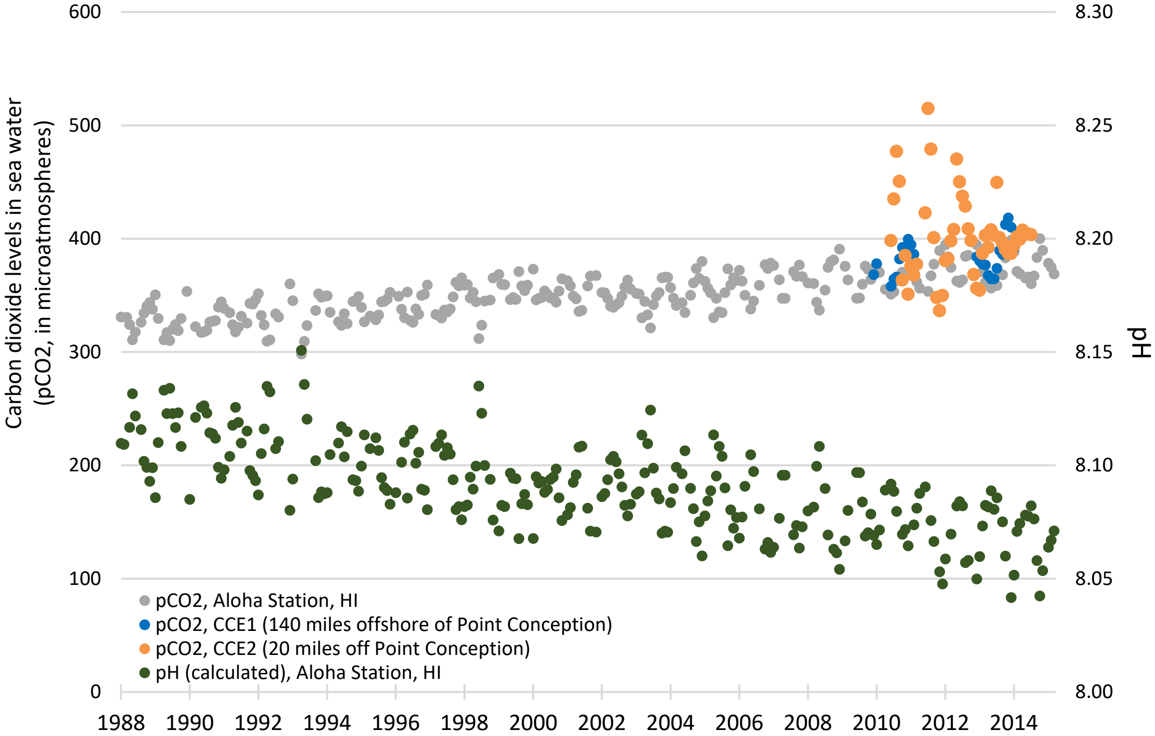
ACIDIFICATION OF COASTAL WATERS

As atmospheric concentrations of carbon dioxide increase, so do levels in the ocean, part of a process known as “ocean acidification.” While long-term data for California waters are limited, the values measured at the offshore location near Point Conception are similar to those from monitoring off Hawaii at the same time points. An increase in seawater carbon dioxide levels accompanied by declining pH (a measure of acidity) have been observed at the Hawaii station.

Figure 1. Seawater carbon dioxide and pH off Hawaii and Point Conception, California*



Source: Hawaii Ocean Time-Series, 2017 (Hawaii);
NOAA PMEL, 2017 and Sutton et al., 2011 (California)

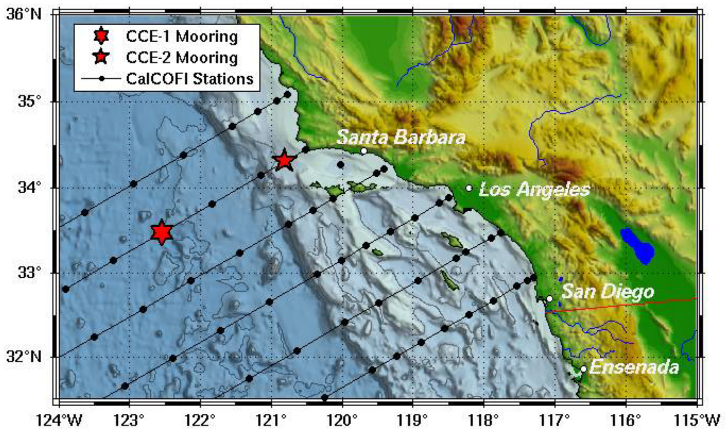
**Carbon dioxide levels are reported as pCO₂, the partial pressure of carbon dioxide, in microatmospheres measured at two California locations off Point Conception designated as CCE1 (blue dots) and CCE2 (orange dots), and Aloha Station, Hawaii (grey dots). pH values are from Aloha Station (green dots).*

What is the indicator showing?

Figure 1 shows that levels of carbon dioxide (CO_2) in seawater measured relatively recently at an offshore location (CCE1) off Point Conception, California near Santa Barbara are similar to those measured at the same time points at Aloha Station off Hawaii; levels at CCE2, a station closer to the California coast, show greater variability. Measurements at CCE1, which began in September 2010, provide the longest-running publicly available data on CO_2 levels in seawater in California. Levels of CO_2 are expressed as the partial pressure of carbon dioxide, or pCO_2 (which refers to the pressure that CO_2 contributes to the total pressure of the mixture of gases present in seawater).

At Aloha Station pCO_2 levels have increased steadily at the rate of 1.92 microatmospheres per year (μatm/year), and the pH (a measure of acidity) has decreased at the rate of 0.002 unit per year from 1988 to 2015. At seven long-term monitoring sites around the globe, measurements of pCO_2 and pH show similar changes over the last three decades: pCO_2 has increased by 1.29 to 2.95 μatm/year, and pH has decreased by 0.0013 to 0.0025 unit/year (Bates et al., 2014). Monitoring at the Aloha Station off Hawaii provides the longest-running measurements of ocean acidity in the North Pacific Ocean.

Figure 2. California CO2 monitoring sites



Source: SIO, 2017

In California, ongoing, continuous monitoring of CO_2 and pH is limited to a few sites (see *Technical Considerations*). Figure 1 presents pCO_2 data from two active monitoring sites off Point Conception (Figure 2): “CCE1,” about 140 miles offshore, and “CCE2,” positioned on the shelf break on the coast about 20 miles off Point Conception (blue and orange dots, respectively). The greater variability in the CO_2 levels in CCE2 (orange dots) is due to its location closer to shore, where levels are influenced by seasonal changes in upwelling (see discussion in *What factors influence this indicator?*). Given the duration of the period covered by the data set, and the gaps in the data, there are insufficient data at these locations with which to derive trends.

Why is this indicator important?

CO_2 is considered to be the largest and most important anthropogenic driver of climate change. It is continuously exchanged between land, the atmosphere, and the ocean through physical, chemical, and biological processes. The ocean absorbs approximately 30 percent of the CO_2 released into the atmosphere by human activities every year (Sabine et al., 2004); this process has significantly reduced the CO_2 concentrations in the atmosphere and minimized some of the impacts of global warming (Rhein et al., 2013). Consequently, as atmospheric CO_2 concentrations continue to increase, so do CO_2 values in the ocean, changing the carbonate chemistry of seawater — a process termed “ocean acidification” (Caldeira and Wickett, 2003; Doney et al., 2009). The mean pH of surface waters in the open ocean currently ranges between 7.8 and 8.4, which means that the ocean is mildly basic (pH > 7). The net result of adding CO_2 to seawater is an increase in hydrogen ions (H+) — which increases seawater acidity and lowers seawater pH — along with decreasing carbonate ion, a fundamental ‘building block’ for organisms forming shells of calcium carbonate.

Many economically and ecologically important West Coast species have been documented to show direct responses to acidification; bivalves, for example, are economically valuable, while also serving an ecological role in providing ecosystem services such as water filtration and habitat for other species. While field observations of impacts on marine organisms are limited (see *Effects of ocean acidification on marine organisms* indicator), laboratory experiments on bivalves have documented mechanisms by which negative effects arise (Miller et al., 2009; Gaylord et al., 2011; Hettinger et al., 2012 and 2013; Barton et al., 2012; Waldbusser et al., 2013) as well as repercussions for species interactions (Sanford et al., 2014). Ocean acidification is also likely to exacerbate the impact of other stressors — including overfishing, input of chemical contaminants, exotic and invasive species, temperature change, and deoxygenation — on coastal ecosystems.

What factors influence the indicator?

The air-sea exchange of carbon dioxide is determined largely by the difference in the partial pressure of CO_2 between the atmosphere and the ocean; as more atmospheric CO_2 is produced, the ocean absorbs some of it to reach equilibrium. Long-term measurements of ocean carbon content at seven monitoring sites around the globe (including the Hawaii Ocean Time Series presented in Figure 1) collectively show consistent and coherent changes in the uptake of CO_2 by the ocean; at decadal time scales, the rate of ocean acidification in these open ocean surface waters generally approximates the rate of CO_2 increase in the atmosphere (Bates et al., 2014).

The air-sea CO_2 interchange is governed by both chemical and biologically-mediated reactions (photosynthesis, respiration, and precipitation and dissolution of calcium carbonate). Photosynthesis and respiration remove and add CO_2 to seawater, respectively. Precipitation of calcium carbonate by marine organism calcifiers also affects the carbonate chemistry of surrounding seawater. These biological processes play an especially key role in determining shorter-term variability in pH and CO_2 in seawater, whereas air-sea exchange processes dominate the longer-term interannual-to-decadal trends.

Along the West Coast, ocean acidification adds to the already naturally high values of carbon dioxide in “upwelled” waters. Upwelling is the wind-driven movement of deep, cool, carbon- and nutrient-rich ocean water to the surface, replacing the warmer, usually nutrient-depleted surface water (see *Coastal ocean temperature* indicator).

In addition to seasonal patterns in ocean chemistry tied to upwelling processes, changes associated with large-scale climate oscillations such as El Niño and the Pacific Decadal Oscillation can alter the oceanic CO_2 sink/source conditions. This can occur through seawater temperature changes as well as through ecosystem variations that occur via complex physical-biological interactions (Chavez et al., 2007). For example, during El Niño, upwelling of high CO_2 waters is dramatically reduced along central California so that flux out of the ocean is reduced; at the same time, ocean uptake of CO_2 is also reduced because of lower photosynthetic activity, as nutrients that would have been carried to the surface by upwelled waters are less available. Modeled estimates of pH and *aragonite saturation state* (another measure used to monitor ocean acidity) along the southern California coast from 1985 to 2014 suggest a persistent shift in ocean acidification-related seawater conditions from the decade prior to the strong 1997–1998 El Niño event to the decade after it (McClatchie et al., 2016). Summertime warming has been shown to increase surface pCO_2 at certain locations, including Station Aloha, so that these waters seasonally transition to being net sources of CO_2 to the atmosphere (Bates et al., 2014). In the southern California Current System, subdecadal (2005–2011) estimates for pH and related parameters reveal a pronounced seasonal cycle and inter-annual variability in the upper water column (Alin et al., 2012).

The variability in the data of pCO_2 levels in Figure 1 (CCE2 location) compared to open ocean waters (CCE1 location) reflects the more complex acid-base chemistry dynamic of coastal waters (NAS, 2010). In addition to climate processes, coastal waters can be affected by localized freshwater and atmospheric inputs, organic matter and nutrients from land, and processes in the underlying sediments. The seasonal, monthly and daily variability that can occur from biological and oceanographic processes has been observed at other monitoring stations along the California coast (e.g., M1 mooring in Monterey, Hog Island Oyster Company store station, Carlsbad Aquafarm shore station) (CenCOOS (Monterey), 2018; IPACOA (shore stations), 2018; see references for URLs to access data from these stations). Knowledge of short-term variability of CO_2 in seawater is important to interpret any changes attributed to anthropogenic processes at a given location.

Technical Considerations

Data Characteristics

Monitoring along the California coast includes moorings with carbon dioxide and pH sensors, regular measurements of inorganic carbon species on oceanographic cruises, calculation of aragonite saturation state, and shore-based observations of carbon chemistry in nearshore waters. These monitoring efforts are included in large-scale monitoring programs, for example within the US Integrated Ocean Observing System (IOOS) and the National Oceanic and Atmospheric Administration (NOAA) ocean acidification observing network, all carried out in collaboration with a wide range of national, regional, and international partners. Many of these efforts can be viewed in real time through an online data portal (IPACOA, 2018).

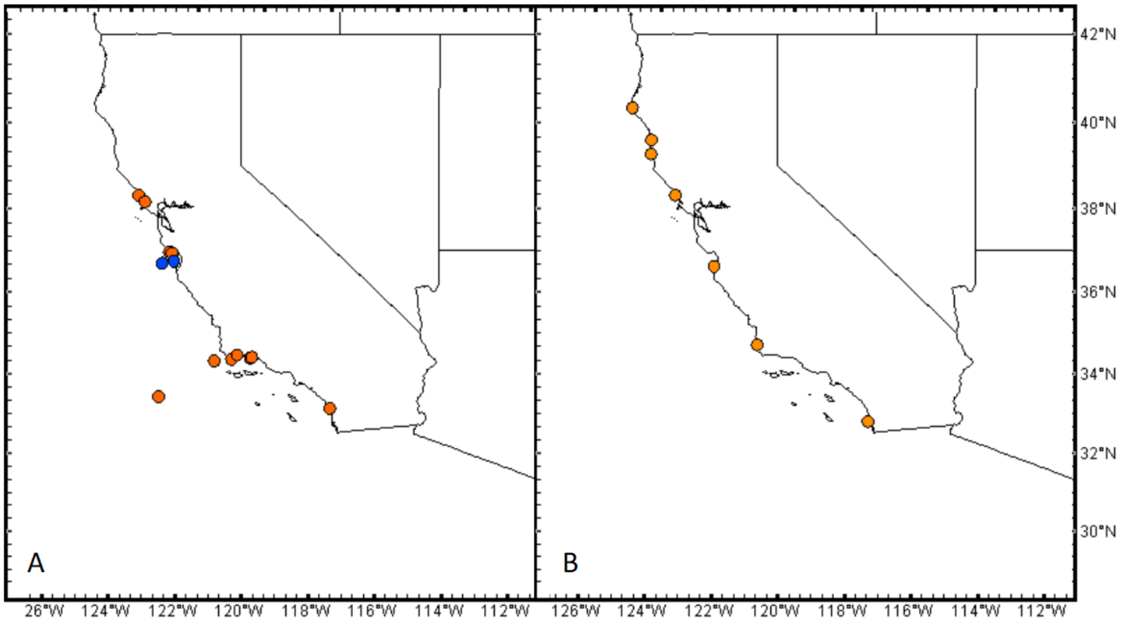
The CCE1 mooring (205 km southwest of Point Conception) was deployed in November 2008 as part of a multi-investigator, multi-disciplinary project by NOAA's Pacific Marine Environmental Laboratory. The project expanded to include the CCE2 mooring, at the shelf break offshore Point Conception, in 2010. Sensors on these moorings measure aspects of biological, chemical, and physical oceanography as well as meteorology; data are collected every 3 hours. This project is closely coordinated with other projects off of Southern California such as the California Cooperative Oceanic Fisheries Investigations (http://www.calcofi.org/), the California Current Ecosystem Long Term Ecological Research (http://cce.lternet.edu/), and the Consortium on the Oceans Role in Climate (http://mooring.ucsd.edu/index.html?/projects/corc).

Figure 1 features data from the Hawaii Ocean Time-series (HOT) program for comparison. This program has been making repeated observations of the chemistry, and biology of the water column at a station north of Oahu, Hawaii since October 1988. Cruises are made approximately once per month to the deep-water Station ALOHA located 100 kilometers north of Oahu, Hawaii. Calculated values of pH and pCO_2 are obtained from measured parameters; direct measurements of pH are also made at sea.

Despite the central importance of data for detecting long-term changes in the ocean’s carbon system, coordinated observing networks in the US coastal and estuarine waters did not exist until recently. Historically, assessments of changes to the carbonate system relied on a handful of data records worldwide (none of which operated in California waters, and the longest of which began only in the early 1980’s) (Bates et al., 2014).

To date, indicators of acidification (pH, pCO_2, and/or aragonite saturation state: a calculation of the stability of shell material) have been monitored at 36 sites (moorings, instrument deployments, or regular bottle sampling) along the California coast (Figure 3) — a small number compared to 300 sites for ocean temperature. In the figure, only publicly available datasets from stationary instruments are presented. The panel on the left shows the datasets that are ongoing (N=13); the panel on the right indicates the datasets that may have been terminated or may not be ongoing. There are no datasets longer than 50 years. There are an additional twelve datasets in California collected on oceanographic vessels that are not displayed here.

Figure 3. Stationary monitoring sites for CO_2-relevant parameters off California



Panel (A) shows carbonate chemistry datasets that are ongoing. Panel (B) shows carbonate chemistry datasets that have been terminated or may not be ongoing.

The colors of the dots refer to dataset length: Blue: 10+years; Orange: 0-9 years

Source: UC Davis Bodega Marine Laboratory, 2016

Strengths and Limitations of the Data

Given that pH and/or pCO_2 of seawater are variable in many of California's marine ecosystems, datasets of these carbonate chemistry parameters will need to be at least a decade or more in length before trends can be detected beyond natural variability (Henson et al., 2016). Hence, a limitation of the ability to detect long-term trends in carbonate chemistry off California's coast is that many of the monitoring sites have not been continuously operated, due to funding limitations, and many focused on ocean acidification were more recently initiated. A surface seawater pH sensor was only recently (September 2012) added to the CCE1 mooring. Measurements of pH in addition to pCO_2, will allow a more accurate and precise evaluation of the changes associated with ocean acidification. Future expansion and extension of the current monitoring network for ocean acidification was a major recommendation of the West Coast Ocean Acidification and Hypoxia Panel (Chan et al., 2016). Ideally this will take shape via a robust, integrated monitoring system for ocean acidification and hypoxia that is integrated with biological monitoring.

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