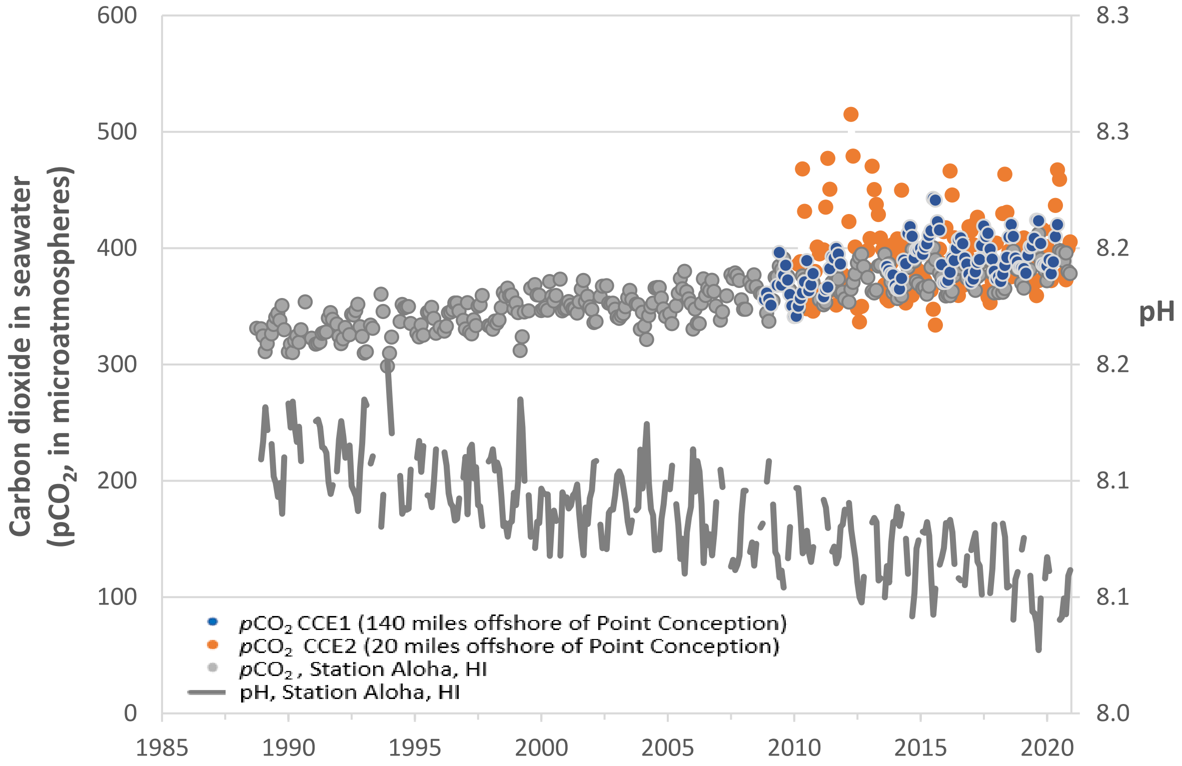
ACIDIFICATION OF COASTAL WATERS

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, carbon dioxide measurements at one offshore location near Point Conception are similar to those from monitoring off Hawaii. They show increases in seawater carbon dioxide levels accompanied by increasing acidity (measured as pH). This phenomenon has been observed at multiple sites in the world's oceans.

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



Source: Hawaii Ocean Time-Series 2022, Dore et al. 2009; NOAA NCEI 2022, Sutton et al., 2012 and 2016

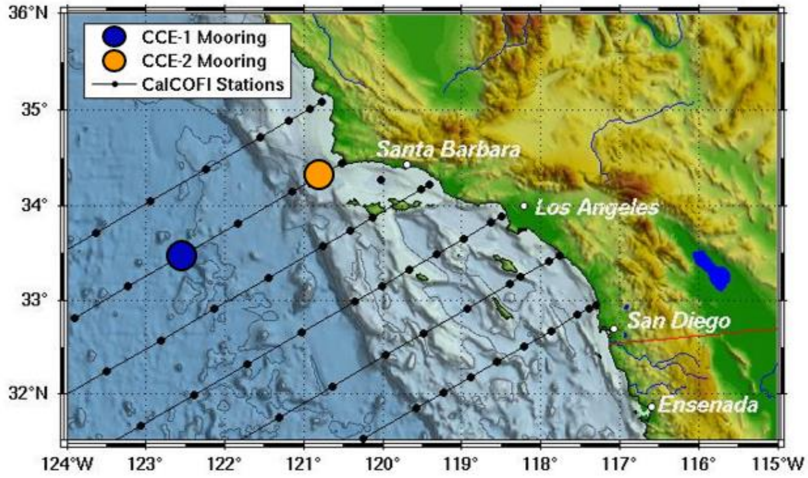
Carbon dioxide (measured as the partial pressure of CO_2 in seawater) from the Hawaii Ocean Time-Series (HOT) site (grey) and two offshore California sites (CCE1 blue, and CCE2, orange). Records of pH are from HOT.

What does the indicator show?

This indicator shows that the oceans are becoming more acidic. This is clear in levels of carbon dioxide (CO_2) and pH (a measure of acidity) in seawater off the coast of Hawaii, as shown in Figure 1. 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). Off the coast of California, the levels of CO_2 measured since 2008 at "CCE1" located 140 miles off Point Conception near Santa Barbara are generally similar to those measured at similar time points at Station Aloha off Hawaii, also shown in Figure 1. At CCE2, a second location 20 miles from Point Conception, levels show greater variability (values range from 330 to 520 microatmospheres (µatm)). This is likely due to its location closer to shore, where concentrations are influenced by seasonal changes in upwelling (Sutton et al., 2019; also see *Coastal ocean temperature* indicator). 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.

Measurements at CCE1, which began in September 2010, provide the longest-running publicly available data on CO_2 levels in seawater in California (there is a 21-month gap in measurements at CCE2). The record at both California locations are not long enough to discern trends. Figure 2 shows where sites CCE1 and CCE2 are located.

Figure 2. Location of CO_2 monitoring sites



Source: Modified from SIO, 2017

At Station Aloha, $p\mathrm{CO_2}$ levels have increased steadily at the rate of about 1.8 µatm/year, and the pH has decreased at the rate of 0.002 unit per year over this time period. At seven long-term monitoring sites around the globe, measurements of $p\mathrm{CO_2}$ and pH show similar changes over the last three decades: $p\mathrm{CO_2}$ 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 Station Aloha off Hawaii provides the longest-running measurements of ocean acidity in the North Pacific Ocean.

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. Since the mid-1980s the ocean has absorbed approximately 20 to 30 percent of the CO_2 released into the atmosphere by human activities (Bindoff et al., 2019; Canadell, et al., 2021; Friedlingstein et al., 2022); 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). As atmospheric CO_2 concentrations continue to increase, so do CO_2 concentrations in the ocean, changing the carbonate chemistry of seawater — a process termed “ocean acidification” (Caldeira and Wickett, 2003; Doney et al., 2009). 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 a decrease in carbonate ion, a fundamental ‘building block’ for organisms known as “calcifiers,” that forming shells or skeletons. The concentration of carbonate ions in seawater is commonly measured using the saturation state of aragonite, a soluble form of calcium carbonate used by calcifiers, expressed as the term Ω. When Ω is less than 1, exposed calcium carbonate structures begin to dissolve (Pershing et al., 2018). Global marine ecosystems face serious threats from ocean acidification, deoxygenation (see *Dissolved oxygen in coastal waters* indicator) and ocean warming (see *Coastal ocean temperature* indicator).

Tracking anthropogenic emissions of CO_2 and the distribution among the atmosphere, land, and ocean provides a better understanding of the global carbon cycle and informs the development of climate policies (Friedlingstein et al., 2022). Future scenarios project that the ocean and land will be less effective as sinks, and thus at slowing the accumulation of CO_2 in the atmosphere with increasing emissions (Gulev et al., 2021). Nevertheless, the ocean holds great potential for uptake and long-term storage of CO_2. Approaches to enhance ocean’s carbon capacity without further acidifying ocean environments are an area of intense research. The National Academies has recommended a research agenda to assess the benefits, risks, and potential for responsible scale-up of ocean-based carbon dioxide removal strategies, and to ensure that no unintended and potentially irreversible harm to natural systems and coastal communities result (NASEM, 2021). Examples include nutrient fertilization to stimulate marine phytoplankton growth, artificial upwelling and downwelling, and seaweed cultivation.

Many economically and ecologically important West Coast species (such as oysters, mussels and crabs) have been documented to show direct responses to acidification (Chan et al., 2016). Although many studies have investigated the effects of ocean acidification on marine species, establishing threshold values for pH that sufficiently capture the concentrations at which harmful responses occur is challenging. For example, thresholds in for a species can vary with endpoints, life stage and spatial and temporal exposure patterns (Bednaršek et al., 2021a, b; Bednaršek et al., 2019). Further ocean acidification, combines with deoxygenation and ocean warming in producing these effects and how this occurs is not well understood. In a review of the literature on possible “tipping points” relating to ocean acidification, the authors concluded that the lack of long-term monitoring and the complexity of ecosystem responses to ocean acidification have made the detection of such tipping points difficult (Heinze et al., 2020).

Several biological processes in marine organisms are sensitive to changes in seawater chemistry. The best-documented and most widely observed biological effects on calcifiers (including plankton, mollusks, and corals) are decreased calcification rates and/or shell dissolution due to reduced carbonate ion levels under reduced pH conditions (e.g., Bednaršek et al., 2014; Bednaršek et al., 2021a, b; Bednaršek et al., 2019; Feely et al., 2018; Gaylord et al., 2011; Hodgson et al., 2018; Lord et al., 2019; Mekkes et al., 2021; Osborne et al., 2020; Rose et al., 2020; Swezey et al., 2020). Controlled laboratory experiments and field observations have documented decreased shell size/thickness in shellfish and elucidated these processes (Barton et al., 2012;

Gaylord et al., 2011; Hettinger et al., 2012 and 2013; Miller et al., 2009; Waldbusser et al., 2013). Impacts on calcifiers can be amplified across marine food webs when they affect sea snails (pteropods), single-celled amoeboid organisms (called foraminifera) and other key links in the marine food chain; can lead to the degradation of the habitat provided by corals, mussels, oysters and other structure-forming taxa; and can reduce the water filtration services provided by bivalves (e.g., Feely et al., 2016; Hollarsmith et al., 2020; Osborne et al., 2020; Mekkes et al., 2021). In Tribal listening sessions, several Tribes, including the Coastal Band of the Chumash Nation and the Santa Ynez Band of Chumash Indians have reported that they have seen a decrease in abalone (a cultural keystone species), Pismo clams and Olivella shells due to ocean acidification (Pala Band of Mission Indians and Santa Ynez Band of Chumash Indians, 2021).

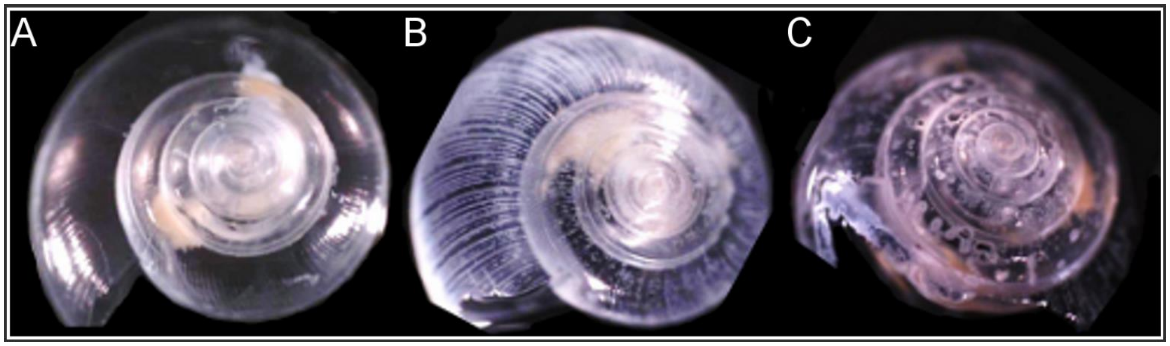
In lower pH ocean waters, organisms face greater challenges in maintaining internal acid-base balance, leading to effects on the physiology and behavior of marine species (e.g., Somero et al., 2016; Hodgson et al. 2018; Jellison et al., 2016; Gaylord et al., 2018; Contolini et al., 2020; Rose et al., 2020). Other potential effects of ocean acidification result from changes in the ionic form of marine nutrients and potentially harmful substances (such as metals); increased photosynthetic rates in carbon-fixing organisms; altered reproduction and survival in organisms; and reduced olfaction (sense of smell) in fish. Broader ecological consequences include trophic mismatch (Kroeker et al., 2021) and altered predator-prey and other species interactions, such as herbivory and competition (e.g., Ferrari et al., 2011; Kroeker et al., 2014; Sanford et al., 2014; Gaylord et al., 2018; Magel et al., 2020; Hodgson et al., 2018; Contolini et al., 2020; Lord et al., 2019).

Regional biological indicators can help improve the understanding of impacts of ocean acidification and other stressors on California's varied smaller-scale ocean ecosystems (Duncan et al., 2019; Duncan et al., 2013). A comprehensive review and analysis of biological responses to ocean acidification has identified possible indicator species and variables to consider in selecting indicators of ocean acidification (Kroeker et al., 2013). Among the most important traits of candidate indicator species are sensitivity to the environmental factor of interest, ecological value, presence over a wide geographic extent, and accessibility and familiarity to local communities (Gaylord et al., 2018). Some potential indicators of the biological impacts of ocean acidification in California waters are:

- The California mussel (*Mytilus californianus),* a familiar and well-recognized intertidal organism throughout the US West Coast. It is a classic "foundation species" that dramatically influences community structure both through its dominant status and its role in providing habitat (mussel beds) for hundreds of other species (Suchanek, 1992; Duncan et al., 2019; Rose et al., 2020). The distribution of *M. californianus* spans the entire west coast of the US (Morris et al., 1980; Rose et al., 2020), including most of the state's shoreline Marine Protected Areas. Life history can play a critical role in mussel response to ocean acidification: newly settled *M. californianus* retain larval shells which have been shown to be smaller when larval stages occurred in lower pH seawater; further, overall health is reduced when lower pH conditions are combined with warmed waters (Gaylord et al., 2018; Rose et al., 2020). Not only are California mussels affected by changes in seawater chemistry, they are accessible on shore when tides recede. *M. californianus* has already been identified as an indicator species by two National Marine Sanctuaries in California (Gaylord et al., 2018).

- Krill, a fundamental and important component of the marine food web. Krill have been shown to be sensitive to ocean acidification, with responses that include reductions in growth rates and increased mortality (e.g., Cooper et al., 2017; McLaskey et al., 2016).
- Pelagic snails (pteropods), that have delicate shells subject to severe dissolution when exposed to low pH seawater (Duncan et al., 2019; Engström-Öst et al., 2019; Mekkes et al., 2021). Dissolution of shells of *Limacina helicina*, the most dominant pteropod within the California Current Large Marine Ecosystem, have been demonstrated to occur in waters with low levels of aragonite (the form of calcium carbonate used by marine calcifiers), thus underscoring the species' susceptibility to ocean acidification (Bednaršek et al., 2014; Bednaršek et al. 2018; Busch et al., 2014; Mekkes et al., 2021) (see Figure 3). Pteropods are ecologically important as prey for commercial fish species.

Figure 3. Dissolution of pelagic snail shells exposed to corrosive seawater



Source: Figure 7, Busch et al., 2014

Images of *Limacina helicina*, a pelagic snail, after week-long incubation in Puget Sound waters at the following levels of aragonite (a form of calcium carbonate, Ω_a) levels: [A] Ω_a ~ 1.59, corresponding to current summer surface conditions; [B] Ω_a ~0.56, current deep water or surface conditions during upwelling; and [C] Ω_a ~0.28, future deep water or surface conditions during upwelling. Corrosion is evident on the ribs of the shell in [B], and [C] shows shell perforations.

The Fourth California Climate Assessment noted that "ocean acidification presents a significant and well-established threat to commercial fisheries and farmed shellfish, and therefore human coastal communities" (Sievanen et al., 2018). This supports a growing body of literature that explores the connections between ocean acidification, coastal economies, and human communities (e.g., Doney et al., 2020).

What factors influence the indicator?

The Intergovernmental Panel on Climate Change (IPCC), in its Sixth Assessment Report, concluded that the uptake of anthropogenic CO_2 emissions is the main driver for the global decline in ocean water pH over the last 40 years (Gulev et al., 2021). 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 the partial pressure of CO_2 in the atmosphere increases with increasing emissions, the ocean absorbs more 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 – which is driven by differences in the amount of CO_2 in air compared to water -- is influenced by biologically-mediated reactions (photosynthesis, respiration, and precipitation and dissolution of calcium carbonate). Photosynthesis and respiration remove and add CO_2 to seawater, respectively. In coastal habitats, kelp forests and seagrass meadows can locally ameliorate high CO_2 concentrations by removal of CO_2 via photosynthesis; these effects, however, are temporary (Hirsh et al., 2020; Ricart et al., 2020). Shell formation by marine calcifiers also affects the carbonate chemistry of surrounding seawater by locally reducing buffering capacity and increasing pCO_2.

While biological processes play an especially key role in determining shorter-term (daily to seasonal) variability in pH and pCO_2 in seawater (Wootton et al., 2008; Hoffman et al., 2011), 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. The unique oceanography of the California Current Large Marine Ecosystem may provide early indication of the impacts of ocean acidification and decreasing dissolved oxygen; California's coastal waters are experiencing more acidified and lower oxygen conditions well earlier than most other regions (e.g., Feely et al., 2008; Hauri et al., 2009; Gaylord et al., 2018; Hodgson et al., 2018; Osborne et al., 2020). The interactions between upwelling, hypoxia, and ocean acidification are well explored (e.g., Cheresh and Fiechter, 2020).

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 ability of oceanic waters to serve as either a sink or a source of CO_2. 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* (a measure of whether calcifying organisms will be able to form shells, or if shells are more likely to dissolve) 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). 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 (15–500 meters depth) (Alin et al., 2012). Changes in the local biogeochemistry, carbon chemistry, and saturation state were also documented during the 2014-2016 heat wave event on the California coast (Lilly et al., 2019).

The variability in the data of $p\text{CO}_2$ 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 upwelling and other climate-related 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), 2021; IPACOA (shore stations), 2021; 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. An analysis of $p\text{CO}_2$ and pH data collected at 40 monitoring stations (in four ocean basins, representing a range of ocean, coastal and coral reef locations) estimated the length of the record needed to distinguish anthropogenic trends from natural variability to be 8 to 15 years at open ocean sites (such as CCE1, estimated at 12 years) and 16 to 41 years at coastal sites (such as CCE2, estimated at 24 years) (Sutton et al., 2019).

Despite the global nature and the widespread implications of ocean acidification, a unified policy response analogous to international efforts to limit greenhouse gas emissions has yet to be developed (Collins et al., 2019). Since it takes decades to millennia for the ocean subsurface to respond to changes at the surface, the ocean is already "committed" to changes resulting from current atmospheric greenhouse gas levels, even after concentrations stabilize; thus, ocean acidification is irreversible on timescales relevant to human societies and ecosystems (IPCC 2019).

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, 2021).

Integrated biological, chemical, and physical oceanographic monitoring may elucidate broad-scale impacts of ocean acidification and climate change. Long-term ecological monitoring programs for intertidal and subtidal ecosystems (e.g., LiMPETS, MARINe, and PISCO), the Marine Protected Area Monitoring efforts (e.g., Ocean Science Trust), and oceanographic monitoring by the Applied California Current Ecosystem Studies (ACCESS) provide essential data to support a better understanding and interpretation of the impacts of ocean acidification for California.

The CCE1 mooring (140 miles 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 closer to Point Conception, in 2010. Sensors on these moorings measure aspects of biological, chemical, and physical oceanography as well as meteorology; data are collected every three hours. This project is closely coordinated with other projects off of Southern California such as the California Cooperative Oceanic Fisheries Investigations, and the California Current Ecosystem Long Term Ecological Research, and the Consortium on the Ocean's Role in Climate.

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 62 miles north of Oahu, Hawaii. Calculated values of pH and $p\mathrm{CO}_2$ 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 the early 2010s, following the establishment of NOAA's Ocean Acidification program (NOAA, 2021). 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). Recent studies have focused on ways in which to build monitoring frameworks and identify gaps (e.g., Turk et al., 2019; Taylor-Burns et al., 2020).

Strengths and limitations of the data

Given that pH and/or $p\mathrm{CO}_2$ of seawater are variable in many of California's marine ecosystems, datasets of these carbonate chemistry parameters will need to be of sufficient length before trends beyond natural variability can be detected (Sutton et al., 2019). Hence, a limitation of the ability to detect long-term trends in carbonate chemistry off California's coast is that the monitoring sites have not been continuously operated, due to funding limitations, and many focused on ocean acidification were more recently initiated. Measurements of pH, in addition to $p\mathrm{CO}_2$, 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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