011a).

This past year, 2012, also marked the lowest recorded sea ice extent in the Arctic (National Snow and Ice Data Center 2012; available at <http://nsidc.org/arcticseaicenews/>). The sea ice has decreased about 40% since record-keeping began in 1979, and scientists estimate that 70-95% of the Arctic melt is due to human activity (Day 2012). This is relevant because it is an anthropogenic source of seawater freshening, which can result in further lowering of pH and undersaturation of aragonite and calcium carbonate. Thus, human-caused sea ice melt is also contributing to corrosive conditions in the Arctic. Yamamoto et al. (2012) used a model to predict pH and aragonite saturation state of the Arctic Ocean due to both CO_2 uptake and freshwater input. The researchers found that surface waters are projected to be undersaturated with respect to aragonite in the annual mean before mid-century. The results show that pH reductions and aragonite undersaturation could occur significantly faster than previously projected because of the rapid pace of sea-ice melt (Yamamoto 2012).

2. The California Current

Observations have already documented significant ocean acidification along the West Coast of the United States, in the California Current upwelling system. The California Current System is particularly sensitive to ocean acidification (Hauri et al.

2009). Already the aragonite saturation horizon has shoaled by ~ 100 m and now reaches the euphotic zone in a few eddies and in near-shore environments during upwelling along the Pacific Coast (Hauri et al. 2009).

Modeling specific to the California Current System predicts rapid changes in pH and aragonite saturation (Hauri et al. 2009). Results of the model show that surface pH decreased from 8.14 to 8.05 between 1750 and 2000, and surface saturation state with respect to aragonite decreased from 2.7 to 2.3. The model indicates that waters that had been $\Omega_{ar} > 2.5$ in 1750 have been completely replaced by $\Omega_{ar} < 2.1$, and a growing percentage of waters at $\Omega_{ar} < 1.5$ (Id.). Gruber et al. predict that by 2030 many of California's coastal waters will be permanently undersaturated with respect to aragonite, with the intensity of ocean acidification increasing 10 fold by mid-century (Gruber et al. 2012). The model shows that nearshore areas will develop summer-long undersaturation in the top 60 m within the next 30 years (Id.). By the year 2050, more than half of the waters are undersaturated year-round, and habitats along the seafloor will become exposed to year-round undersaturation within the next 20 to 30 years (Id.).

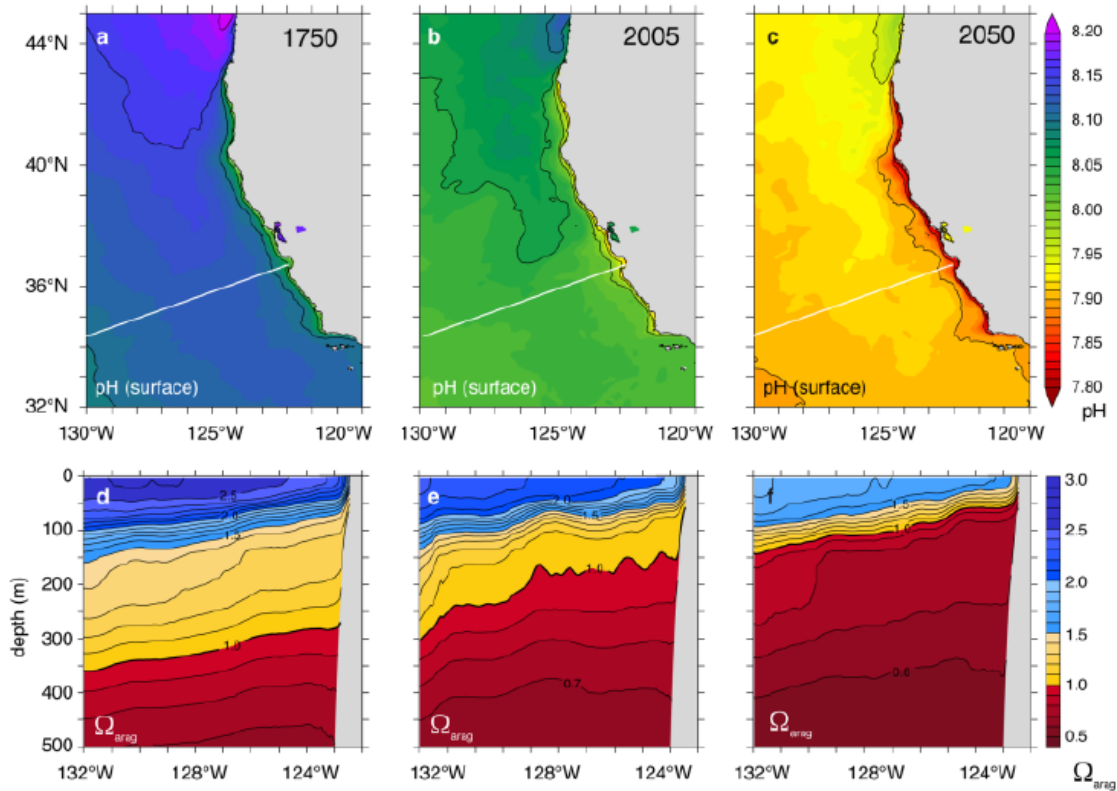


Figure 2. Temporal evolution of ocean acidification in the California Current System from 1750 until 2050 for the A2 scenario. (A to C) Maps illustrating the evolution of annual mean surface pH, illustrating the decrease in pH for the three time slots 1750, 2005, and 2050. (D to F) Offshore depth sections depicting the general decrease of the annual mean saturation state of seawater with regard to aragonite, Ω_{ar} , and the shoaling of the saturation depth, i.e., $\Omega_{ar} = 1$, for the same three time slots. The white lines in (A) to (C) indicate the position of the offshore section (Gruber et al. 2012)

Based on observations from cruise surveys, Feely et al. (2012a) report that in the Pacific Ocean there has been a decrease of the saturation state of surface seawater with respect to aragonite and calcite as well as an upward shoaling of the saturation horizon by about 1-2 meters per year on average (Feely et al. 2012a). The California Current has experienced a remarkable shoaling of the aragonite saturation horizon of 5 meters per year on average, due in part to changes in ocean circulation as well as atmospheric CO₂ (Feely et al. 2012a). Because the saturation horizon has shoaled, the corrosive waters come up onto the continental shelf along the entire coast from Washington to Southern California during the upwelling season (Feely et al. 2008). The surveys found undersaturated bottom waters with pH of < 7.75 units, and these undersaturated waters are reaching the mid-continental shelf and even surface waters in northern California (Id.). The upwelled waters in northern California were last at the surface about 50 years ago when CO₂ levels were much lower than they are today (Id.).

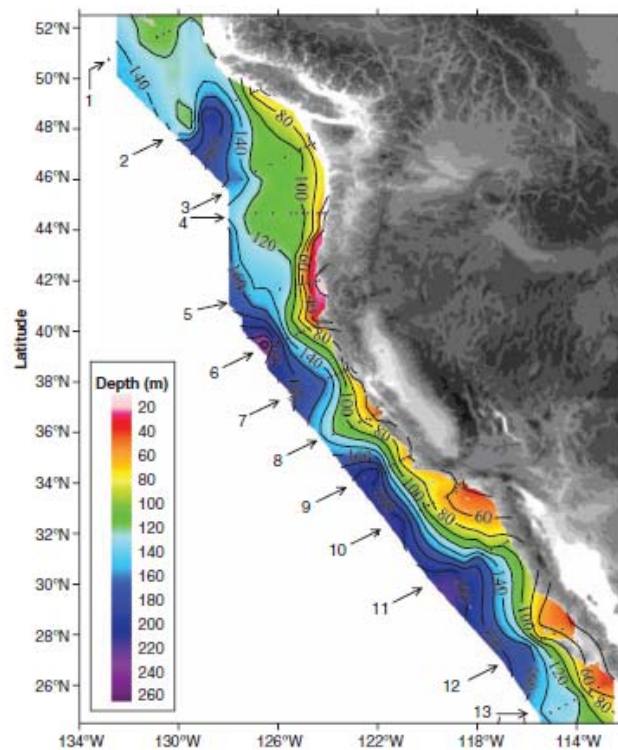


Figure 3. Distribution of the depths of the undersaturated water (aragonite saturation < 1.0; pH < 7.75) on the continental shelf of western North America from Queen Charlotte Sound, Canada, to San Gregorio, Baja California Sur, Mexico. On transect line 5, the corrosive water reaches all the way to the surface in the inshore waters near the coast. The black dots represent station locations (R.A. Feely et al. 2008).

In the Pacific Northwest, an extensive study on the coast of Washington, Wootton et al., found that pH declined by 0.045 units annually (Wootton et al. 2008). Accordingly, during the eight-year period pH declined an average -0.045 units annually thus resulting in a total decrease of 0.36 pH units between 2000 and 2008 (Id.). Continuing monitoring documented that the declining trend continues, and that the pH changes are an order of magnitude greater than predicted models (Wootton & Pfister

2012). Parallel trends from other observations indicate that it is a regional trend (Id.). Wooten & Pfister (2012) tested and ruled out numerous potential drivers of the pH shifts, indicating a primary role of inorganic carbon (Id.).

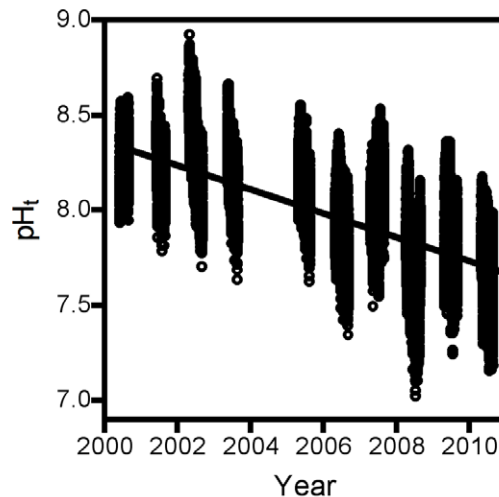


Figure 4. Trends in ocean pH taken from Tatoosh Island, Washington, from 2000–2010, expressed on the total scale. 2004 not reported because of probe failure. N= 37,038 (J. Wootton & C. Pfister 2012).

The Puget Sound has exhibited extremely low pH and an increase in the presence of undersaturated waters. Corrosive waters have been observed every year since 2008 in the Puget Sound (Moore et al. 2011; Feely et al. 2012a). Feely et al. (2010) estimated that pH has declined in the Puget Sound by 0.11 units since the pre-industrial era, and that aragonite saturation has declined by 0.09-0.33, with larger decreases in some areas during the summer (Feely et al. 2010). They attribute 24-49% of the pH decrease observed to anthropogenic CO₂, which will account for 49-82% of the pH decrease over time when carbon dioxide in the atmosphere reaches 560 ppm (Feely et al. 2010). Before the end of the century, ocean acidification is predicted to be the dominant contributor to reductions in pH and aragonite saturation in the Puget Sound.

3. Coral Reef Waters

Waters with coral reefs are especially vulnerable to ocean acidification because these ocean ecosystems are highly dependent on calcification. Coral reefs provide many ecosystem services that are jeopardized by ocean acidification. Coral reefs are associated with 25% of the oceans' species. We are dependent on coral reefs for biological diversity, fisheries, shoreline protection, tourism, recreation, cultural practices, livelihoods, and subsistence.

Tropical waters have experienced declining saturation states due to ocean acidification. Models show that by the end of the century, most coral reef areas will no longer have aragonite saturation states that are optimal for coral growth (*see* Figure 5).

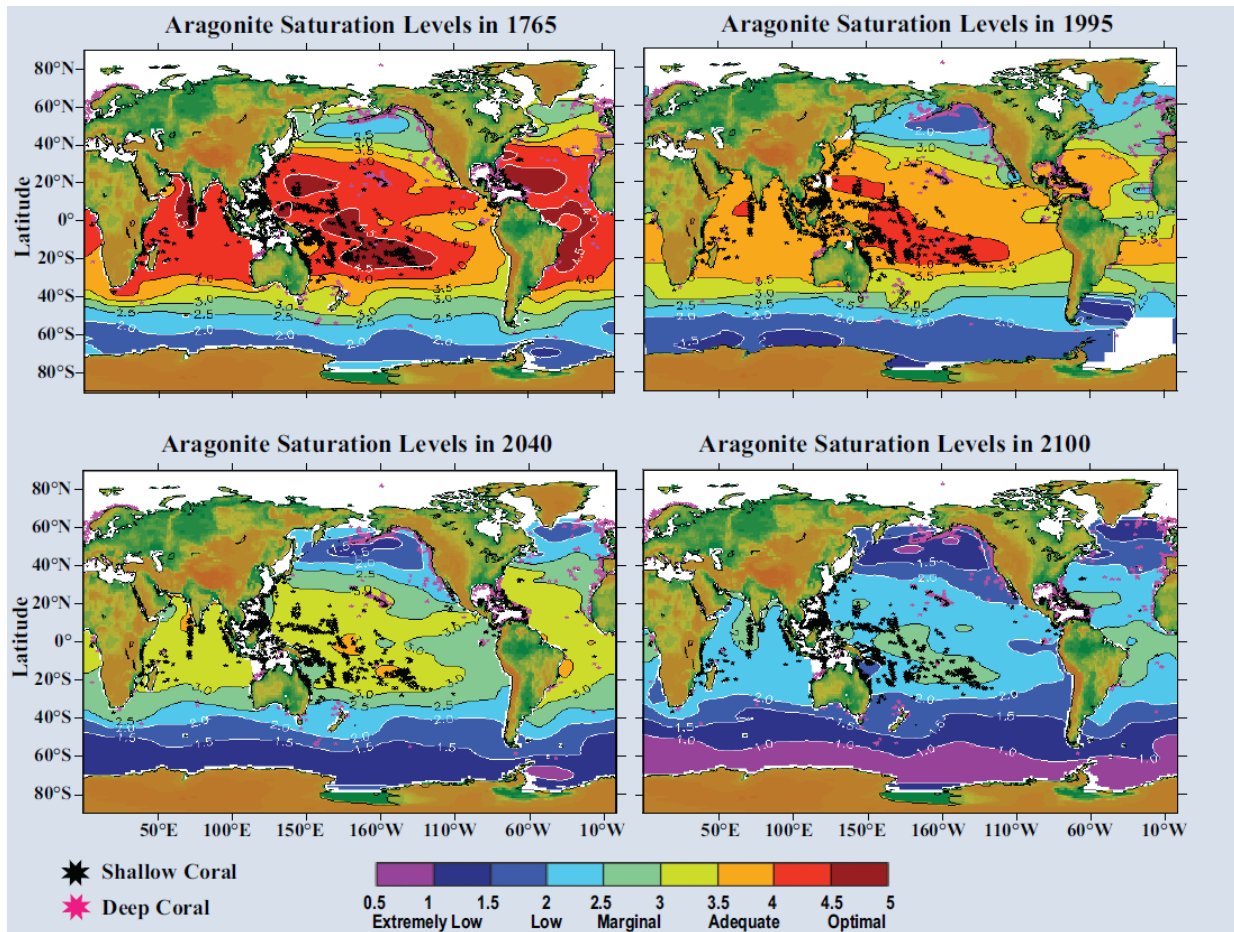


Figure 5. Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely *et al.*, submitted), based on the modeling results of Orr *et al.* (2005) and a Business-As-Usual CO₂ emissions scenario. The distributions of deep-sea coral banks are from Guinotte *et al.* (2006). (J. A. Kleypas *et al.* 2006a)

A recent 10 year study of the Greater Caribbean Region found a strong decrease in aragonite saturation state as a consequence of rising atmospheric carbon dioxide and resulting ocean acidification (Gledhill *et al.* 2008). The study found a regional decline in aragonite from 4.05 to 3.9 from 1996-2006, at a much faster rate of decline than previously reported (currently: -0.012 ± 0.001 , previously: -0.007 ± 0.002). Modeling predicts that under various emissions scenarios the coral reefs in the Caribbean will be thermally and chemically stressed between now and 2030 (Meissner *et al.* 2012). They found that even under the most optimistic scenario, 98% of reefs would be stressed by 2050 (Id.). Under an intensive emissions scenario, the model shows mean annual open ocean surface water aragonite saturation thresholds for corals (3.3Ω) exceeded by mid-century (Id.).

The Caribbean has experienced the largest regional trends with the observed surface aragonite saturation state having declined 0.09 per decade (Friedrich *et al.* 2012). This change over approximately 20 years is as much as 100 times the glacial-interglacial rate of change (Id.). By around 1980, the anthropogenic signal exceeded the natural range in this region by a factor of ten (Id.).

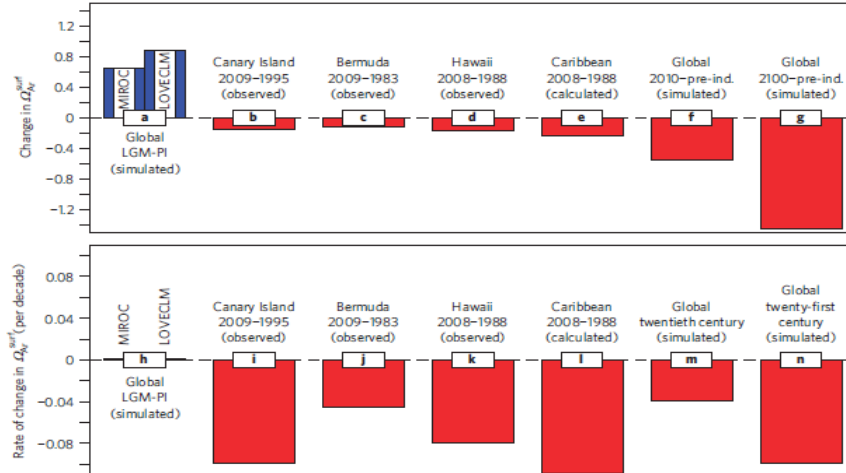


Figure 3 | Current Ω_{Ar}^{surf} trends in the context of the Last Glacial Termination. **a**, Globally averaged change in Ω_{Ar}^{surf} between pre-industrial (PI) times and the Last Glacial Maximum as simulated by the LOVECLIM and the MIROC model respectively. **b-e**, Trends in Ω_{Ar}^{surf} for the European Station for Time series in the Ocean (1995-2009) (**b**), the Bermuda Atlantic Time-series Study (1983-2009) (**c**), Station ALOHA (1988-2008) (**d**) and the Caribbean region (1988-2008; ref. 20) (**e**). **f,g**, Globally averaged change in Ω_{Ar}^{surf} as simulated by the MPI-ESM for the years 2010 (**f**) and 2100 (**g**) respectively (with respect to the pre-industrial average). **h-n**, Rates of change in Ω_{Ar}^{surf} (per decade) for glacial-interglacial as in **a** (**h**), observations as in **b-e** (**i-l**) and the twentieth (**m**) and twenty-first century (**n**), respectively.

Figure 6: Trends in surface aragonite saturation states (Friedrich et al. 2012).

In the Pacific, there are nearly 20 years of time-series measurements of seawater pH in the central North Pacific Ocean near Hawaii (Dore et al. 2009). Dore et al. documented a significant long-term decreasing trend of $-0.0019 \pm 0.0002 \text{ y}^{-1}$ in surface pH, which is indistinguishable from the rate of acidification expected from equilibration with the atmosphere (Id.). This is in agreement with a basin-wide survey of the Pacific found that surface ocean waters in the North Pacific Ocean have experienced an annual decline of 0.0017 pH units between 1991 and 2006, and that this rate of change is accelerating (Byrne et al. 2009). The long-term pH trend at 175m at HOT is -0.001930 y^{-1} (See figure 7) (Beman et al. 2011).

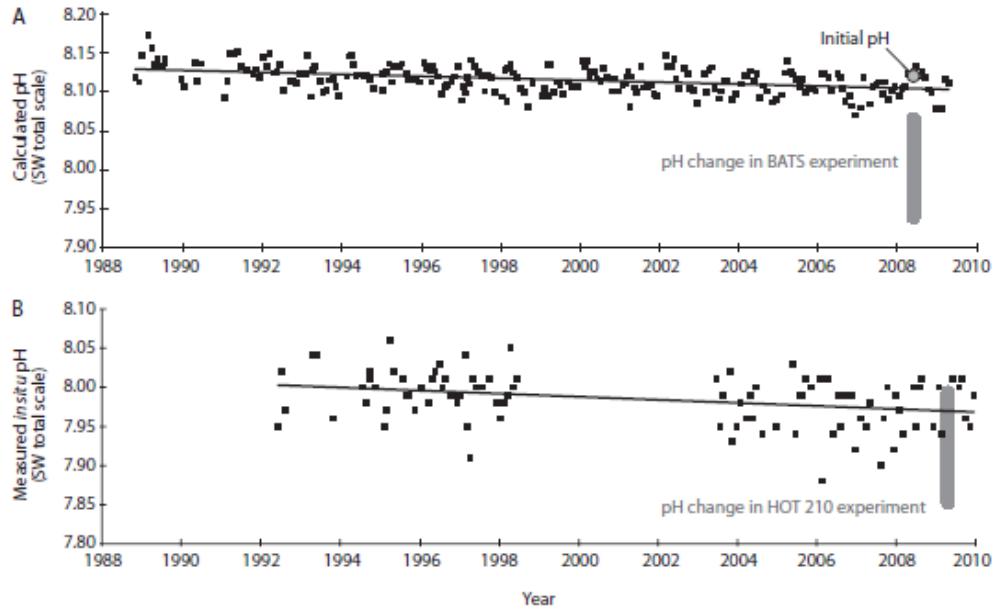


Figure 7. Experimental pH manipulation at 150m at BATS(A) and 175m at HOT(B) in relation to pH variation over time. Vertical gray bars denote the pH changes induced in both experiments, with higher values occurring in control incubations and lower values in acidified treatments. DIC and TA were immediately measured on seawater collected at BATS (“initial pH”) and then for controls and acidification treatments at the end of the incubation; HOT data represent single end-point measurements. pH is not directly measured at 150m at BATS, and data points therefore represent pH values calculated from DIC and TA measurements made at 140 and 160m. At HOT, pH values are measured spectrophotometrically and are more limited in number, but are highly similar to calculated values(3). HOT data from 1992 through 1998 represent direct measurements at 175m depth; from 2003 to present, no measurements were made at 175m, and so pH values were calculated from measurements made at 150 and 200m. All pH values are reported on the seawater total scale, are typically ~0.1 unit higher at BATS than at HOT, and range more widely at HOT. On the basis of these data, the long-term pH trend at 150m at BATS is $-0.001263y-1$ and at 175m at HOT is $-0.001930y-1$ (Beman et al. 2011; Beman 2011 Supporting Information).

Hawaii’s coastal waters have a range of CO_2 levels with some areas being relatively stable like the open ocean measurements at station ALOHA, meanwhile other coastal areas are highly variable ranging between 100-1000 p CO_2 , including levels predicted for the end of the century (Drupp in press). Dulaiova et al. (2010) examined 22,200 near-shore pH measurements in Hawaii and reported that seawater pH in Hawaii between 2003-2009 showed a significantly declining trend of -3.14×10^{-5} /day pH units (three times the offshore trend at station ALOHA reported above) (Dulaiova et al. 2010). The report found that 27 of the sites had significant acidification, a negative pH trend, occurring at sites on the islands of Hawaii, Kauai, Oahu, and Maui. The report also explains that “the reefs on Maui that have experienced most dramatic decline in reef health have also been exposed to the greatest decrease in pH values” (Dulaiova 2010:4). While Dulaiova et al. were unable attribute the changes in pH to a single cause, they acknowledge that it can be related to anthropogenic sources including CO_2 , land use, and other causes.

Finally, even ocean waters not at high latitude, in upwelling systems, or containing coral reefs ecosystems are, or will soon be, exhibiting signs of ocean acidification. Observations of East Coast waters during all seasons show that they remain

supersaturated with respect to aragonite (Jiang et al. 2010). Aragonite saturation states in the surface water of the South Atlantic Bight ranged from 2.5 to 4.2 (Id.). They were lowest close to the coast and increased offshore. By the end of this century, saturation states of aragonite and calcite will decrease by 20–40%, with the lowest Ω_{ar} 1.3 in some seasons (Id.).

b. Biological Effects of Ocean Acidification.

The leading ocean acidification scientists warn that changes in our oceans chemistry are having significantly adverse impacts on marine life (Caldeira & Archer 2007). Even a 0.2 pH change – the current federal marine water quality criterion for pH – will result in major negative impacts on corals and other marine organisms that build calcium carbonate skeletons, and whose success is largely controlled by carbonate chemistry.

In a meta-analysis of over 400 experiments examining the impacts of ocean acidification on marine organism response, Kroeker et al. (2013) found the biological effects to be generally large and negative. This analysis was restricted to experiments with pH manipulations of less than 0.5 units, in order to reflect the predicted level of ocean acidification by the end of the century (IPCC 2007). By limiting the analysis to small variations in pH, this study shows that even chemistry changes within the range allowed under the current federal criterion there will be “profound repercussions for marine organisms” (Kroeker et al. 2010). While the negative effect of ocean acidification was most pronounced for calcification and survival (27% reductions in both responses), the study also revealed significant negative effects on growth and reproduction (11 to 19%, respectively). In addition, abundance was reduced by 15%. The strength of this analysis suggests that the patterns highlighted in this study are a robust representation of the current literature on ocean acidification.

Over 90 national academies of sciences, including the United States, have signed a statement that ocean acidification will “cause grave harm to important marine ecosystems as CO₂ concentrations reach 450ppm and above” (Interacademy Panel 2009). At 550 ppm, ocean acidification will be “disastrous for sensitive oceanic ecosystems in many parts of the world.” A concentration of 550 ppm corresponds to an ocean pH of approximately 7.9, or 0.2 units below current worldwide levels.

Beyond its effects on individual species, elevated acidity will disturb entire communities and have repercussions throughout the food web. Many calcifying species are located at the bottom or middle of global ocean food webs, therefore changes in abundance of shelled organisms due to ocean acidification will alter predator-prey relationships and the effects will be transmitted throughout the ecosystem and global marine food web. In addition to the likely disruptions through large components of the marine food web, a loss or change in biodiversity could have significant ecological consequences (Convention on Biological Diversity 2009).

For example, calcifying pteropods are a key food component for carnivorous zooplankton and fish. The decline of pteropod densities, as predicted for high latitude

regions in the near future, will influence the predator-prey relationships of many species, such as cod, pollock, and mackerel, and could result in greater predation pressure on juvenile fish, such as salmon (Fabry et al. 2008). Fish that feed on pteropods will experience greater energetic foraging costs as they struggle to find sufficient prey. The commercially important pink salmon, which preys almost entirely on the pteropod *Limacina helicina* will experience drastically reduced body mass as pteropod populations in the North Pacific crash (Fabry et al. 2009). *Gonatus fabricii*, among the most abundant squid species in the North Atlantic, is the most important prey item to a number of marine mammals and may be responsible for their seasonal occurrence in some regions. Because squid metabolic rates are high, they are predicted to be highly sensitive to increases in acidity (id.), and a decline in their abundance will impact marine mammal populations and migrations.

Using a multi-year data set from coastal benthic communities in the Pacific Northwest, Wootton et al. (2008) predict a substantial shift in the species dominating the coastal habitat as a consequence of both direct effects of reduced calcification and indirect effects arising from the web of species interaction. Although coastal and surface waters make up only a small portion of the world's oceans, they are focal point for ocean production and human activity; any changes to the dynamics of these communities will have far reaching ramifications.

Not only will ocean acidification affect global food webs and ecosystems, it will have a direct effect on the global economy. The U.S. economy is very dependent on the health of the ocean. In 2009, the ocean economy contributed over \$223 billion annually to the U.S. gross domestic product and provided more than 2.6 million jobs (NOAA, <http://oceanservice.noaa.gov/facts/oceanconomy.html>). Cooley and Doney (2009) estimate that if just a 10-25% decrease in United States mollusc harvests from 2007 were to occur today, \$75-187 million in direct revenue would be lost each year henceforth, with a net loss of \$1.7-10 billion through mid-century, when pH levels are approximately 0.3 units below pre-industrial values.

Tropical coral reefs provide ecosystem services, such as habitat and nursery functions for commercial and recreational fisheries and coastal protection. As reefs decline in acidified waters, there will be an ecological phase shift to a new ecosystem state dominated by less commercially valuable species. The annual economic damage of ocean acidification induced coral reef loss is estimated to escalate rapidly over time due to economic growth, reaching \$870 billion by 2100 (Brander et al. 2009a). Other services provided by the oceans, for example providing a site for the release of wastes and pollutants, are less well accounted for by standard economic measures. Attempts to quantify some of these services have produced estimates of many billions of dollars. Even subtle changes in environmental conditions may have strong effects on ecosystem functioning, with yet unforeseen consequences for the continued provision of key services (Convention on Biological Diversity 2009).

Hundreds of studies have documented the impacts that will occur throughout the marine environment as a result of ocean acidification. Many of these scientific

experiments have reported their manipulations of carbonate chemistry as a function of total alkalinity (TA), dissolved inorganic carbon (DIC), calcium carbonate saturation state (Ω), or carbon dioxide concentration ($p\text{CO}_2$). In order to standardize their results, we have converted those figures, where possible, to pH, using the below table. This was done in order to demonstrate that harmful biological responses that will occur as a result of marine organisms living in ocean waters with pH values allowed under the current federal water quality criterion, for which we seek additions.

TABLE 1. Forecasts of atmospheric CO_2 concentrations and their impact on the ocean chemistry

Aspect	Glacial	Preindustrial	Today	2 × preindustrial	3 × preindustrial	4 × preindustrial	5 × preindustrial	6 × preindustrial
Atmospheric concentration of CO_2	180	280 ppm	380 ppm	560 ppm	840 ppm	1120 ppm	1400 ppm	1680 ppm
H_2CO_3 (mol/kg)	7	9	13	19	28	38	47	56
HCO_3^- (mol/kg)	1666	1768	1867	1976	2070	2123	2160	2183
CO_3^{2-} (mol/kg)	279	225	185	141	103	81	67	57
Total dissolved inorganic carbon (mol/kg)	1982	2003	2065	2136	2201	2242	2272	2296
Average pH of surface oceans	8.32	8.18	8.07	7.92	7.77	7.65	7.56	7.49
Hydrogen ion (H^+) ($\mu\text{mol/kg}$)	4.79×10^{-3}	6.92×10^{-3}	8.92×10^{-3}	12.3×10^{-3}	17.4×10^{-3}	—	—	—
Calcite saturation	6.6	5.3	4.4	3.3	2.4	1.9	1.6	1.3
Aragonite saturation	4.3	3.4	2.8	2.1	1.6	1.2	1.0	0.9
Temperature ($^\circ\text{C}$)	15.7	19	19.7	20.7	22.7	—	—	—
Salinity (ppt)	35.5	34.5	34.5	34.5	34.5	—	—	—

Figure 8. Forecasts of ocean carbonate chemistry (Abbasi and Abbasi 2011).

i. Corals

EPA must promulgate water quality criteria that will adequately protect corals from the detrimental impacts of acidification. Coral reefs exhibit negative effects in marine waters with pH inside the federally allowed deviation. Coral reefs cannot exist below 7.8 pH units (Fabricius et al. 2011), and the threshold for coral growth is $3.3 \Omega_{\text{ar}}$ (Meissner et al. 2012).

Corals are among the ecosystems most threatened by ocean acidification. To date, most scientific investigations into the effects of ocean acidification on coral reefs have been related to the reefs' unique ability to produce voluminous amounts of calcium carbonate (Kleypas & Yates 2009). The persistence of carbonate structures on coral reefs is essential in providing habitats for a large number of species and maintaining the extraordinary biodiversity associated with these ecosystems. As a consequence of ocean acidification, the ability of marine calcifiers to produce calcium carbonate will decrease, resulting in a transition from a condition of net accretion to one of net erosion, with drastic consequences for the role and function of these ecosystems (Kleypas & Yates 2009).

Coral reefs are predicted to drastically lower their calcification rates in the near future, and historical records show that calcification rates have already fallen relative to pre-industrial values. According to scientists, the main reef building organisms will calcify up to 50% less relative to pre-industrial rates by the middle of this century (Id.). A

drop of approximately 60% coral reef calcification is projected for the end of the century, when pH is predicted to fall 0.5 units below pre-industrial values (Caldeira & Archer 2007). Many studies suggest calcification rates could be reduced between 20-60% at 560ppm, or 7.9 pH, and that a reduction of this magnitude would fundamentally alter reef structure and function (Convention on Biological Diversity 2009). According to the model of Silverman et al. (2009), developed from field observations from more than 9,000 reef locations, all coral reefs are expected to reduce calcification by more than 80% relative to their pre-industrial rate at 560 ppm (0.3 pH change), and at this point “all coral reefs will cease to grow and start to dissolve.” The Interacademy Panel on International Issues concurs; “at current emission rates models suggest that all coral reefs and polar ecosystems will be severely affected by 2050 or potentially even earlier.”

In a meta-analysis on coral calcification responses to ocean acidification, the coral calcification declined by a mean of 15% per unit decrease in aragonite saturation state ($2 < \Omega < 4$) (Chan and Connolly 2013). On current emission trends, calcification will decline 22% on average for corals by the end of the century (Id.). This falls to the lower range of responses that have been predicted by ocean acidification researchers and described above, which the authors believe reflects variation in the calcification responses of different corals.

Calcification rates at coral reef locations in the western tropical Pacific and the Caribbean may have already declined by 15%, (Caldeira & Archer 2007), and data from the Great Barrier Reef indicates a 14% decline in calcification rates between 1990 and 2005 (De'ath et al. 2009). Other studies in the Great Barrier reef indicate a decline of approximately 21%, and analysis of coral growth records confirm that this decline is unprecedented in recent centuries (Cooper et al. 2008). A model based on field samples shows that calcification of coral reefs in French Polynesia declined 15% between the pre-industrial period and 1992, and that rates will decline 40% by 2050, when CO₂ levels reach 560 ppm (pH 7.9)(Anthony et al. 2011). Near Bermuda, historical records show that coral skeletal density has decreased 33%, and coral calcification rates have declined by 52% as a result of changes in seawater carbonate chemistry (Bates et al. 2010). These observed changes have occurred even before a 0.2 unit decline in ocean pH; as atmospheric CO₂ continues to rise and lower pH values, calcification rates will maintain their precipitous decline.

Ocean acidification acts in concert with ocean warming and coral bleaching in furthering coral reef decline. Studies projecting the combined impacts of ocean acidification and ocean warming on corals predict that coral erosion will exceed calcification rates at atmospheric CO₂ concentrations of 450 to 500 ppm, (Hoegh-Guldberg et al. 2007), and all coral reefs will begin dissolve at CO₂ concentrations of 560 ppm (Silverman et al. 2009). These figures correspond to a 0.2 and 0.3 unit drop in pH, respectively, as compared to pre-industrial values. In the Caribbean, a recent study concluded that “coral reef communities are likely to be essentially gone from substantial parts of the Southeast Caribbean by the year 2035” (Buddemeier et al. 2011). The Great Barrier Reef has lost 50% of its coral cover since 1985 as a result of the combined effects of ocean acidification, global warming, coral bleaching, coral predation by starfish, and

cyclone damage (De'ath et al. 2012). In short, due to the synergistic impacts of ocean acidification, mass bleaching, and local impacts, coral reefs are projected to experience “rapid and terminal” declines worldwide at atmospheric CO₂ concentrations 450 ppm, or pH 8.0, a level that is expected before mid-century (Veron et al. 2009).

Many experimental studies have show declining calcification rates and other ill effects when corals are exposed to acidified waters. Decreases in calcification rates across a suite of benthic species and calcifying systems range from 3 to 60% for a doubling in pCO₂, which corresponds to a 0.3 reduction in pH (Abbasi & Abbasi 2011). The average response of corals is a 30% decline in calcification in response to a doubling in pCO₂ (Id.). In a study of an assemblage of corals exposed to conditions designed to mimic the change that may be experienced in the next 50-100 years (pH decline of 0.22 to 0.28 units), calcification rates declined between 44% and 80%. Abbasi and Abbasi (2011) compiled a table of calcification responses to increased CO₂, including the responses of many corals, and this table is included at Figure 9, below.

TABLE 3. Impact of increased pCO₂ concentrations on calcification responses (adopted from Guinotte and Fabry, 2008; Kleypas et al., 2006)

Organism	% change in calcification at pCO ₂			Reference
	Associated mineral	2 × preindustrial	3 × preindustrial	
Coralline red algae <i>Porolithon gardineri</i>	Calcite	-25		Agegian, 1985
Coccolithophores <i>Emiliania huxleyi</i>	Calcite	-9	-18	Riebesell et al., 2000
<i>E. huxleyi</i>	Calcite	-25		Sciandra et al., 2003
<i>Gephyrocapsa oceanica</i>	Calcite	-29	-66	Zondervan et al., 2001
Foraminifera <i>Globigerinoides sacculifer</i>	Calcite	-4 to -6	-6 to -8	Bijma et al., 2002; Bijma et al., 1999
<i>Orbulina universa</i>	Calcite	-8	-14	Spero et al., 1997; Bijma et al., 1999
Mussel <i>M. edulis</i>	Calcite		-25 ^a	Fabry, 2008
Oyster <i>C. gigas</i>	Calcite		-10 ^a	Fabry, 2008
Scleractinian corals <i>Acropora cervicornis</i>	Aragonite	-40	-59	Renegar and Riegl, 2005
<i>Acropora eurystroma</i>	Aragonite	-55		Schneider and Erez, 2006
<i>Acropora verweyi</i>	Aragonite	-12	-18	Marubini et al., 2003
<i>Fungia sp.</i>	Aragonite	-47	-69	Hossain and Ohde, 2006
<i>Galaxea fascicularis</i>	Aragonite	-12	-18	Marubini et al., 2003
<i>G. fascicularis</i>	Aragonite	-56	-83	Marshall and Clode, 2002
<i>Porites compressa</i>	Aragonite	-17	-25	Marubini et al., 2001
<i>P. compressa</i> + <i>Montipora capitata</i>	Aragonite	-40	-59	Langdon and Atkinson, 2005
<i>Pavana cactus</i>	Aragonite	-14	-20	Marubini et al., 2003
<i>P. lutea</i>	Aragonite	-38	-56	Ohde and Hossain, 2004
<i>P. lutea</i>	Aragonite	-33	-49	Hossain and Ohde, 2006
<i>P. porites</i>	Aragonite	-16		Marubini and Thake, 1999
<i>Stylophora pistillata</i>	Aragonite	-14	-20	Gattuso et al., 1998
<i>S. pistillata</i>	Aragonite	0 to -50		Reymaud et al., 2003
<i>Turbinaria reniformis</i>	Aragonite	-9	-13	Marubini et al., 2003

^a2.6 × preindustrial.

Figure 9. All of the above species experienced a decrease in calcification at pCO₂ levels which correspond to a decline in 0.2 pH, the current federal marine pH water quality criterion (Abbasi & Abbasi 2011).

The coral *Acropora palmata* (listed as threatened under the Endangered Species Act), once the dominant reef building coral in the Caribbean, experiences impaired fertilization, settlement, and growth with increasing pCO₂ (Albright et al. 2010). The cumulative impact of ocean acidification on fertilization and settlement success is an

estimated 52% and 73% reduction in the number of larval settlers on the reef under pCO₂ conditions projected for the middle and end of this century, respectively (0.2 and 0.5 decline in pH) (Id.). After only 8 days of high CO₂ conditions (pH 7.75), *Acropora* experiences a statistically significant (18%) reduction in calcification rate (Murubini et al. 2003).

Experimental studies evaluating the effects of ocean acidification on early life history stages of corals generally conclude that primary polyp growth is hindered by increasing acidity (Albright et al. 2010, Cohen & Holcomb 2009). Renegar and Riegl (2005) showed a significant decrease in the growth rate of *Acropora cervicornis* larvae at pH levels 0.3-0.5 units below control. Larvae of the common Atlantic golf ball coral, *Favia fragum*, shows significant delays in both the initiation of calcification and subsequent growth of the primary corallite in acidic waters (8.17 – 7.54 pH) (Cohen & Holcomb 2009). Visible changes in the skeletal development were observed in all non-control treatments, and in the most acidic waters skeletal development was 75% less than the control.

Acidification also affects cold water corals. Cold water corals have a worldwide but patchy distribution, and are often found in areas with highly productive fisheries (De Mol et al. 2002; Kenyon et al. 2003). Overall, more than two-thirds of all known coral species are cold water corals (Roberts & Hirshfield 2012; Cairns 2007). Recent exploration and research that has begun to search for, map, and observe cold water corals has found that these organisms are fragile, long-lived, slow-growing, very sensitive to physical or environmental disturbance and adapted for a specific environmental niche (McDonough & Puglise 2003). Alaskan waters are already showing widespread evidence of ocean acidification as a result of greenhouse gas emissions (Mathis et al. 2011a). By 2100, 70% of cold-water corals will be exposed to corrosive waters (Convention on Biological Diversity 2009). Conditions in waters typically inhabited by cold-water corals are even less favorable for calcification than those experienced by warm water corals; this may cause cold-water corals to be affected earlier and more strongly by CO₂-related ocean acidification than their warm water counterparts (Abbasi & Abbasi 2011).

The vulnerable early developmental and reproductive stages of cold water corals may be especially strongly impacted (Kurihara 2008; Dupont & Thorndyke 2009; Kroeker et al. 2010). In an experiment on the cold-water coral *Lophelia pertusa*, lowering the pH by 0.3 units relative to the ambient level resulted in calcification being reduced by 56% (Maier et al. 2009). Lower pH reduced calcification more in fast growing, young polyps (59% reduction) than in older polyps (40% reduction). Thus, corals' larvae and young corals are significantly more susceptible to ocean acidification than adults, and will likely show a higher degree of reduced calcification and growth with reduced pH, making young and larval corals less likely to survive to maturity as the ocean continues to absorb anthropogenic CO₂ and as climate change progresses.

Acidification alone decreases calcification, and acidification combined with warming results in extremely drastic reductions in calcification rates (Anlauf et al. 2011)(observing a 3% reduction in acidification with a 0.2 decline in pH, and a 30%

decline when acidification is coupled with 1° C warming). While natural variability in the annual cycle and interannual variability may account for some of the observed change in coral growth rates, scientists are “virtually certain” that anthropogenic trends already exceed natural variability (Friedrich et al. 2012).

In addition to reduced calcification rates, the strength of cementation may also be reduced in waters with a lower pH, promoting higher rates of physical and bio-erosion (Manzello et al. 2008). Once coral reefs experience lowered calcification and poor cementation, erosion and reef flattening can result, which severely reduced the structural heterogeneity of reefs and lowers its potential to support biodiversity. An important new study of reef bioerosion determined that the combined effects of lower calcification with increased bioerosion can significantly degrade coral reefs (Wissshak et al. 2012). In the study, a common bioeroding sponge in the Great Barrier Reef was observed on massive *Porites*. The sponge was more effective at bioerosion of the corals at high CO₂, ranging from 17% increase from present day levels to 61% increase at the highest CO₂ treatment. The researchers describe the important role of balancing the antagonistic processes of calcification and bioerosion in a reef for a healthy coral ecosystem, and predict detrimental consequences under ocean acidification as calcification declines and bioerosion increases.

Bioerosion may result in a loss of change in fish assemblages, lower densities of commercially important species, and lower rates of larval fish recruitment (Feary et al. 2007). Weaker reef calcification and cementation also increases the potential for reef damage as storm frequency and intensity increases with continued global warming, leading to further reef degradation (Id.). In a study looking at the impacts of storm damage and ocean acidification, researchers concluded that table coral populations are vulnerable to collapse (Madin et al. 2012). In the Indo-Pacific, table corals provide an important role in the reef ecosystem by creating reef structure and sheltering other reef species. They are also particularly vulnerable to ocean acidification, thermal stress, bleaching, disease and stress from storm waves. The table corals will become more vulnerable to storm waves as ocean acidification reduces calcification and increases bioerosion, therefore weakening their cementation and structure. Madin et al. (2012) found that a coral colony was four times more likely to be dislodged by a storm wave by the end of the century ocean acidification levels. Because of this vulnerability, the results showed that table corals are prone to large and rapid declines in coral cover.

Numerous biological responses independent of calcification are also negatively impacted by ocean acidification. Corals in acidifying waters are likely to be in a nutritionally or energetically stressed state and thus less likely to initiate reproduction, or successfully reproduce, due to negative impacts of ocean acidification on all stages of the reproductive cycle (Maier et al. 2009; McCulloch et al. 2012). Sperm flagellar motility also declines in response to decreasing pH. If sperm lose their ability to find eggs in the vast extent of the sea, the life of marine organisms is potentially limited. Sperm flagellar motility, which is indispensable for fertilization, is regulated by an elevation of intracellular sperm pH (Morita et al. 2010). While 69% of *Acropora* sperm were motile at pH 8.0, 46% were motile at pH 7.8, and fewer than 20% at pH 7.7 (Id.). Additionally, the

physiological costs associated with reproduction are more likely to result in the demise of the organism due to the compounding stressors from ocean acidification and climate change (Wood et al. 2008, Cohen & Holcomb 2009). Significant reductions in metabolism have been observed for coral larvae following exposure to waters with a 0.2 decline in pH, levels projected to occur by the middle of this century (Albright & Langdon 2011).

Albright et al. (2010) concluded that with increased CO₂ concentrations to those projected to occur in this century (560 atm to 800 atm, or a 0.3 to 0.5 decline in pH from pre-industrial values), the fertilization success of the tropical reef-building coral *Acropora palmata* decreased by 12-13%, settlement success reduced 45-69%, and linear extension was significantly reduced. The compounding effect of these impacts translated to 52-73% reduction in the number of larval settlers on the reef. Albright et al. (2010) predicted that the net impact on recruitment would actually be greater than that given that the depressed post-settlement growth is likely to result in elevated rates of post-settlement mortality. This corroborates other studies showing negative impacts on early-stage tropical corals.

Albright and Langdon (2011) tested the effects of ocean acidification on sexual recruitment of tropical corals. Larval metabolism was depressed by 27% at acidification levels expected by mid-century (0.3 pH reduction) and 63% at end-of-century acidification levels (0.4-0.5 pH reduction). Settlement was also reduced 42-45% and 55-60% at the mid and end-of-century levels respectively, relative to controls (Albright & Langdon 2011). Another study of larvae of tropical corals showed that short-term or long term exposure of larvae to ocean acidification decreased their metamorphosis (Suwa et al. 2010). This means that even when larval survivorship is unchanged, the success of recruiting new corals could be inhibited by ocean acidification (Id.). Additionally, under conditions of acidification planktonic larvae lose their preference for settlement on the optimal crustose coralline algae communities (Doropoulos et al. 2012). Crustose coralline algae in turn, will experience a lower recruitment rate as marine waters become more acidic. Crustose coralline algae, a red calcifying algae, is of key importance in coral reef ecosystems, stabilizing reef structures and providing an important food source for benthic organisms (Convention on Biological Diversity 2009). Crustose coralline algae form a major calcifying component of the marine benthos from polar to tropical regions and are considered to influence the settlement of coral recruits. With a mean pH change of 0.26 between control and treatment, Kuffner et al. (2007) found that crustose coralline algae growth rates declined by 40%, and recruitment rate and percentage cover decreased by 78% and 92%, respectively.

In sum, reproduction is critical to maintaining a healthy population, and the long-term impacts of ocean acidification on reproduction, especially on larval settlement and growth, may significantly reduce the corals' ability to recover or maintain a population in the face of human caused disturbances and anthropogenic CO₂ emissions. This would result in a lack of reproductive capacity, genetic bottlenecks, and population collapse (Dupont et al. 2010; Ross et al. 2011).

As the world's oceans become more acidic and less saturated with carbonate minerals, corals are expected to build weaker skeletons and experience slower growth rates, which will make it more difficult for corals to retain competitive advantage over other marine organisms (Guinotte et al. 2006). As coral skeletons weaken, they will become increasingly at risk of storm damage and bioerosion, which will reduce the structural complexity of the reef system, reducing habitat quality and diversity alongside the loss of coastal protection functions (Hoegh-Guldberg et al. 2007). At greater than 550 ppm, coral reef ecosystems will be reduced to "crumbling frameworks." (Id.). Extensive studies have demonstrated that changes of only 0.2 pH will cause a suite of negative impacts, from reduced calcification rates to lowered reproductive success.

ii. Molluscs, Echinoderms, and Crustaceans

Molluscs, echinoderms, and crustaceans are also negatively impacted by ocean acidification. Ocean acidification not only impairs their ability to calcify, but affects reproduction and larval development (Pörtner et al. 2004).

In response to reported shellfish hatchery problems in Oregon, Barton et al. reported the results of their observations from the Whiskey Creek Hatchery on Netarts Bay in the summer of 2009 (Barton et al. 2012). Unlike previous laboratory experiments, this study analyzed calcifying organism responses in the naturally fluctuating ambient-water CO₂ chemistry of Oregon's coastal upwelling system. Larval production and mid-stage growth (~120 um to ~150 um) of the oyster, *Crassostrea gigas*, were both significantly negatively correlated with the pH of waters in which larval oysters were spawned and reared for the first 48 hours of life. These waters ranged in pH from 7.6 to 8.2. Although the impact of the exposure was not immediate, the delayed reaction caused a significant decline in growth for mid-sized oyster larvae and reduced overall production. The findings corroborate other laboratory studies that show that many marine species, especially at the larval stage, are adversely affected by ocean acidification.

Scientific studies have demonstrated that even modest pH declines affect the sensitive and vulnerable early developmental stages of organisms because these life histories have specific environmental needs (Kurihara 2008)(see Figure 10, below, showing negative effects from low pH treatments). A number of studies have found a delay in development or less development, degraded shells, decreased rate of metamorphosis, shell thickness, and loss of hinge integrity (Ross et al. 2011a). The resulting reduced larval size can reduce the feeding efficiency of larvae, and smaller larvae are more susceptible to starvation because they encounter comparatively less food (Kurihara & Shirayama 2004). Sub-lethal effects of elevated acidity can severely alter the composition and fitness of larvae, and given the high mortality rates of larvae in the water column and during the transition to benthic settler, small perturbations to larvae potentially may have large alterations to settlement dynamics, post-settlement mortality, recruitment, and ultimately adult populations (Ross et al. 2011).

Watson et al. (2009) exposed one day-old oyster larvae to a range of pH conditions, from 7.6 to 8.1, for 10 days and showed significant decline in the survival and growth of young larvae at lower pH. Waldbusser et al. (2010), in a study on the Chesapeake Bay, showed that even modest changes in pH present conditions that are corrosive to shells and have physiological impacts on adult and larval oysters. Biocalcification declined significantly with a reduction of 0.2 pH units, making juvenile bivalves more susceptible to predation and other mortality factors (Id.). Negative effects have been seen on the metamorphosis, size, and survival of larval hard clams (*Mercenaria mercenaria*), bay scallops (*Argopecten irradians*), and Eastern oysters (*Crassostrea virginica*) at levels of CO₂ predicted to occur in the 21st century (Talmage & Gobler 2011). At 650 ppm, or an approximate drop of 0.3-0.4 from pre-industrial values, both *M. mercenaria* and *A. irradians* larvae exhibited dramatic declines (over 50%) in survivorship as well as significantly delayed metamorphosis and significantly smaller size. *C. virginica* also experienced lowered growth and delayed metamorphosis at this level, an indicator that current and future increases in CO₂ populations may deplete or alter the composition of shellfish populations in coastal ecosystems (Id.).

The Olympia oyster, *Ostrea lurida*, a foundation species in estuaries along the Pacific coast, exhibits clear decline in larval growth and settlement as pH declines (Hettinger et al. 2012). Oysters in this experiment were raised at three levels of seawater pH, including a control (8.0) and two additional levels (7.9 and 7.8). Larvae reared under pH 7.8 exhibited a 15% decrease in larval shell growth rate, and a 7% decrease in shell area at settlement, compared to larvae reared under control conditions. Impacts were even more pronounced a week after settlement, with juveniles that had been reared as larvae under reduced pH exhibiting a 41% decrease in shell growth rate. Oysters on the Atlantic coast also experience the ill effects of ocean acidification. Dickinson et al. (2012) found negative effects on juvenile eastern oysters after exposure to water with a 0.2 pH change. Exposure of the oysters to elevated acidity led to a significant increase in mortality, reduction of tissue energy stores and negative soft tissue growth, indicating energy deficiency. At low pH levels, thermal tolerance is impaired in oyster larvae, leading to reduced development, size and increased abnormality (Ross et al. 2011; Parker et al. 2010). Similar results have been found in red abalone, with thermal tolerance impaired at pH 7.87 compared to control (pH 8.05) (Zippay and Hoffman 2010).

In studies with edible mussel (*Mytilus edulis*) and Pacific oyster (*Crassostrea gigas*) researchers found a strong decline of calcification as pH decreased (Gazeau et al. 2007). Based upon these results, researchers concluded that mussel and oyster calcification may decrease by 25% and 10%, respectively, by the end of the century,” when pH has fallen by 0.3 units (Id.). Oysters and mussels also exhibit development abnormalities when exposed to low pH (Kurihara 2008). When oyster eggs were reared under pH 7.8, they showed malformations of their shell, and when reared under pH 7.4, more than 70% of the larvae were either completely non-shelled, or only partially shelled, and only 4% of CO₂ treated embryos developed into normal larvae by 48 hours after fertilization, in contrast to about 70% successful development in control embryos.

The shrimp *Palaemon pacificus* displayed variable responses at different developmental stages, pH and length of exposure (Kurihara 2008). Following long term (30 weeks) exposure of adults to pH 7.89 and 7.64, survival and egg production in early developmental stages decreased in both treatments. Findlay et al. (2010) found a slower rate of development of embryos in the common intertidal northern hemisphere barnacle *Semibalanus balanoides* with an estimated 19 days delay in reaching 50% hatching stage at pH 7.7. Other amphipods have exhibited metabolic changes in response to acidification levels greater than what is allowed under the federal criterion (Hauton et al. 2009).

Echinoderms exhibit delayed and asymmetrical development when exposed to acidified conditions. In the absence of adequate adaptation or acclimation, lowered pH levels will have a range of sub-lethal effects on sea urchins, brittlestar and seastar larvae from a range of geographical regions (Ross et al. 2011). Larvae of the ecological keystone brittlestar, *Ophiothrix fragilis*, either were abnormal, had altered skeletal proportions, or asymmetry during skeletogenesis, and there was a delay in development at pH levels of 7.9, or approximately 0.3 units below current surface levels (Gutowska et al. 2009). Other experiments on brittlestar in low pH waters resulted in dramatic results; acidification of 0.2 units induced 100% larval mortality within an eight day period. Control larvae showed 70% survival over the same period. Because the calcite skeleton of the larval brittlestar aids key functions such as feeding and vertical migration, and defense against predators, abnormal development of the skeleton will have drastic consequences for fitness. The developmental abnormalities may be exacerbated by temperature increases predicted for the end of the century; some scientists suggest that this may result in the disappearance of echinoderms from the surface oceans within the next 50-100 years (Ross et al. 2011a).

Reproductive success is compromised by ocean acidification. The fertilization rate of sea urchins decreases with increasing CO₂ concentrations (8.1 to 6.8 pH) (Kurihara 2008). In another sea urchin experiment utilizing six CO₂ concentrations, with a pH between 8.01 (control) and 6.83, cleavage rate, developmental speed, and larval morphology all declined with increased CO₂ concentration (Kurihara & Shirayama 2004). At a 0.2 change from control, effects could be seen on the morphology and development of the larvae, and these effects became more pronounced with greater pH changes (Id.)(see Figure 10, below). The authors concluded that “all the effects of raised CO₂ concentration observed in this study would have a negative impact on the survival of sea urchin embryos in their early life history.” A recent study showed that sea urchin sperm flagellar motility was significantly reduced when seawater pH decreased by .3 units, from 8.0 to 7.7 (Suwa et al. 2010). As discussed above, decreased flagellar motility has severe consequences for fertilization and subsequent population dynamics; if sperm lose their ability to find eggs, the population size will necessarily diminish.

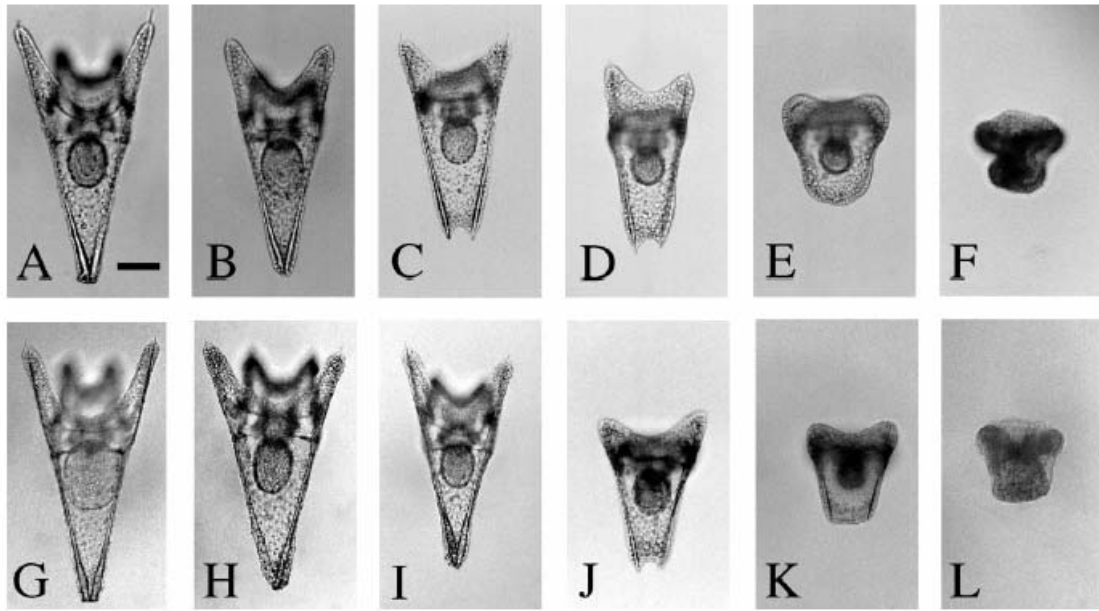


Fig. 6. *Hemicentrotus pulcherrimus*. Morphology of 4-armed pluteus larvae cultured for 3 d in (A–F) CO₂-seawater and (G–L) HCl-seawater. (A & G) control (pH 8.0); (B & H) +500 ppm (pH 7.8); (C & I) +1000 ppm (pH 7.6); (D & J) +2000 ppm (pH 7.4); (E & K) +5000 ppm (pH 7.0); (F & L) +10 000 ppm (pH 6.8). Scale bar = 50 μ m

Figure 10. Declining development of sea urchin larvae exposed to acidified waters (Kurihara & Shirayama 2004).

Even moderate increases in atmospheric CO₂ and ensuing acidification adversely affect the growth of both gastropods and sea urchins (Shirayama & Thornton 2005). Before the end of this century, atmospheric CO₂ is likely to increase by more than 200 ppm, decreasing the pH of the ocean by approximately 0.3 units from pre-industrial levels. Two species of sea urchin as well as the gastropod *Strombus luhanus* were exposed for six months to waters with this level of elevated CO₂, and all three species exhibited similar consequences. Increased CO₂ negatively affected growth rate, calcification, shell height and body mass, and metabolic activity (Shirayama & Thornton 2005). The developing embryos of the gastropod and intertidal snail *Littorina obtusata* also demonstrate slower overall development time, altered embryonic movement, and modification of shell shape in hatchlings while exposed to acidified waters (pH 7.6) (Ellis et al. 2009).

Arnold et al. (2009) investigated the effect of ocean acidification on lobsters and found that indirect disruption of calcification and carapace mass may adversely affect the competitive fitness and recruitment success of larval lobsters with serious consequences for population dynamics and marine ecosystem function. Even squid are not immune from increasingly acidic waters. Reducing pH by 0.3 pH caused a 31% decline in metabolic rate and a 45% decrease in activity level for the jumbo squid, an important predator in the Easter Pacific (Rosa & Seibel 2008).

Reduced metabolism is expected to impair predator-prey interactions, as well as have consequences for growth, reproduction, and survival. Metabolic suppression has

previously been reported to occur in a variety of adult marine invertebrates, including crabs, squid, worms, bivalves, pteropods and amphipods (Albright 2011). Slowed metabolism is generally achieved by halting energy-expensive processes, such as protein synthesis, and therefore may lead to reductions in growth and reproductive potential (Id.). The blue mussel *Mytilus edulis* has strong physiological mechanisms by which it is able to protect body tissues against short-term exposure to acidified seawater, but these come at an energetic cost, and will result in reduced growth during long term exposures (Bibby et al. 2008). Consequently, the predicted long-term changes to sea water are likely to have a significant effect on the health and survival of blue mussel populations (Id.). Mussel beds are a dominant coastal habitat and provide food and structure for a diverse array of species in an otherwise physically stressful environment; any decline in their population structure will lead to a reduction in appropriate habitat for a myriad of other species.

In summary, acidified waters impact the development, growth, and reproductive success of a suite of echinoderms, crustaceans, and molluscs. A growing body of information is becoming available on the effecting of declining pH on these organisms and their ecosystems. The results of these studies are clear; as pH falls even 0.2 units from pre-industrial values, these organisms will struggle to survive in their increasingly acidic environment.

iii. Plankton

Plankton, which comprise the basis of the marine food web, are among the calcifying organisms adversely affected by ocean acidification. Changes to calcifying zooplankton, such as pteropods and foraminifera, have the potential to affect the ecological and trophic dynamics which govern the exchange of energy and cycling of nutrients throughout the marine food web (Gattuso & Hansson 2011). For example, the shelled pteropod, *Limacina helicina*, an Arctic pelagic mollusc, is a food source for higher predators such as fishes, whales and birds that are particularly important in high latitude areas.

Studies have shown that pteropods exposed to a pH value predicted for the end of this century exhibited a 28% decrease in calcification (Comeau et al. 2009). Experiments on *Limacina helicina* showed that changes from 8.05 pH to 7.89 pH (Δ -0.16 units) caused shell dissolution and cracks appeared at 7.76pH, and linear extension of the shell decreased as a function of declining pH (Comeau et al. 2012). Pteropods form integral components of food webs, and are considered an overall indicator of ecosystem health (Orr et al. 2005). The pteropod *Clio pyramidata* kept in aragonite undersaturated waters began to dissolve within two days (Orr et al. 2005). A decline of pteropod population would likely cause dramatic changes to various pelagic ecosystems, and impact the commercially important salmon fishery.

Some coccolithophorids are also susceptible to ocean acidification. Studies showed that carbon dioxide related changes to seawater caused reduced calcification, resulting in malformed and incomplete shells. Calcification of coccolithophorids declined

15-44%, and their shells were malformed as pH changed up to about 0.3 units (Riebesell et al. 2000). Coccolithophorids are globally distributed and bloom in massive areas affecting the optical properties of the ocean, reflecting light from the earth, and play a major role in the ocean carbon cycle.

Elevated carbon dioxide concentrations also reduce the shell mass of foraminifera (Kleypas et al. 2006). Modern shell weights of foraminifera in the Southern Ocean are 30–35% lower than those from preindustrial sediments, which is consistent with reduced calcification induced by ocean acidification (Moy et al. 2009).

Ocean acidification may already be increasing the toxicity of harmful algal blooms known as “red tides.” High CO₂ levels in seawater magnify the toxins of harmful algae. These toxic red tides poison shellfish, marine mammals, fish, and even cause paralytic shellfish poisoning in people. Some globally distributed diatoms produce a neurotoxin, domoic acid, which can result in human illness and even death. Studies of this genus *Pseudo-nitzsca* show that the toxicity of these diatoms increases significantly under ocean acidification conditions. A -0.5pH change caused toxin production in the diatoms to increase 4.2-fold and a -0.3pH unit change increased the toxicity 2.5-fold (Tatters et al. 2012). Already, these harmful algal blooms have been related to mass mortalities of fish and marine mammals and these studies suggest that the damage will become much worse.

iv. Fish

While lower pH values correspond to a decreased ability by calcifying organisms to build shells or skeletons from calcium carbonate, the negative physiological affects of ocean acidification are not confined to invertebrates. For example, the gametes, embryos, and larvae of vertebrates such as fish are vulnerable to changes in ocean chemistry and have shown impairments in their homing and predator/prey detection capabilities.

Laboratory experiments have shown that ocean acidification at levels expected to occur within this century impairs larval orange clownfish and damselfish sensory abilities and behavior, making it more difficult for them to locate suitable settlement sites on reef habitat and avoid predators. Specifically, ocean acidification disrupts smell, hearing, and behavior of larval orange clownfish, (Munday et al. 2009; Nilsson et al. 2012), making larval clownfish attracted to odors from predators and unfavorable habitat (Munday et al. 2010; Dickson et al. 2010). Olfactory cues that prompted avoidance or neutral behavior in controls (pH 8.15) stimulated strong preference behavior in larvae raised at pH 7.8, in addition to significant reduction in response to usually positive preferences. Ocean acidification also impairs the hearing capacity of larval clownfish, which is predicted to have negative effects on settlement success and survival (Simpson et al. 2011).

Similarly, research on six damselfish species found that ocean acidification impairs larval damselfish smell, vision, learning, behavior, and brain function, leading to higher risk of mortality. For example, in acidified waters, larval damselfish (1) become attracted to predator odors and display much riskier behaviors, making them more prone

to predation; two species suffered a five-fold to nine-fold increase in predation rate at CO₂ levels of 700 to 850 ppm, or 0.3 pH units below control (Munday et al. 2009; Ferrari et al. 2011); (2) cannot discriminate between habitat olfactory cues, making it more difficult to locate appropriate settlement habitat (Devine et al. 2011); (3) settle on the reef during dangerous times—the full moon rather than new moon—when they are more vulnerable to predation (Devine et al. 2011); (4) fail to visually recognize or evade important predator species; (5) cannot learn to respond appropriately to a common predator by watching other fish react or by smelling injured fish, unlike fish under normal conditions (Id.); and (6) suffer disruption of an important neurotransmitter which is thought to result in the sensory and behavioral impairment observed in acidified conditions (Nilsson et al. 2012).

As seawater becomes more acidic, changes in the oceans' acoustic properties may also affect marine mammals. Sound travels 70% further with the ocean pH change resulting from a doubling of preindustrial CO₂, a change which is expected to occur by midcentury (Brewer & Hester 2009). Marine mammals in particular will have to adapt their communications to an environment with higher background noise levels. While the precise impacts of acoustic changes are yet to be determined, a noisy ocean environment will undoubtedly affect the interactions between marine mammals such as whales and dolphins, shipping channels, and military sonar.

The scientific community has provided overwhelming evidence that changes of 0.2 pH will have serious negative consequences to marine aquatic life. Indeed, these changes are already occurring; according to one scientist, “adverse impacts of ocean acidification have begun to manifest in no uncertain terms.” (Abbasi & Abassi 2011). Meta-analyses suggest that the biological effects of ocean acidification are “generally large and negative.” (Kroeker et al. 2010). While there are still large unknowns on the biological consequences of ocean acidification, the science we have is clear: from shellfish to corals, and from pteropods to fish, our marine resources are threatened by the acidification of our ocean waters. In order to better understand this process and its biological effects, EPA must promulgate water quality criteria that measure parameters in addition to marine pH. Because “application of a pH criterion alone will be inadequate to monitor ocean acidification and its impacts on coastal marine ecosystems,” EPA must set additional criteria that will guide states in the setting their own state water quality standards (Ocean Carbon and Biogeochemistry Program 2009).

5. EPA is Failing its Duty Under the Clean Water Act to Protect Our Nation's Water

a. Clean Water Act Background

Congress enacted the Clean Water Act, 33 U.S.C. §§ 1251 et seq., with the express purpose of “restor[ing] and maintain[ing] the chemical, physical, and biological integrity of the Nation's waters.” 33 U.S.C. § 1251(a) (2008). According to the Supreme Court, the “Act does not stop at controlling the ‘addition’ of pollutants, but deals with ‘pollution’ generally . . . which Congress defined to mean the ‘manmade or man-induced

alteration of the chemical, physical, biological, and radiological integrity of water.” *S.D. Warren v. Maine Bd. of Env’tl Protection*, 126 S.Ct. 1843, 1852 (2006). The national goals of the Clean Water Act are to guarantee “water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation” and to promptly eliminate water pollution. 33 U.S.C. § 1251(a).

Toward those goals, the Clean Water Act requires that EPA publish and “from time to time thereafter revise” criteria for water quality accurately reflecting the latest scientific knowledge

(A) on the kind and extent of all identifiable effects on health and welfare including, but not limited to, plankton, fish, shellfish, wildlife, plant life, shorelines, beaches, esthetics, and recreation which may be expected from the presence of pollutants in any body of water, including ground water;

(B) on the concentration and dispersal of pollutants, or their byproducts, through biological, physical, and chemical processes; and

(C) on the effects of pollutants on biological community diversity, productivity, and stability, including information on the factors affecting rates of eutrophication and rates of organic and inorganic sedimentation for varying types of receiving waters.

33 U.S.C. § 1314(a)(1). EPA must also publish “and from time to time” revise information on four topics necessary to protection of water quality. The publication of this information is critical because it provides states with the necessary information to evaluate the needs of the waters in their jurisdiction, which may require modification of state water quality standard or pollution control requirements. 33 U.S.C. § 1314(a)(2).

The national water quality criteria and information required by section 304 establish a baseline for nationwide implementation of the Clean Water Act. States must either adopt the national recommended water quality criteria in their water quality standards or provide a science-based explanation for their alternate criteria. 40 C.F.R. § 131.11(b) (“In establishing criteria, States should: (1) Establish numerical values based on: (i) 304(a) Guidance; or (ii) 304(a) Guidance modified to reflect site-specific conditions; or (iii) Other scientifically defensible methods”). EPA oversees water quality standards and must either approve the states’ standards or promulgate standards for that state guided by the national water quality criteria. Additionally, EPA uses the water quality criteria for promulgating federal water quality regulations under section 303(c) of the Clean Water Act.

State water quality standards are the foundation of the Clean Water Act and are at the heart of each strategy of pollution control under the Act. A water quality standard defines the water quality goals for a water body by “designating the use or uses to be made of the water and by setting criteria necessary to protect the uses.” 40 C.F.R. § 131.2. Accordingly, water quality standards designate specific uses for each water body

and set narrative or numeric criteria for the water that will support those designated uses. Id. at § 131.3(b) & (f). Water quality standards include all numeric criteria, narrative criteria, waterbody uses, and antidegradation requirements. 40 C.F.R. § 130.7(b)(3). In specifying the uses and criteria for a water body, the standards must take into account the water's "use and value for public water supplies, propagation of fish and wildlife, recreational purposes, and agricultural, industrial, and other purposes...." 33 U.S.C. § 1313(c)(2).

State water quality standards are important in developing regulatory controls on the discharge or release of pollutants. For example, water quality standards are transformed into individual point source obligations through NPDES discharge permits, which requires polluters to obtain permits and adhere to effluent limitations and technology controls necessary to meet water quality standards. 33 U.S.C. §§ 1342, 1311. Section 401 requires applicant for any federal permit or license to obtain state certification that the permitted activity will comply with state water quality standards. 33 U.S.C. § 1341.

Relevant here, state water quality standards are used to determine whether a water body is "impaired" for failing to meet an applicable standard. Section 303(d) of the Clean Water Act requires states to establish a list of impaired water bodies within their boundaries for which existing pollution controls "are not stringent enough to implement any water quality standard applicable to such waters." 33 U.S.C. § 1313(d). States must conduct a water quality assessment and list of impaired waters every other year. 40 C.F.R. § 130.7(d). Once a water body is listed as impaired pursuant to Clean Water Act § 303(d), the state has the authority and duty to control pollutants from all sources that are causing the impairment. Specifically, the state or EPA must establish total maximum daily loads of pollutants that a water body can receive and still attain water quality standards. 33 U.S.C. § 1313(d). States then implement the maximum loads by controlling pollution from point sources and nonpoint sources. The goal of section 303(d) is to ensure that our nation's waters attain water quality standards whatever the source of pollution.

Section 304 criteria and guidance are at the very heart of protection of water quality across the nation. The result is that the national water quality criteria set the lower limit for water quality standards. When the federal criteria are outdated, water quality throughout the nation suffers.

b. EPA Must Publish Additional Water Quality Criteria To Address Ocean Acidification

The Center for Biological Diversity formally requests that EPA initiate a rulemaking pursuant to the Clean Water Act, 33 U.S.C. 1314(a)(1), to promulgate new water quality criteria for ocean acidification. Additional criteria, acting in concert with the already existing marine pH criterion, will more effectively address water quality threats posed by ocean acidification. Accordingly, we petition EPA to publish the following criteria for marine waters:

- 1) Aragonite saturation state (Ω_{ar}) shall not fall below 1.0, or for marine waters with tropical corals aragonite saturation state shall not fall below 3.3; and
- 2) Calcification rates for target calcifiers should not measurably decline.

If EPA should decline to adopt some of all of these specific criteria, the Center alternatively requests that EPA promulgate water quality criteria for ocean acidification that are scientifically defensible.

Federal water quality criteria published under Section 304 of the Clean Water Act serve an important regulatory function. They provide guidance to states and tribes in the development and adoption of water quality standards that protect the designated uses for their waters. *See National Recommended Water quality Criteria for the Protection of Human Health*, 68 Fed. Reg. 75507, 75509 (Dec. 31, 2003). States must revise their water quality criteria to reflect changes in the published section 304 guidelines. *See, e.g.*, 63 Fed. Reg. 67548 Part III (1998). Therefore, the federal criteria form an important baseline in the nationwide implementation of the Clean Water Act.

In 1976, EPA published the “Red Book” which contained the water quality criteria for pH in marine waters. It provides that pH “should not be changed more than 0.2 units outside the naturally occurring variation or in any case outside the range of 6.5 to 8.5.” (Quality Criteria for Water 1976: 342-43). The EPA recently reaffirmed this federal water quality criterion for its applicability to ocean acidification. In 2009, EPA published a notice in the Federal Register of its intent to “review the current aquatic life criterion for marine pH to determine if a revision is warranted.” EPA received over 17,000 comments expressing support for EPA to take immediate action; however, EPA ultimately decided not to modify the marine pH water quality criterion.

While the current marine pH water quality criterion can be used to detect ocean waters impaired by ocean acidification, as recognized by EPA, scientists have identified additional seawater chemistry parameters that are useful for monitoring ocean acidification (National Research Council 2010). Furthermore, while all coastal states have water quality standards for marine pH, many states have inconsistent standards. Additional water quality criteria that are exacting for ocean acidification are needed because they will help states and EPA monitor and detect ocean acidification.

New water quality criteria for ocean acidification can be useful for areas with information gaps about naturally occurring pH conditions. Whether or not a threshold for aragonite saturation is being attained can be determined even without information about historic conditions. In contrast, EPA’s marine pH criterion, that pH should not be changed more than 0.2 units from the naturally occurring variation, is useful for measuring ocean acidification; but it requires knowledge of pH conditions absent anthropogenic pollution. This has limitations because many states claim that they lack fine-scale, long-term pH monitoring. Moreover, seawater pH is very sensitive to

temperature, and temperature is not always recorded or measured at sufficient accuracy to constrain the pH measurement. Even though it is possible to model historic pH conditions and to understand long-term trends from historic pH monitoring, new standards could prove easier to implement.

New biological criteria for ocean acidification will also facilitate better water quality assessments than existing standards, which generally protect aquatic life beneficial uses. Biological criteria can be very effective because they provide quantifiable objectives to protect aquatic life uses. For example, EPA advises that states may benefit from developing biocriteria for coral reefs because they:

- a) directly assess impairments in ambient biota from adverse impacts on the environment;
- b) are defensible and quantifiable;
- c) document improvements in water quality resulting from agency action;
- d) reduce the likelihood of false positives;
- e) provide information on the integrity of biological systems that is compelling to the public.

(EPA, *Coral Reef Biological Criteria*, 2010.)

Water quality criteria that are specific to ocean acidification can help states and EPA develop appropriate monitoring programs. The National Research Council recommends monitoring of several seawater chemistry parameters as well as biological indicators (National Research Council 2010). By defining new water quality criteria specific to ocean acidification, states will be better informed about which parameters they should be monitoring to understand how ocean acidification is affecting seawater quality. Then states can develop good monitoring programs that are useful for biennial water quality assessments. This will also help to harmonize water quality monitoring among coastal states to better understand regional trends.

Finally, the Clean Water Act was established to respond to new water quality problems. The intent of Congress to keep standards updated was clear when it directed EPA to review and revise water quality criteria periodically. This allows for water quality criteria to respond to new scientific advancements in either the understanding of a pollutant's impacts or to new pollutants. Here, new information on the impacts of carbon dioxide pollution has triggered EPA's duty to public additional water quality criteria because the "latest scientific knowledge" derogates the sole reliance upon pH for measuring ocean acidification. 33 U.S.C. § 1314(a)(1). Because additional water quality criteria acting in concert with the 0.2 pH criterion would be more effective in preventing harmful biological effects, EPA must promulgate water quality criteria to measure ocean acidification and guide states in setting protective water quality standards. Additional water quality criteria can be used to more effectively measure and monitor ocean acidification and will provide states with the tools under the Clean Water Act to prevent ocean pollution.

i. The Latest Scientific Knowledge Supports Promulgation of Additional Criteria

Section 304 of the Clean Water Act requires the EPA to publish and revise “water quality criteria “from time to time” to “accurately reflect the latest scientific knowledge.” 33 U.S.C. § 1314(a)(1). As presented herein, the promulgation of new water quality criteria, in addition to the marine pH criterion, will more effectively protect marine life from the adverse effects of ocean acidification. Pursuant to its duties under the Clean Water Act, EPA must consider this new information and consequently update the national water quality criteria to reflect the latest scientific information.

The water quality criteria must reflect the latest scientific knowledge related to the effects of pollutants on, *inter alia*, “plankton, fish, shellfish, wildlife, plant life, shorelines, beaches, esthetics, and recreation” and human health. 33 U.S.C. § 1314(a)(1)(a). The criteria must also reflect the latest scientific knowledge “on the concentration and dispersal of pollutants, or their byproducts, through biological, physical, and chemical processes; and . . . on the effects of pollutants on biological community diversity, productivity, and stability.” 33 U.S.C. § 1314(a)(1)(b)-(c). In light of recent information demonstrating that marine pH alone is a less effective metric to evaluate the impacts of ocean acidification, EPA must promulgate criteria on alternative ocean acidification parameters.

Scientists recognize that using a single criterion is difficult to gauge the effects of ocean acidification and effectively protect marine organisms. “Application of a pH criterion alone will be inadequate to monitor ocean acidification and its ecological impacts.” (Ocean Carbon and Biogeochemistry Program 2009). A pH change of 0.2 is seen as a guardrail for the harmful impacts of ocean acidification (Schubert & Németsország, 2006), but it has also been brought into question with regard to the latest scientific research (Zeebe et al. 2008: “These standards must be reevaluated based on the latest research on pH effects on marine organisms.”). Not only does a 0.2 unit pH criterion provide organisms with a poor buffer from the detrimental effects of acidification, as detailed above, there are technical and historical reasons for the inadequacy of the criterion. “Showing that a waterbody is more than 0.2 units outside of its ‘natural’ range requires being able both to document the present day pH with specificity (a technical hurdle), and to put that measurement in the context of its historical variation (the more significant hurdle).” (Kelly & Caldwell 2012), *see also* (Ocean Carbon and Biogeochemistry Program 2009) (“Although pH in seawater has been measured for many decades, a reliable long-term trend of ocean water pH cannot be established due to data quality issues, in particular the lack of strict and stable calibration procedures and standards.”). Because there are few baseline data on historical marine pH, it is exceedingly difficult to demonstrate departures from the past range of a particular waterbody. Consequently, scientists and policy makers are asking “whether alternative forms of water quality standards might better defend existing designated uses.” (Kelly & Caldwell 2012).

The latest science knowledge supports promulgation of additional criteria, and federal and state policymakers are awaiting EPA action on this issue. In the 2010 memo from EPA to states regarding the use of 303(d) lists to address ocean acidification, EPA acknowledged that marine pH is not an ideal parameter for measuring ocean acidification because of inadequate data on baselines and seasonal and diurnal variability. In spite of this, EPA stated that states must use marine pH as a proxy for ocean acidification “until additional ocean acidification criteria are adopted.” The implicit assumption in this statement is that additional federal criteria would be forthcoming. Now is the time to remedy the inadequacies in our federal criteria regarding ocean acidification.

Washington State’s Blue Ribbon Panel on Ocean Acidification recently voiced its desire for EPA to publish additional federal criteria. This panel, convened at the request of the governor and consisting of experts in the scientific community as well as representatives from industry and state government, concluded that while “pH is the only water quality criteria that can be readily associated with ocean acidification. . . recent scientific research suggests that other ocean chemistry parameters and biological indicators may be relevant to local acidification.” (Blue Ribbon Report: 49). Therefore, EPA should “**evaluate the applicability of other water quality criteria** identified by recent research or recommended by scientific experts in the fields of ocean acidification and water quality.” Id. (emphasis added). With regards to Washington’s oyster industry, the panel concluded that additional monitoring criteria would better protect the industry from future crises:

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.

(Blue Ribbon Report: 70)(emphasis added).

In a letter to Nancy Stoner, Acting Assistant Administrator for the Office of Water, EPA, the Director of Washington’s Department of Ecology, Ted Sturdevant, highlighted the inadequacies of a pH standard for identifying water quality impacts due to ocean acidification. Relevant here, the letter highlights the recommendations of the Blue Ribbon Panel to chart a course for addressing the effects of ocean acidification on Washington’s shellfish resources and other marine organisms.

Scientific panel members pointed to recent scientific research suggesting that other ocean chemistry parameters and biological indicators may be more relevant to local acidification. Given the national significance of recommending water quality standards for identifying ocean acidification impacts, it was **recommended that US EPA should take the lead in evaluating the applicability of other water quality criteria** identified by

recent research or recommended by scientific experts in the fields of ocean acidification and water quality.

(Emphasis added). EPA's failure to take any affirmative steps towards promulgating additional acidification criteria leaves states without the necessary guidance to fulfill their duties under the Clean Water Act.

States have an independent obligation to protect water quality under the Clean Water Act, yet states that might otherwise begin revising their water quality standards as part of their triennial review are foregoing that process in the belief that EPA is addressing the issue at a national level. Washington has indicated that the state's work in developing additional water quality criteria for ocean acidification has been "preempted" by the Blue Ribbon Panel, which has, in turn, asked EPA to take the lead in evaluating the applicability of additional water quality criteria. Susan Braley at Washington Department of Ecology explained the state's position in an email dated January 11, 2013:

[T]he Blue Ribbon Panel work and Governor Gregoire's Executive Order 12-07 on ocean acidification has somewhat preempted our anticipated work as part of the triennial review. As you may be aware, one of the recommendations of the Panel was to ask EPA at the national level to take the lead in evaluating the applicability of water quality criteria for identifying impacts from ocean acidification and developing nationally recommended criteria if needed. . . . We will be following closely the efforts of EPA to develop criteria for ocean acidification and will be involved where we can provide regional or state specific expertise and background on these issues.

Therefore, not only does the scientific consensus command the promulgation of additional criteria, but EPA's inaction on this issue is obstructing otherwise viable efforts by states to address ocean acidification.

ii. New Water Quality Criteria Will Better Protect Marine Life from Ocean Acidification

The scientific literature has established that multiple criteria will more effectively measure and monitor the effects of ocean acidification. (Ocean Carbon and Biogeochemistry Program 2009) ("Application of a pH criterion alone will be inadequate to monitor ocean acidification and its ecological effects."). We request rulemaking for additional water quality criteria. While we acknowledge the regional chemical and biological variation inherent in ocean waters, effective national criteria exist that will set important thresholds independent of location. We suggest that EPA publish criteria establishing that for marine waters,

1) Aragonite saturation state (Ω_{ar}) shall not fall below 1.0, or for marine waters with tropical corals aragonite saturation state shall not fall below 3.3; and

2) Calcification rates for target calcifiers should not measurably decline.

If EPA should decline to adopt some of all of these specific criteria, the Center alternatively requests that EPA promulgate water quality criteria for ocean acidification that are scientifically defensible.

These suggested criteria provide two parameters, one chemical and one biological, by which states can measure and monitor the threats of ocean acidification.

1. Aragonite Saturation State

Experimental studies have demonstrated that it is the saturation state (Ω) rather than the pH that controls the response of many calcifying organisms. (Langdon et al. 2003; Meissner et al. 2012). In particular, scientists have identified the aragonite saturation state (Ω_{ar}) as being particularly indicative of ocean acidification's effects on marine organisms. (Barton et al. 2012). Because application of a pH criterion alone is less effective in monitoring ocean acidification and its ecological impacts, the scientific community supports the adaptation of an aragonite saturation state criterion in order to more successfully prevent ocean pollution (Ocean Carbon and Biogeochemistry Program 2009).

As anthropogenic CO₂ is absorbed by seawater, chemical changes occur that increase the CO₂ partial pressure and reduce both seawater pH and the concentration of carbonate ion. The loss of carbonate ions produce lower saturation levels for the carbonate minerals, aragonite and calcite, which are the primary mineral phases of the shells and skeletons of many marine plants and animals. Models predict that under the continuously increasing CO₂ emissions scenario, Southern Ocean surface waters begin to become undersaturated with respect to aragonite by the year 2050. In the Arctic Ocean, one model predicts that such undersaturation will occur as early as 2016 during one month per year in 10% of the Arctic. In addition, the aragonite saturation horizon (the interface between understaturated waters below and supersaturated waters above) will move upward (shoal) throughout the ocean (Comeau et al. 2012).

Of even more immediate concern is the rate at which aragonite saturation state is declining in certain areas, such as along the West Coast of the United States, where mixing processes, upwelling, and colder temperatures naturally precondition the water column to have lower saturation state values (Fabry et al. 2008; Feely et al. 2010). Recent observations in the sub-Arctic North Pacific Ocean have revealed areas of seasonal undersaturation throughout the water column, while models predict widening areas of aragonite saturation in the coming decades (Mathis et al. 2011b). Along with parts of the Arctic, seasonal upwelling of undersaturated waters occurs along the West Coast of the United States and has negative ramifications for the marine ecosystems and the multifaceted economies that depend on them (Feely et al. 2008).

The saturation state of aragonite directly affects the ability of calcium carbonate secreting organisms to produce their shells or skeletons. When seawater is supersaturated with respect to aragonite and calcite (saturation levels are greater than 1), calcification is favored more than dissolution (Feely et al. 2009; Miller et al. 2009: “ Ω is therefore a proxy for the ease with which organisms can produce calcium carbonate”). Below Ω_{ar} 1.0, a wide array of organisms experience a severe negative response. Oysters, mussels, and clams all show negative responses to lowered aragonite saturation state values, with larvae the most susceptible developmental stage of marine bivalves. (Barton et al. 2012). Barton et al. reported the results of their observations from the Whiskey Creek Hatchery on Netarts Bay in the summer of 2009 (Barton et al. 2012). Unlike previous laboratory studies, this study analyzed calcifying organism responses in the naturally fluctuating ambient-water CO_2 chemistry of Oregon’s coastal upwelling system. Larval production and mid-stage growth (~120 μm to ~150 μm) of the Pacific oyster, *Crassostrea gigas*, were both significantly negatively correlated with the aragonite saturation state of waters in which larval oysters were spawned and reared for the first 48 hours of life. The study demonstrated that during times of low aragonite saturation, larval oysters experienced adverse effects. Although the impact of the exposure was not immediate, the delayed reaction caused a significant decline in growth for mid-sized oyster larvae and reduced overall production. The findings corroborate other laboratory studies that show that many marine species, especially at the larval stage, are adversely affected by ocean acidification.

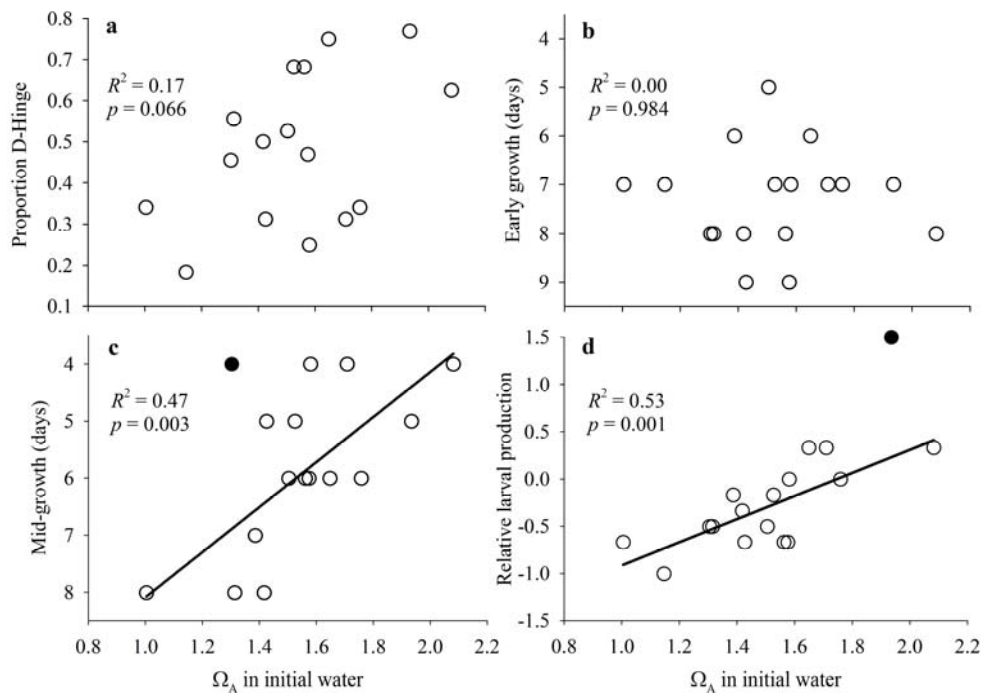


Figure 11. Relationship between saturation state of aragonite and a) proportion of larvae developing to D-hinge stage, b) number of days for larvae to reach a nominal 120 μm size, c) number of days for larvae to grow from 120 to 150 μm nominal size, and d) overall relative production of each cohort (Barton et al. 2012).

Laboratory studies show that calcification rates for the edible mussel and Pacific oyster decline linearly with increasing CO₂, and for the mussel, calcification ceases when aragonite saturation reaches 1.0 (Gazeau et al. 2007). For the Pacific oyster, calcification declines by more than 50% at the aragonite saturation horizon (Id.). Eastern oysters, bay scallops, and hard clams also experience pronounced negative effects on their survival as aragonite saturation falls below 1.0 (Talmage & Gobler 2009). For the Eastern oyster, the rate of oyster larvae metamorphosis is significantly delayed by exposure to undersaturated conditions – after two weeks, one third of oyster larvae exposed to current CO₂ conditions had fully metamorphosed, while only 3% had done so in undersaturated conditions (Id.). Likewise, only 2% of bay scallops survived to metamorphosis at undersaturated conditions (compared to 52% at control conditions); for the hard clams, fewer than 20% of larvae survived to metamorphose into juvenile clams, compared to 76% at the ambient, control treatment. Not only do undersaturated conditions affect the rate of metamorphosis and survivorship of larvae, but lower saturation state also leads to a significant reduction in size. The negative effects of elevated CO₂ on shellfish larvae extend beyond those observed during the experiment. For example, the delayed metamorphosis of shellfish larvae, and reduced size, would likely translate into prolonged predation and would further decrease survival of larvae in the field (Id.).

Pteropods and other plankton are also expected to be greatly affected by declining aragonite saturation state (Comeau et al. 2012; Bednarsek et al. 2012). Due to their sensitivity to undersaturated conditions, pteropods are considered a valuable bioindicator of future ocean acidification (Bednaršek et al. 2012; Orr et al. 2005). Because pteropods are widely distributed through all oceans and their vertical migrations can cover several hundred meters, they are major contributors to fluxes of calcium carbonate in the deep ocean, and are highly sensitive to changes in sea water chemistry because their external calcareous shells are made of aragonite. In a study that linked model projections for chemistry with laboratory data on pteropod calcification rates, scientists estimate that in parts of the Arctic pteropods will become unable to precipitate CaCO₃ during the second half of this century, when Ω_{ar} falls below 1.

Pteropods may be unable to maintain their shells in waters that are undersaturated with respect to aragonite (Orr et al. 2005). Data from sediment traps indicate that empty pteropod shells exhibit pitting and partial dissolution as soon as they fall below the aragonite saturation horizon. New experimental evidence suggests that even the shells of live pteropods dissolve rapidly once surface waters become undersaturated with respect to aragonite (Feely et al. 2004). When exposed for two days to waters undersaturated with aragonite pteropod shells show dissolution marks, casting additional doubt on their ability to achieve a positive balance between precipitation and dissolution of calcium carbonate (Orr et al. 2005). Without growing a protective shell, we cannot expect pteropods to survive in waters undersaturated with aragonite. As the aragonite saturation state shoals, pteropods might be exposed to increasingly corrosive waters during their daily vertical migrations, and may be forced to reduce their range both within the water column, and southwards towards waters with a naturally higher saturation state.

Even at levels above 1.0 Ω_{ar} , bivalves and other calcifiers show negative responses to lowered saturation state values (Barton et al. 2012). Recent studies have shown that the calcification rate of calcifiers, such as corals, coccolithophores, foraminifera and bivalves, decreases with increasing pCO_2 , even in seawater supersaturated with respect to calcium carbonate (Gattuso et al. 1998). In numerous species of corals, the relative rate of calcification relative to pre-industrial values sharply declines as aragonite saturation state is lowered, as illustrated in Figure 7.2 of Gattuso and Hansson (page 141). Other laboratory studies have demonstrated the negative consequences to food web dynamics as a result of a lowered aragonite saturation state (Kleypas et al. 2006).

However, regardless of whether calcification in marine organisms has been observed to increase in response to lowered Ω_{ar} , deposition of calcium carbonate is thermodynamically less favorable under such conditions. Some organisms may be able to up-regulate their metabolism and calcification to compensate for increased acidity of seawater. Nonetheless, this comes at a substantial energetic cost, energy that would otherwise have been spent on other essential processes such as protein synthesis, growth, and reproduction, and this upregulation is not sustainable in the long run. (Gattuso et al. 2009).

Scientists have suggested that EPA can take advantage of the empirical relationship between the gross calcification rates ($CaCO_3$ precipitation) and aragonite saturation state Ω_{ar} (Comeau et al. 2012). Others have noted that a linear relationship exists between aragonite saturation state and coral calcification rates. (Friedrich et al. 2012). Experiments that specifically control the concentrations of the various components of the carbonate system suggest that calcification responds to saturation state rather than pH or some other component of the surrounding seawater environment (Kleypas et al. 2006). Aragonite saturation state, coupled with pH, would therefore provide a more accurate measure of the biological response of many calcifying organisms to the effects of ocean acidification.

A federal water quality criterion which mandates that marine waters remain supersaturated with respect to aragonite would act as a geochemical threshold to guard against the worst effects of ocean acidification. While marine organisms exhibit negative responses to waters with aragonite saturation states *above* 1.0, establishing a federal water quality criterion at the threshold between undersaturated and saturated waters would provide a helpful benchmark to monitor unfavorable ocean conditions (Ocean Carbon and Biogeochemistry Program 2009) (“[m]any of the laboratory studies discussed above document biological sensitivity to reduced carbonate ion concentration simply when the extent of the calcium carbonate supersaturation is reduced, but remains well above 1.”).

Establishing an aragonite saturation state threshold of 1.0 would provide a certain level of protection to many calcifying organisms. However, corals are especially sensitive to the aragonite saturation state with a higher biogeochemical threshold. Many mesocosm studies show direct impact on coral reef calcification from lowering Ω_{ar} . Kleypas et al. (1999) compiled statistically derived environmental averages and extremes among

present day reefs and found a minimum average open ocean aragonite saturation of 3.28. Laboratory and field studies confirm that at aragonite saturation values of 3.3 tropical coral accretion approaches zero or becomes negative (Hoegh-Guldberg et al. 2007). These findings are supported by the fact that reefs with net carbonate accretion today are restricted to waters where aragonite saturation exceeds 3.3 (Meissner et al. 2012). Studies of shallow volcanic seeps in Papua New Guinea show that tropical reefs with high coral cover can still exist at seawater with 2.5 Ω_{ar} , but only with severe losses in biodiversity, structural complexity and resilience (Fabricius et al. 2011). Other investigations have defined classes for annual mean open ocean seawater aragonite saturations; over 4 being “optimal, 3.5-4 being “adequate,” 3-3.5 being “marginal,” and values below 3 being “extremely low.” (Guinotte & Fabry 2008). However, the general scientific consensus defines the minimum average value of 3.3 as the threshold for open ocean Ω_{ar} .

Aragonite saturation state “speaks directly to one of the more alarming biological effects of ocean acidification: shell dissolution that threatens key designated uses such as shellfish harvesting and marine habitat.” (Kelly & Caldwell 2012). Setting a water quality criterion at the aragonite saturation threshold, the point at which calcium carbonate shells begin dissolving in seawater, or at 3.3 for waters with tropical corals, gives water quality managers a standard that is easy to measure and that is relevant to both the chemistry and biology of ocean acidification. Monitoring and enforcing a pre-determined, quantitative threshold of aragonite saturation state, based upon the ecological response to ocean acidification, would allow EPA to further the Clean Water Act’s statutory purpose of “restor[ing] and maintain[ing] the chemical, physical and biological integrity of the nation’s waters.”

2. Calcification Rates of Target Calcifiers

EPA should promulgate a criterion that takes into account the growth rates of the calcifying organisms that are most affected by ocean acidification. Biological criteria, unlike numeric criteria, are based on the species inhabiting a waterbody and describe the biological condition of aquatic communities inhabiting those waters. Rather than applying a numeric water quality criterion to a system with naturally dynamic background chemistry, an impairment threshold can be set that is based upon the ecological response of a particular waterbody to ocean acidification. EPA has promulgated biological standards for other criteria, and has recognized the applicability of these types of standards to ocean acidification:

Biological standards, by tracking the condition of target organisms, establish a direct process to determine whether a waterbody is achieving its biological goals. Biocriteria are complementary--they do not supersede or replace physical and chemical criteria. Biocriteria may be particularly important for coral reefs because bioassessments reflect the integrated effects of multiple and cumulative stressors, detect impairment that might be missed by physical and chemical criteria (e.g., overfishing or habitat loss), resonate with managers and stakeholders, and have been found (at least in freshwater systems) to be cost effective.

(EPA, *Coral Reef Biological Criteria*, 2010).

Like nutrient loadings, where EPA recommends ecosystem effects-based criteria, ocean acidification operates against a background of naturally dynamic chemistry. “Marine pH is a regulatory challenge that is highly analogous to that of nutrient pollution, given the large spatial and temporal fluctuations in water chemistry that occur naturally. And because of the practical difficulty of testing the present water quality criterion for marine pH, establishing a more easily trackable, ecosystem-based criterion is an attractive idea.” (Kelly & Caldwell 2012).

Moreover, scientists are already measuring calcification rates in order to investigate the biological effects of ocean acidification. From corals (e.g., Kleypas, et al. 2006; Fabricius, et al. 2011; Albright 2011), to shellfish (e.g., Barton et al. 2012; Gazeau et al. 2007), to pteropods and echinoderms (e.g., Comeau et al. 2012; Kurihara 2008; Orr et al. 2005), scientists have developed the tools and know-how necessary to implement a criterion that requires careful monitoring of long term calcification trends. Furthermore, the “Guide to best practices for ocean acidification research and data reporting” describes the best practices for researching and reporting such biological responses to ocean acidification (Riebesell et al. 2010). For example, the study describes five methods that are in wide use for the study of calcification of benthic organisms, including buoyant weight of the organism, skeletal density banding, direct measurement of shell or skeleton weight, change in total alkalinity of the incubation water, and measurements of radioisotopes (Id.).

Regional variations in calcification rates and other ecological parameters make the process of establishing a national biological criterion related to ocean acidification difficult. However, as detailed in EPA’s Report on Coral Reef Biological Criteria, there are mechanisms for taking into account spatial and temporal variability (EPA 2010). EPA should mandate that states identify target calcifying species in order to monitor their calcification rates, or shell densities, to gauge the effects of ocean acidification of the waterbody in which they reside. Scientists at NOAA have recommended that biological criteria measure long-term regional changes in growth rates of target taxa in response to ocean acidification (NOAA 2012). When calcification rates, or calcium carbonate shell densities, reach a pre-determined, statistically significant deviation from the norm, the waters in which those organisms are found would be listed as impaired.

A biological criterion to measure ocean acidification could also be evaluated at the community scale. Studies conducted on calcifying communities in the natural environment or in experimental mesocosms have shown that there is a strong positive coupling between seawater carbonate saturation state and the net community calcification rate (Bates et al. 2010; Langdon & Atkinson 2005). The chemical threshold at which different systems become subject to net dissolution varies, but as calcium carbonate saturation states continues to decline, calcification will decrease and carbonate dissolution increase, potentially pushing calcifying systems past their critical thresholds and towards a condition of net dissolution (Gattuso & Hansson 2011). Measuring

calcification in the aggregate would allow water quality managers to account for differences in individual species response. For example, Andersson et al. (2009) observed marginal daily net dissolution in replicated subtropical coral reef communities incubated in continuous-flow mesocosms exposed to Ω_{ar} 1.4; while individual corals appeared healthy and continued to deposit calcium carbonate, other calcifiers were not as successful is dealing with high CO₂ conditions and were very negatively affected.

There has been a long-standing interest in biological criteria to characterize ecological conditions and to inform regulatory applications (*see, e.g., EPA, Coral Reef Biological Criteria*, 2010; EPA website). EPA has published technical reports on biocriteria for a variety of ecosystems; from lakes and streams, estuaries and coastal waters, to wetlands and coral reefs, biocriteria have proven effective in improving the health of our nation's waterbodies (*see EPA website*). While there may exist a variety of measurements to characterize ecosystem health in the face of ocean acidification, EPA has the capacity and the ability to develop biological indicators that effectively assess the effects of carbon dioxide pollution in the marine environment.

c. EPA Must Publish Guidance on Ocean Acidification

The Clean Water Act provides EPA with broad authority to take action on ocean acidification. EPA also has a duty to publish information on water quality. Accordingly, the Center for Biological Diversity officially requests that EPA publish information pursuant to Section 304(a)(2). Specifically, the EPA must:

Publish information to provide guidance on ocean acidification, including:

- **the factors necessary to prevent deleterious changes in seawater chemistry due to anthropogenic carbon dioxide emissions;**
- **the factors necessary to prevent adverse impacts of ocean acidification on fish, shellfish, and wildlife;**
- **the recommended methods for measuring ocean acidification parameters and considering data and information on ocean acidification; and**
- **recommendations for developing and implementing total maximum daily loads for ocean acidification.**

The Clean Water Act requires that EPA publish and “from time to time thereafter revise” information regarding four factors of water quality: (A) the maintenance of chemical, physical, and biological integrity of all of the nations waters; (B) the protection and propagation of fish, shellfish, and wildlife; (C) measurement and classification of water quality; and (D) which pollutants are suitable for measuring maximum daily loads related to water quality (33 U.S.C. § 1314(a)(2)). States require this information to adequately conduct their water quality assessments and to identify waters impaired by ocean acidification. In addition, the information may play a valuable role in the education of state personnel and for management of state water resources.

It is prudent for EPA to publish new information under section 304(a)(2) because of new scientific knowledge. The legislative history of the Act demonstrates that this provision of the Act was intended to provide up-to-date information as needed to protect water quality. When the Clean Water Act of 1977 was adopted by the Senate: “The Administrator is required to publish information on the factors needed to assure attainment of that degree of water quality. I sponsored the amendment [sections 304(a)(4)-(6)] requiring this because of the inadequacies of EPA’s earlier efforts under section 304(a)(2) of the 1972 law.” (95th Cong. Senate Debates 1977: 39197). Thus, the EPA has a non-discretionary duty to publish guidance information on ocean acidification.

The need for guidance on ocean acidification is clear for many reasons: (1) EPA already determined that ocean acidification guidance is warranted; (2) states rely on EPA for guidance about ocean acidification; (3) new scientific information about ocean acidification must inform state’s water quality protection programs; and (4) long-term water quality monitoring is needed to detect ocean acidification related problems. In order to comply with the Clean Water Act, and to fulfill the goals of its enactment, the information contained in this guidance should mirror the four statutory requirements of Section 304(a).

i. Guidance on Ocean Acidification Is Warranted

EPA has already determined that guidance on ocean acidification is warranted and has committed to publishing such guidance. On November 15, 2010, EPA issued a memorandum to provide tribes, states, and regions with assistance in preparing their integrated reports related to impacts of ocean acidification under sections 303(d), 305(b), and 314 of the Clean Water Act (Environmental Protection Agency 2010b). EPA affirmed that states and tribes have the authority to address ocean acidification under section 303(d) of the Clean Water Act. EPA acknowledged the seriousness of aquatic life impacts of ocean acidification and threat of ocean acidification as a water quality problem, and EPA concluded that

States should list waters not meeting water quality standards, including marine pH [water quality criteria], on their 2012 303(d) lists, and should also solicit existing and readily available information on [ocean acidification] using the current 303(d) listing program framework.

(EPA, *Memo*, 2010). EPA also recommended that states focus on vulnerable waters that are at risk from ocean acidification, including waters with coral reefs, marine fisheries, and shellfish resources.

In 2010, EPA committed to providing guidance on ocean acidification:

EPA will provide additional 303(d) guidance to the States when future [ocean acidification] research efforts provide the basis for improved monitoring and assessment methods...This future [ocean acidification]

guidance may be in the form of stand-alone [ocean acidification integrated report] guidance, or as part of EPA's routine, biennial [integrated report] update.

EPA's role in interpreting the Clean Water Act and assisting states and tribes with their water quality assessments as they relate to ocean acidification is vital. EPA has taken important steps forward in recognizing the water quality threat of ocean acidification. To further fulfill that role and its duties under the Clean Water Act, EPA must publish guidance on ocean acidification.

ii. States Need Ocean Acidification Guidance

EPA guidance on ocean acidification is necessary because states rely on such information in conducting their water quality assessments and preparing their lists of impaired waters. States and tribes are already responsible for evaluating information on ocean acidification, so the need for EPA guidance already exists. For example, in response to comments for their draft 2010 integrated reports numerous states – including Oregon, Maine, New Hampshire, New York, North Carolina, Rhode Island, and South Carolina – indicated that they anticipated EPA direction on the issue of ocean acidification. States need information pursuant to section 304(a)(2) on ocean acidification to (a) guide water quality standards; (b) improve monitoring and water quality assessments; and (c) reduce pollution causing ocean acidification.

While there is a national network of ocean observing systems, states either do not bother to gather such data or they don't know how to access these repositories of information.

iii. Significant Scientific Information Exists to Inform Guidance

The scientific understanding of ocean acidification has developed rapidly in recent years, and a vast body of scientific information is now available. The Clean Water Act requires that EPA and states take this new information into account. While some of the specifics about biological responses to ocean acidification are still being investigated, there is ample scientific information to develop meaningful guidance on ocean acidification. There is broad-based consensus among ocean acidification scientists that can serve as a foundation for EPA guidance. As detailed in this petition, there have been significant advancements in our understanding of the causes and impacts of ocean acidification. There are also well-defined methods for ocean acidification monitoring and research.

An evaluation of scientific articles, books, and book chapters about ocean acidification indicates a steep increase in research (Gattuso & Hansson 2011). From 1989-2003, there were an average of only nine articles per year, with 213 articles published in 2010 and accelerating in 2011 (Id.). Articles on the biological response to ocean acidification increased six-fold between 2004-2010 (Id.). There have also been significant contributions to ocean acidification science from federally funded programs

(Interagency Working Group on Ocean Acidification 2011). This includes monitoring ocean chemistry and biological impacts through observations, surveys and time-series; as well as research on key species, mesocosm studies, and ecosystem studies done in situ and in laboratory studies (Id.). As part of the Interagency Working Group on Ocean Acidification, EPA is well-aware of the significant advances in ocean acidification science and the well-established methods for monitoring and research.

Most importantly, at least two reports have addressed strategies for monitoring and research of ocean acidification. “Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean” discusses a strategy for monitoring waters, and “Guide to Best Practices in Ocean Acidification Research and Data Reporting” provides recommendations for methods for monitoring and researching the biological impacts of ocean acidification (National Research Council 2010; Riebesell et al. 2010). Monitoring and assessment methods are also described by the Ocean Carbon and Biogeochemistry (OCB) Program in its comments to EPA on the Notice of Data Availability and Notice of Call for Public Comment on 303(d) Program and Ocean Acidification (Ocean Carbon and Biogeochemistry Program 2009; Ocean Carbon and Biogeochemistry Program 2010). These important guidance documents can serve as a foundation for EPA guidance.

Finally, EPA guidance can and should be updated as new information arises. This is what the Clean Water Act requires. Section 304 demands that guidance mirror current scientific knowledge; it does not permit EPA to wait indefinitely for new science. 33 U.S.C. § 1314(a).

iv. Water Quality Assessments Should Gather Baseline and Impacts Information on Ocean Acidification

State water quality assessments provide an excellent opportunity to improve our scientific understanding of ocean acidification and monitor its impacts. In 2010, EPA recommended that states solicit information on ocean acidification and begin monitoring and assessing ocean acidification with a focus on vulnerable waters, such as those with corals, shellfish, and fisheries.

Yet, few states, if any, have experience monitoring and assessing the impacts of ocean acidification. EPA must provide guidance to ensure that states can fulfill this recommendation and comply with their obligations under the Clean Water Act to conduct biennial water quality assessments.

There is a need for more high-resolution, site-specific coastal data on ocean acidification. It is vital that states and tribes have information about how ocean acidification is affecting marine water quality and aquatic life uses. Enhanced monitoring and assessment of ocean acidification should be a high priority for EPA, as well as coastal states and tribes.

There is a critical need for long-term monitoring of ocean acidification to determine the environmental baselines and the impact of ocean acidification on seawater

chemistry and ocean ecosystems (National Research Council 2010). Guidance for states will encourage states to begin monitoring ocean acidification and such data can be used to develop baseline environmental information. Long-term monitoring is also important to detect changes in ocean chemistry and the biological impacts of ocean acidification. Accordingly, states have an important role to play in national water quality monitoring for ocean acidification.

v. Guidance Information

The Clean Water Act requirement that EPA publish and “from time to time thereafter revise” information regarding four factors of water quality provides a good roadmap for what should be included in EPA’s guidance on ocean acidification: (A) the maintenance of chemical, physical, and biological integrity of all of the nations waters; (B) the protection and propagation of fish, shellfish, and wildlife; (C) measurement and classification of water quality; and (D) which pollutants are suitable for measuring maximum daily loads related to water quality (33 U.S.C. § 1314(a)(2)).

Accordingly, the guidance should include information on (1) the impact of carbon dioxide on seawater chemistry; (2) the impacts of ocean acidification on fish, shellfish, and wildlife; (3) the recommended methods for measuring ocean acidification parameters and considering data and information on ocean acidification; and (4) recommendations for developing and implementing total maximum daily loads for ocean acidification.

1. Information about carbon dioxide’s impact on seawater chemistry

When addressing the requirements of Section 304(a)(2)(A), the EPA should publish information on ocean acidification, including an explanation of the effects of carbon dioxide emissions on ocean chemistry.

The guidance should explain that ocean acidification is caused by anthropogenic CO₂. As discussed above, the scientific literature provides extensive evidence that anthropogenic carbon dioxide emissions are the direct cause for the precipitous decline in ocean pH that has occurred since beginning of the industrial revolution. Atmospheric CO₂ is at ~392 ppm and worldwide emissions continuing to increase by more than 2 ppm each year (<http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>). Guidance should explain the process of ocean acidification (*see e.g.*, Kleypas et al. 2006). It should describe the changes that have already occurred, for example that pH has declined by about 0.1 units on average since the beginning of the industrial (Caldeira & Wickett 2003). It can draw on section 4(a), above, which describes the chemical ocean conditions in regions that are vulnerable to ocean acidification such as those with upwelling, high latitudes, and coral reef waters.

Next, the guidance should explain that ocean acidification is predicted to worsen. There are several studies that have modeled future projections of ocean acidification through the end of the century. It is estimated that ocean pH will decline up to 0.3 units

on average before the end of the century (Caldeira & Wickett 2003). Modeling of the oceans' aragonite saturation predicts that by the end of the century up to 75% of ocean volume could be undersaturated with respect to aragonite (Joos et al. 2011). Modeling showed that even under the most optimistic scenario, 98% of coral reefs will be chemically and thermally stressed by 2050 (Meissner et al. 2012). Regional predictions are also available, for example, a model of the California Current shows that by 2030 many of California's coastal waters will be permanently undersaturated with respect to aragonite (Gruber et al. 2012). States will benefit from having information about the projected changes in ocean chemistry because it will help with management and adaptation to ocean acidification.

Finally, the guidance should emphasize the importance of reducing local CO₂ sources to address ocean acidification. While paths to global CO₂ reductions are complex, state and local governments should understand the importance of reducing CO₂ locally. Incremental reductions and even delayed increases in CO₂ can narrow the spectrum of harms resulting from ocean acidification. The United States has been responsible for the greatest contribution of CO₂ to the atmosphere to date and therefore should bear the burden of significant reductions in CO₂. Reducing emissions even on a state-by-state basis can ratchet back acidification. U.S. states contribute enormous amounts of CO₂ to the atmosphere, and therefore reductions even in those states can slow ocean acidification. For example, if Texas were a country it would rank 7th globally in CO₂ emissions, and California would rank 17th. Accordingly, states should understand the role they play in managing water quality for ocean acidification.

2. Information about the biological and socio-economic consequences of ocean acidification

EPA guidance on ocean acidification should provide information on the biological consequences of ocean acidification. Many of the key biological impacts of ocean acidification are summarized above in section 4(b). Meta-analyses can provide a big picture view of the most common results of ocean acidification studies (Kroeker et al. 2010; Kroeker et al. 2013; Chan & Connolly 2013). There are also several review publications that EPA may draw upon for guidance on the biological consequences of ocean acidification (Abbasi & Abbasi 2011; Turley et al. 2006; Albright 2011; Hofmann et al. 2010; Ross et al. 2011; Guinotte & Fabry 2008; Branch et al. 2012; Convention on Biological Diversity 2009; Fabry et al. 2008; Royal Society 2005; J. A. Kleympas et al. 2006a; National Research Council 2010).

At present there are several studies of the socio-economic impacts of ocean acidification can provide a basis for the guidance (Cooley & Kite-Powell 2009; Cooley & Doney 2009; Brander et al. 2009; Branch et al. 2012; Royal Society 2005; Narita 2012; Griffith 2012; Brander *forthcoming*; Kaplan *in progress*). These studies look at the impacts of ocean acidification on mollusk harvests, coral reefs, and seafood production.

3. Monitoring and classification of water bodies

The guidance should include information on accurate ocean acidification monitoring methods and how to make classifications of waterbodies during water quality assessments, which must be published pursuant to Section 304(a)(2)(C).

a. Monitoring

For monitoring the chemical indicators of ocean acidification, the National Research Council recommended that measurements include temperature, salinity, oxygen, nutrients critical to primary production, and at least two of the following four carbon parameters: dissolved inorganic carbon, pCO₂, total alkalinity, and pH (National Research Council 2010). The National Research Council in its report on ocean acidification concluded that “[t]he chemical parameters that should be measured as part of an ocean acidification observational network and the methods to make those measurements are well established” (National Research Council 2010). “Guide to best practices for ocean CO₂ measurements” contains the most up-to-date information available on the chemistry of CO₂ in seawater and the methodology of determining carbon system parameters (Dickson et al. 2007). Methods are also described in “Guide to best practices for ocean acidification research and data reporting” and the Ocean Carbon and Biogeochemistry comments to EPA (Riebesell et al. 2010; Ocean Carbon and Biogeochemistry Program 2010; Ocean Carbon and Biogeochemistry Program 2009).

Additionally, EPA should recommend and describe methods for monitoring biological indicators of ocean acidification. The National Research Council suggested that measurements of the following indices would have value for understanding changes brought about by ocean acidification: (1) rates of calcification, calcium carbonate dissolution, carbon and nitrogen fixation, oxygen production, and primary productivity; (2) biological species composition, abundance, and biomass in protected and unprotected areas; (3) the relative abundance of various taxa of phytoplankton (i.e., diatoms, dinoflagellates, coccolithophores); and (4) settlement rates of sessile calcareous invertebrates, such as mussels and oysters (National Research Council 2010). If EPA adopts the growth rate criteria recommended by this petition, it should provide guidance for how states can identify indicator species and methods for measuring growth rates.

Biological data can be monitored by remote collection techniques or through direct measurement by scientists. Data about primary production (photosynthesizing activity) can be collected from buoys through measurement of chlorophyll a, nutrient levels and oxygen. Biologists have many techniques for collecting biological data in the field, both from ships and on shorelines. Biological responses are measured by scientists with calcification rates, shell growth, behavior, otolith growth (for fish), metabolic rate, reproduction, among others parameters. For example, calcification can be measured by shell mass, high-resolution scans, growth bands, and other methods. There are also developments in using microbial methods and gene expression to detect physiological responses.

The “Guide to best practices for ocean acidification research and data reporting” describes the best practices for researching and reporting such biological responses to

ocean acidification (Riebesell et al. 2010). For example, the study describes five methods that are in wide use for the study of calcification of benthic organisms, including buoyant weight of the organism, skeletal density banding, direct measurement of shell or skeleton weight, change in total alkalinity of the incubation water, and measurements of radioisotopes (Id.). EPA can draw from this guide for its own guidance.

b. Assessments

EPA must also provide states with guidance on how to make water quality attainment determinations for ocean acidification. There are several water quality standards that implicate assessment for ocean acidification, these include marine pH, aquatic life standards, and antidegradation standards. New standards, as requested in this petition, should also be developed. States need information on how to conduct assessments.

First, EPA and states need information on how to obtain ocean acidification data because they have a duty “evaluate all existing and readily available water quality-related data and information to develop the list.” 40 C.F.R. § 130.7(b)(5); *see also Sierra Club v. Leavitt*, 488 F.3d 904 (11th Cir. 2007). There is ample information and data on ocean acidification that is being developed by federal and academic research institutions. EPA and states have a duty to evaluate this data to make attainment determinations for ocean acidification.

There are several sources for high-quality ocean acidification data. EPA’s guidance should act as a clearinghouse for data on ocean acidification. Moreover, EPA maintains a water quality database, which should be periodically updated with the best available data on ocean acidification. At minimum, EPA should guide states on how to obtain ocean acidification data and evaluate it from existing monitoring databases. Specifically, the following resources maintain ocean acidification data:

The United States Integrated Ocean Observing System

(<http://www.ioos.noaa.gov/>)

The National Oceanographic Data Center (<http://www.nodc.noaa.gov/>)

Ocean Margin Ecosystems Group for Acidification Studies

(<http://omegas.science.oregonstate.edu/>)

NOAA Ocean Acidification Monitoring Program

(<http://www.pmel.noaa.gov/co2/OA/>)

The Ocean Carbon and Biogeochemistry Program also provided list of ongoing programs with high-quality inorganic carbon chemistry data in its prior comments to EPA (Ocean Carbon and Biogeochemistry Program 2010). EPA must provide guidance for states on what to do with the raw ocean acidification data that is available from these databases.

Second, there is also a growing body of ocean acidification research available in the scientific literature that must be evaluated by states and EPA in making attainment determinations. EPA guidance should direct states to make inferences about their coastal

waters based on available information. Despite the lack of site specific data documenting ocean acidification, the best available information must be used to infer water quality of ocean and coastal water segments. For example, states should take into account not only site-specific monitoring, but also studies of offshore monitoring, predictive modeling, knowledge about atmospheric carbon dioxide levels and rates of increase, as well as laboratory studies on the impacts of ocean acidification on organisms to identify threatened and impaired waters. States need direction on what inferences can be made from the scientific literature about their coastal waters. EPA should also acknowledge that the research being done by federal agencies and academic institutions on ocean acidification is sufficient to meet data quality standards required by EPA for water quality assessments. EPA should facilitate the use of scientific literature on ocean acidification because most researchers do not obtain pre-approval of quality assurance protocol from states, thus presenting a major obstacle to science-based water quality management. Additionally, the synergistic effects of global warming, pollution, with ocean acidification should be considered.

Third, while there is regional variability in coastal pH and other ocean chemistry parameters, in many cases the envelope of natural variability can be gleaned from historical information. Most states have sources for coastal pH monitoring, while this may not be ideal to understand the contribution of ocean acidification to pH changes it can nonetheless be used to develop baseline information about coastal waters (Ocean Carbon and Biogeochemistry Program 2009; Ocean Carbon and Biogeochemistry Program 2010). Such baseline information can then be used to determine if there are trends, for example if pH is declining in a region. This can and should play a role in determining if water quality is declining due to ocean acidification.

4. Recommendations for developing and implementing total maximum daily loads

The guidance should include information for states on developing total maximum daily loads (“TDMLs”) for ocean acidification. A TMDL is a calculation of the maximum amount of a pollutant that a water body can receive and still safely meet water quality standards. To address ocean acidification, a TMDL would set a target amount how much carbon dioxide can be added to ocean waters that assures that those seawaters attain water quality standards for pH, designated uses, and other applicable standards.

The Center recommends that EPA develop guidance for cooperative regional or nationwide approaches to developing TMDLs, as have been used to reduce atmospheric mercury pollution (*See e.g.* Northeast Regional Mercury Total Maximum Daily Load (CT, ME, MA, NH, NY, RI, and VT) (Oct. 24, 2007)). Moreover, carbon dioxide targets and allocations can complement targets and requirements under the Clean Air Act, state programs for greenhouse gas reductions, or any other programs aimed at limiting greenhouse gases.

For example, EPA could start with the global and national emissions reductions necessary to achieve a 350 ppm standard, meaning that emissions need to be reduced by 40-45% from 1990 levels by 2020. Using the greenhouse gas inventories already completed or underway in most states, EPA can then determine each state’s proportional contribution to

the necessary reduction. Next EPA or states would then determine the sources of carbon dioxide and allocate the TMDL accordingly. There are already good sources for this information being developed in conjunction with efforts to regulate greenhouse gases under the Clean Air Act. Sources with NPDES permits should be required to reduce their carbon dioxide emissions in a manner that is compatible with the TMDL, and for other sources of CO₂ states may use regulatory (i.e. condition permits on compliance) or incentive programs to control CO₂ emissions.

While the most effective TMDL would be a nationwide approach adopted by EPA, with sufficient guidance there are other approaches that could help to address ocean acidification.

6. Conclusion

Our oceans are facing a crisis. EPA must fulfill its statutory duties and update the federal water quality criteria in order to accurately reflect the “latest scientific information” on ocean acidification. Additional water quality criteria will allow states to adopt more effective water quality standards in order to protect marine life. EPA must also publish information on ocean acidification to provide much needed guidance to states on how to address ocean acidification within their coastal waters.

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