SCCWRP #0866

Core Principles of the
California Current Acidification Network

LINKING CHEMISTRY, PHYSICS, AND ECOLOGICAL EFFECTS

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Phytoplankton blooming in an upwelled area off California. *Image courtesy of the SeaWiFS Project, NASA/Goddard Space Flight Center, and ORBIMAGE*

> "The [California Current Acidification Network] workshops facilitated broad agreement on a set of core principles that can be used to coordinate measurements and practices to generate a data set that is regional in scope and of sufficient quality to enhance understanding of [ocean acidification] impacts on nearshore ecosystems."

ABSTRACT. Numerous monitoring efforts are underway to improve understanding of ocean acidification and its impacts on coastal environments, but there is a need to develop a coordinated approach that facilitates spatial and temporal comparisons of drivers and responses on a regional scale. Toward that goal, the California Current Acidification Network (C-CAN) held a series of workshops to develop a set of core principles for facilitating integration of ocean acidification monitoring efforts on the US West Coast. The recommended core principles include: (1) monitoring measurements should facilitate determination of aragonite saturation state (Ω_{arag}) as the common currency of comparison, allowing a complete description of the inorganic carbon system; (2) maximum uncertainty of ±0.2 in the calculation of Ω_{arag} is required to adequately link changes in ocean chemistry to changes in ecosystem function; (3) inclusion of a variety of monitoring platforms and levels of effort in the network will insure collection of high-frequency temporal data at fixed locations as well as spatial mapping across locations; (4) physical and chemical oceanographic monitoring should be linked with biological monitoring; and (5) the monitoring network should share data and make it accessible to a broad audience.

INTRODUCTION

The ocean absorbs one-quarter of global carbon dioxide (CO_2) released into the atmosphere by anthropogenic activities (Doney et al., 2009). When anthropogenic CO_2 dissolves in seawater, it lowers pH and reduces the concentration of available carbonate ions, a process called ocean acidification (OA; Dickson, 2010). Waters undersaturated with carbonate ions are corrosive to many organisms that produce calcium carbonate exoskeletons, such as some shellfish, corals, and some species of plankton that comprise the base of marine food webs (Fabry et al., 2008; Hofmann et al., 2010). Losses of these calcifying organisms and changes in marine food webs could significantly alter global marine ecosystems, impacting

harvests that provide 110 million metric tons of food for humans and that were valued at US$160 billion in 2006 (Cooley et al., 2009; Kroeker et al., 2011).

In coastal oceans and estuaries, numerous factors, such as freshwater inputs, tidal forcing, water stratification, nutrient over-enrichment, algal blooms, and hypoxia, can interact with OA (Fabry et al., 2008; Borges and Gypens, 2010; Breitburg et al., 2015, in this issue). As a result, these ecosystems may be increasingly vulnerable to ecological and biogeochemical perturbations from OA (Doney et al., 2009; Howarth et al., 2011). However, our understanding of coastal feedback mechanisms is poor, and development of models that better define the relative influence of different factors

on ecosystem structure and function is hampered by the absence of coordinated monitoring necessary to provide the data on which the models may be built. Historically, different monitoring programs have had different goals, and as a result, there is a lack of uniformity and continuity in the measured physical, chemical, and biological parameters among programs. For example, most US regulatory monitoring programs include measurement of pH, but scientific ocean monitoring typically encompasses a more complete description of the seawater carbonate system that is at a higher level of precision and is tied to reference standards to determine accuracy of the data. There is also a disconnect between the types of data collected. Most biological data are spatially located inshore (e.g., at shellfish hatcheries), whereas most physical and chemical measurements are taken offshore on moorings or during ship-based sampling events. These differences make it challenging to link data sets for spatial and temporal analysis of status and trends associated with OA, and to understand the effects of changing ocean chemistry on ecosystem function.

Recent observations of the California Current System have found the chemical condition of nearshore waters to already be at a level that was not predicted for open-ocean surface waters for several decades into the future (Feely et al., 2008; Hauri et al., 2009; Gruber et al.,

2012). Furthermore, the aragonite saturation horizon is shoaling and reaches the surface during strong upwelling events (Feely et al., 2008; Leinweber and Gruber, 2013). Recognizing the serious impacts of OA on West Coast shellfish production, as well as impacts on coastal environments and other fisheries, leaders from the shellfish industry reached out to resource managers and the scientific community to develop a response. These efforts led to creation of the California Current Acidification Network (C-CAN, http://c-can.msi.ucsb.edu), which began working toward a synchronized, uniform monitoring network. Beginning in 2010, C-CAN sponsored a series of western US workshops designed to bring together these different sectors to increase collective understanding of the effects of OA on the nearshore environment and develop recommendations for how to proceed in enhancing this understanding into the future.

There was broad agreement that existing data sets are insufficient to explain the impacts and effects of OA on nearshore ecosystems, and that the main barrier to implementing a nearshore OA monitoring network was a lack of an organizing framework, including standardized data collection methods, for example, the *EPOCA Guide to Best Practices for Ocean Acidification Research and Data Reporting* (Riebesell et al., 2010). A coordinated OA network would serve several purposes: (1) greatly improve the numerous but scattered existing efforts, (2) aid in establishing the status and trends in OA along the California Current, (3) enhance both fundamental and applied knowledge of OA for a range of users, and (4) ultimately be cost effective, as resources across the network could be leveraged. Pieces of a coordinated monitoring program are in place, notably US-wide OA monitoring via the Integrated Ocean Observing System (IOOS, http://www.ioos.noaa.gov) and its regional associations, as well as international monitoring networks such as the Global OA Observing Network

(GOA-ON, http://www.goa-on.org) and as proposed by Feely et al. (2010). The goal of C-CAN was to facilitate interaction among existing efforts, as well as coordinate among the diverse sectors affected by OA, including industry, academic, and non-academic monitoring programs, in order to develop a sound basis for design and development of a nearshore OA monitoring network. The C-CAN workshops facilitated broad agreement on a set of core principles that can be used to coordinate measurements and practices to generate a data set that is regional in scope and of sufficient quality to enhance understanding of OA impacts on nearshore ecosystems.

RECOMMENDATIONS FOR CORE MONITORING PRINCIPLES
Recommendation 1: Measurements should facilitate determination of aragonite saturation state (Ω_{arag}) and a complete description of the carbonate system, including pH and pCO$_2$.

A fundamental aspect of an effective nearshore OA monitoring network is that data can be compared spatially and temporally. This requires a common variable to be defined as the basis for comparison. Several experiments have shown that many organisms are dependent on the saturation state of the calcium carbonate polymorph, aragonite (e.g., Fabry et al., 2008; Hofmann et al., 2010; Barton et al., 2012). Furthermore, in characterizing aragonite saturation state, the entire inorganic carbon system is constrained and, thus, a number of indices for evaluation of biological effects of changing ocean chemistry can be inferred (Doney et al., 2009), if not measured primarily. This realization has led to widespread adoption of aragonite saturation state as a key indicator for OA effects, and it was adopted by C-CAN as the common currency for a nearshore network. The focus on aragonite as the common currency was driven largely by high interest in and partnership with the

shellfish industry, to which this parameter is particularly relevant. However, other currencies for comparison may be more relevant in some systems, such as H$^+$ and CO$_2$ concentration (Ishimatsu et al., 2008; Ries, 2011; Roleda, et al., 2012), and thus reporting all data used in calculation of aragonite saturation state is critical to network success.

When CO$_2$ dissolves in seawater, a new equilibrium is established that influences the concentrations of other key molecules: hydrogen (H$^+$) and bicarbonate (HCO$_3^-$) ion concentrations increase, carbonate ion (CO$_3^{2-}$) concentration decreases, and the saturation state of biologically important forms of calcium carbonate (CaCO$_3$) declines (Dickson, 2010; Box 1). There are two important forms of biogenic CaCO$_3$, calcite and the more-soluble aragonite. Aragonite is the form used by corals and pteropods and is the preliminary form precipitated by bivalves in larval stages. The aragonite saturation state is defined as the ratio between the product of calcium ions and carbonate ions estimated for the sample and the value this product would have if the seawater were at equilibrium with aragonite (i.e., the stoichiometric solubility product for aragonite). When saturation state is greater than 1, seawater is over-saturated with respect to aragonite, and spontaneous net precipitation from seawater is thermodynamically possible; at a saturation state less than 1, seawater is undersaturated with respect to aragonite, and spontaneous net dissolution is thermodynamically possible.

Presently, there is no widely accepted method for direct measurement of carbonate ion concentration, and thus aragonite saturation state must be calculated from concurrent determination of at least two other parameters: pH, pCO$_2$, TCO$_2$, or total alkalinity (TA), together with the equilibrium constants for the CO$_2$ system: K$_H$, K$_1$, K$_2$. Use of TA requires additional knowledge of the total concentration and equilibrium constant(s) of any other significant acid-base systems in seawater (Dickson et al., 2007; Box 2). Indeed, this

practice has already been implemented by a number of shellfish hatcheries in the Pacific Northwest (Barton et al., 2015, in this issue). By defining aragonite saturation state as the unifying parameter in the OA network, participants gain flexibility in selecting the specific parameters they measure, and, by extension, a number of additional potential indices that may be more biologically relevant can be calculated.

Recommendation 2: A ±0.2 maximum uncertainty in the aragonite saturation state (Ω) calculation is required to adequately link changes in ocean chemistry to changes in ecosystem function.
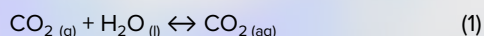
A key goal for any observing network is to ensure that measurements are of appropriate quality for their intended purposes, and that they are comparable with one another even if made at different times, in different places, and by different instruments. To be useful, a cohesive network must employ existing technology suitable for use by a large number of participants and yet yield data adequate for understanding drivers of ocean acidification and ecosystem response. The C-CAN community agreed that a maximum uncertainty of ±0.2 in calculation of aragonite saturation state was
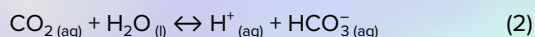
Box 1. Definition of Aragonite Saturation State

One of the California Current Acidification Network's core principles is to monitor chemical parameters that allow for determination of aragonite saturation state (Ω) and a complete description of the carbonate system with a minimum uncertainty of ±0.2. The parameters that can be measured to meet this objective are defined by the equilibrium established through a series of reactions when CO_2 dissolves in seawater (Dickson, 2010):

CO_2 gas dissolves in and reacts with water to form a mixture of aqueous CO_2 ($CO_{2\,(aq)}$) and carbonic acid (H_2CO_3) that is dominated by $CO_{2\,(aq)}$:

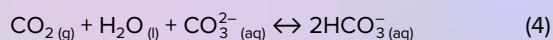$$CO_{2\,(g)} + H_2O_{(l)} \leftrightarrow CO_{2\,(aq)} \tag{1}$$

This operationally defined quantity then forms hydrogen ion and bicarbonate ion:

$$CO_{2\,(aq)} + H_2O_{(l)} \leftrightarrow H^+_{(aq)} + HCO^-_{3\,(aq)} \tag{2}$$

and most of the hydrogen ions formed from this dissociation react with carbonate ions to form bicarbonate:

$$H^+_{(aq)} + CO^{2-}_{3\,(aq)} \leftrightarrow HCO^-_{3\,(aq)} \tag{3}$$

The sum of the reactions shows the direct reaction between $CO_{2\,(g)}$ and $CO^{2-}_{3\,(aq)}$:

$$CO_{2\,(g)} + H_2O_{(l)} + CO^{2-}_{3\,(aq)} \leftrightarrow 2HCO^-_{3\,(aq)} \tag{4}$$

The above reactions are all essentially in instantaneous thermodynamic equilibrium, and the relationships between the concentrations of these species can be simplified to:
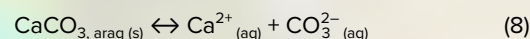
$$K_H = \frac{[CO_2]}{x(CO_2) * P} \tag{5}$$

$$K_1 = \frac{[H^+][HCO^-_3]}{[CO_2]} \tag{6}$$

$$K_2 = \frac{[H^+][CO^{2-}_3]}{[HCO^-_3]} \tag{7}$$

where $[CO_2]$, $[HCO^-_3]$, $[CO^{2-}_3]$, $[H^+]$, and $[Ca^{2+}]$ are the molar concentrations of the aqueous species carbon dioxide, bicarbonate, carbonate, hydrogen, and calcium ions in seawater, respectively; $x(CO_2)$ is the mole fraction of carbon dioxide gas, P is the equilibration pressure, and K_H, K_1, and K_2 are the equilibrium constants for reactions, which are known functions of temperature, salinity, and pressure.

The dissolution and precipitation reaction of aragonite,

$$CaCO_{3,\,arag\,(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3\,(aq)} \tag{8}$$

is almost never in thermodynamic equilibrium, so we usually relate the abundance of calcium and carbonate ions to the thermodynamic solubility product, $K_{sp\,(arag)}$, a known function of temperature, salinity, and pressure, through the saturation state (Ω_{arag}):

$$\Omega_{arag} = \frac{[Ca][CO^{2-}_3]}{K_{sp\,(arag)}} \tag{9}$$

The concentration of calcium ion in open-ocean seawater, $[Ca^{2+}]$, is present in near-constant proportion to salinity and can thus be assumed to be a function of salinity (S):

$$[Ca^{2+}] = \frac{0.01028 * S}{35} \tag{10}$$

A value for the saturation state of a seawater sample with respect to aragonite, Ω_{arag}, can thus be estimated for a seawater sample if the carbonate ion concentration $[CO^{2-}_3]$ is determined and the temperature, salinity, and pressure are known. Carbonate ion concentration cannot be directly measured, but can be estimated through characterization of the seawater CO_2 system and the three equilibrium relationships between these concentrations, K_H, K_1, and K_2. Thus, determination of aragonite saturation state of a seawater sample requires independent measurements of chemical parameters that can characterize two of the carbon system species, as well as temperature, salinity, and pressure.

both technologically achievable and biologically meaningful. This uncertainty encompasses multiple sources of error, including, but not limited to, measurement reproducibility and repeatability, accuracy relative to a standard, and uncertainty in the solubility product constants (De Bièvre, 2008). This is similar to target uncertainties developed by GOA-ON, which states that a maximum allowable uncertainty of 10% in aragonite saturation state is necessary to identify relative spatial patterns and short-term variation in OA, which for a saturation state of 2.0 is ±0.2 ("weather objective"; Newton et al., 2014).

Biologically important thresholds of aragonite saturation state, and other relevant carbonate system parameters, are lacking for a number of target species (Hofmann et al., 2010), but one threshold that is thought to be critical for marine organisms is when surface waters become undersaturated with respect to their shell mineralogy (Doney et al., 2009). The calcification threshold for many organisms does not necessarily coincide with the chemical threshold where saturation state is 1, but instead can occur at both higher and lower values. Many reef-building corals, for example, appear to cease calcification at aragonite saturation as high as 2.0 (Doney et al., 2009; McCulloch et al., 2012), and oyster larvae have been shown to have severe mortalities at aragonite saturation states less than 1.8 (Barton et al., 2012). While ± 0.2 is inadequate for ocean chemists looking for small temporal changes in saturation state, it provides adequate context for interpreting biological response.

Because aragonite saturation state is a calculated parameter, it depends not only on the independent measurements of chosen pairs of pH, pCO_2, TCO_2, or TA, and co-located measures of temperature and salinity, but also on the thermodynamic constants that determine the relationships of the carbonate species to each other. There are uncertainties associated with both measurement of carbon system parameters and the constants used to calculate Ω_{arag}. Despite the best work of marine physical chemists over the last several decades, there is not yet perfect agreement on the values of these thermodynamic constants, even in the relatively constant-condition open ocean, and considerably less certainty for values in the brackish-mesohaline environments typical of many estuarine and coastal environments. As a result, even with perfect (zero uncertainty) measurements

Box 2. Possible Parameters to Constrain the Seawater CO_2 System

Many alternate combinations of measurements of the four parameters described in Box 1 can be used to determine the carbonate ion concentration and thus characterize the aragonite saturation state The recognized methods currently available (Dickson et al., 2007, provides a review) for measuring these parameters are described briefly here.

Seawater pH, measured on the total scale, is a measure of the hydrogen ion concentration in seawater:

$$pH = -\log[H^+] \tag{11}$$

The partial pressure of carbon dioxide of a small gaseous headspace in equilibrium with seawater pCO_2 is expressed as

$$p(CO_2) = \frac{[CO_2]}{K_H} \tag{12}$$

Total dissolved inorganic carbon (C_T or TCO_2), the sum of the dissolved inorganic carbon species in seawater is expressed as

$$TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{13}$$

Total alkalinity (TA) is a charge balance equation representing a solution's ability to neutralize an acid, effectively the stoichiometric sum of bases minus acids in solution:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]... \tag{14}$$

where the ellipses stand for additional minor acids or base species that are present in such small amounts that they may be neglected in some cases.

Calculation of the carbonate ion concentration requires knowledge of at least two of the parameters pH, $p(CO_2)$, TCO_2, or TA, together with the equilibrium constants for the CO_2 system, K_H, K_1, and K_2. Use of total alkalinity requires additional knowledge of the total concentration and equilibrium constant(s) of any other significant acid-base systems in seawater. For open-ocean surface seawater, this usually only involves the borate and water systems, which are well constrained. In coastal environments with restricted exchange with the open ocean, there may be significant contributions from other acid-base systems. Some of these, such as phosphate, silicate, and ammonium, have equilibria that are reasonably well characterized; others, such as organic acids and bases, are less well understood.

Publicly available computer programs, such as CO2SYS, CO2calc, or Seacarb, are typically used to calculate carbonate ion concentration from measured data. See Dickson et al. (2007) for a detailed review of the relevant calculations.

of pH, pCO_2, TCO_2, or TA, calculation of Ω_{arag} will nevertheless have an associated uncertainty. Furthermore, the magnitude of this uncertainty will depend on the pair of analytical parameters chosen for the calculation. Intercomparison of data within a network will be meaningless if calculations are performed with different assumed sets of thermodynamic constants, and participants in an integrated network should rely on a common set of thermodynamic constants based on the same pH scale. In this case, C-CAN recommends the total pH scale. Recommendations for equilibrium constants for use at salinities greater than 20 ppt are: Lueker et al. (2000) for the temperature and salinity-dependent constants for first and second dissociation constants of carbonic acid, K_1, and K_2 on the total pH scale; Mucci (1983) for the solubility product constant for aragonite ($K_{sp\,(arag)}$); Weiss and Price (1980) for the Henry's Law constant for the partial pressure of CO_2 in water or Weiss (1974) for the fugacity of CO_2; Lee et al. (2000) for relationship between boron and total alkalinity; Dickson (1990) for the dissociation constant for hydrogen sulfide ion; and Wanninkhof (1992) for air-sea carbon dioxide exchange. There will likely be further evolution of the scientific community's understanding of these thermodynamic parameters, and growing consensus regarding the appropriate use of certain formulations of the temperature and salinity dependences. If all network participants retain detailed records of primary chemical measurements and quality control data, and utilize the same set of constants, straightforward and consistent community-wide recalculation should be possible, if deemed necessary.

Any two (or more) CO_2 system parameters can be used to calculate aragonite saturation state. Mathematically, all choices should be equivalent, but in practice this is not the case. Each parameter is an experimental quantity with an associated uncertainty (Dickson and Riley, 1978; De Bièvre, 2008). These uncertainties can propagate through the

calculations, resulting in uncertainties in the calculated values (e.g., Ω_{arag}). As discussed above, in addition to uncertainties in the measured CO_2 parameters, there are also uncertainties, for example, in the various equilibrium constants, in the total concentrations of other acid-base systems such as boron, and in the completeness of the expression for total alkalinity. Therefore, it is essential to document the uncertainty associated with each of the measured and/or calculated parameters reported in coastal ocean acidification studies. A full analysis of the sources of uncertainty is beyond the scope of this paper, though proper assessment is critical, and discussion of potential sources of uncertainty is starting to be assessed by others (Hoppe et al., 2012; Bockmon and Dickson, 2015). Table 1 provides an expectation for technologically achievable uncertainties in measurable carbonate system parameters, as well as the uncertainties associated with

the thermodynamic constants, indicating that an overall uncertainty of ±0.2 or less in Ω_{arag} is reasonable (a relative combined uncertainty of 10% is equivalent to ±0.2 with Ω_{arag} of 2). Table 2 demonstrates the effect of these uncertainties and the choice a pair of carbonate system parameters has on the calculated value of Ω_{arag}.

C-CAN emphasizes the importance of continuous collection of monitoring data in order to understand short-term variability in aragonite saturation state. While selection of a pair of carbonate parameters with a strong positive covariation could inflate combined errors, such non-ideal pairing could still provide critical data. For example, pCO_2 and pH strongly covary; however, commercially available sensors for continuous monitoring of each of these parameters is available, and the information generated from such time-series measurements could constrain variation in aragonite saturation state in critical coastal habitats.

Table 1. Expectation for achievable uncertainties in measurable carbonate system parameters and uncertainties associated with thermodynamic constants (95% confidence).

Parameter	Absolute Uncertainty $u(x)$
TCO_2	10 µmol kg^{-1}
pH	0.02
pCO_2	12 µatm (at 400 µatm)
Total Alkalinity (TA)	10 µmol kg^{-1}
pK_0	0.004
pK_1	0.015
pK_2	0.030

Parameter	Relative Uncertainty $u(x)/x$
$u(TCO_2)/TCO_2$	0.5%
$u[H^+]/[H^+]$	3%
$u(p(CO_2))/p(CO_2)$	3%
$u(TA)/TA$	0.5%

Table 2. Calculated combined relative uncertainties for a seawater sample with a pH ~ 8.1 and Ω_{arag} ~ 2.0 using uncertainties from Table 1. A relative uncertainty of 10% in Ω_{arag} is equivalent to the bound of the C-CAN recommended ±0.2. Each line reflects a different pairing of carbonate system parameters with the values in bold reflecting the measured parameters. Overall uncertainty includes uncertainty associated with constants.

Pairing	pH	TCO_2	TA	pCO_2	Ω_{arag}
pH + TCO_2	0.3%	0.5%	1%	6%	8%
pH + pCO_2	0.3%	7%	7%	3%	13%
TCO_2 + TA	0.6%	0.5%	0.5%	12%	14%
TCO_2 + pCO_2	0.3%	0.5%	1%	3%	7%

Until widespread technology is available to support a more ideal carbonate system pairing for continuous measurement, monitoring programs will be constrained to work with less ideal combinations.

Regardless of which parameters are used to determine aragonite saturation state, all participants in the OA monitoring network would be expected to implement best practices with a quality assurance and quality control (QA/QC) program to ensure that aragonite saturation state can be calculated with known uncertainty. The QA/QC program includes regular calibration with reference materials as well as routine intercalibration with partner laboratories. Bottle samples should be used to ground truth sensors and improve data quality for all autonomous measurements and, wherever possible, co-located sensors should be deployed (Bresnahan et al., 2014). Bottle samples for intercalibration should be collected and run in house and at a series of partner laboratories at least twice per year to ensure precision and comparability of network monitoring stations.

Recommendation 3:
Inclusion of a variety of monitoring platforms and levels of effort in the network will ensure collection of high-frequency temporal data at fixed locations as well as spatial mapping across locations.

Two primary types of data sets should be incorporated into an OA network: (1) continuous, high-frequency data at fixed locations from one or more depths, and (2) high spatial coverage maps and vertical profiles. Data collected at high frequency can provide information on short-term changes and cycles in OA parameters (e.g., tidal, diurnal). At sentinel sites, it is important to collect continuous, high-frequency data in order to understand diurnal and seasonal patterns in the carbonate system. However, because such monitoring is resource intensive, spatial coverage is likely to be limited. Synoptic mapping expeditions

that cover large areas can help fill in the gaps and provide information on spatial variability that would not otherwise be captured at a fixed station. An OA monitoring network should incorporate both types of data. However, because biological activity (photosynthesis and respiration) and physical processes strongly affect the carbonate system, particularly in coastal waters, limited, discrete sampling at a single location or synoptic studies of limited scope will be of little network value because of challenges in interpreting such data sets.

To maximize available resources, an OA network should be broadly inclusive, recognizing that not all organizations will possess equal levels of technical expertise and/or financial capability. To this end, a nested sampling design will ensure that all sites are collecting a minimum set of priority measurements; secondary measurements can be added for those with greater resources. Priority measurements include: temperature, salinity, dissolved oxygen, and two of the four carbonate system parameters, allowing for direct calculation of aragonite saturation state and a full characterization of the seawater CO_2 system (Newton et al., 2014). Secondary measurements may include: additional carbonate system parameters, current speed and direction, meteorology (e.g., air temperature, wind speed and direction, solar irradiance), atmospheric pCO_2, photosynthetically available radiation (PAR), nutrient concentrations, trace metal concentrations, particulate organic carbon, particulate inorganic carbon, export production, stable isotopic measures of nutrients and carbon (e.g., $\delta^{18}O$ of water, $\delta^{13}C$ of particulate organic matter, $\delta^{18}O$ and $\delta^{15}N$ of dissolved nitrate, $\delta^{15}N$ of dissolved ammonia), and measures of rates of nutrient and carbon cycling (e.g., nutrient uptake kinetics, nitrification, denitrification, nitrogen fixation, primary production and respiration, net ecosystem metabolism). These measurements are important for parameterization of coupled biogeochemical and physical models.

Recommendation 4:
The monitoring network encourages linkage of physical and chemical oceanographic changes with changes in biological communities.

Understanding ecological interactions and feedbacks is critical to characterizing the impacts and drivers of ocean acidification in the nearshore environment (Alin et al., 2015, in this issue). Changing ocean chemistry directly affects biological communities, which, in turn, influence ocean chemistry (Melzner et al., 2012; Duarte et al., 2013). A key component of the OA monitoring network is to establish linkages between chemical and physical data sets and biological data sets to advance understanding of interactions between them.

First, the effects of changing ocean chemistry on biological communities must be defined. This is a twofold process. First, co-location of seawater monitoring sensors with biological measurements will allow for documentation of how organisms respond to in situ changes in ocean chemistry (Hofmann et al., 2011), and the data thus collected can then be used to guide targeted experiments. Addition of complementary parameters to existing monitoring programs can help clarify causes and effects and can be used to develop correlations between chemical parameters and biological responses. These effects can then be further tested in the laboratory to more clearly define the relationships. Second, experiments must be implemented that will allow for understanding the adaptive capacity of organisms (e.g., Dawson et al., 2011) in a context of future acidification. This will involve characterizing the physiological tolerances and capacities of species in a population (in order to identify vulnerability or the lack of plasticity to future changes) as well as the degree to which a species can adapt to a rapidly changing environment (Hoffmann and Sgrò, 2011).

Second, the influence of biological communities on the expression of OA must be characterized. As acidification

alters biological community structures, species shifts may result in changes in carbon and nutrient cycling. Many near-shore pelagic and benthic calcified organisms are integral parts of marine food webs, and ecological consequences will potentially follow loss of foundational species (Cooley et al., 2009; Kroeker et al., 2011). In particular, filter feeders play key roles in nutrient cycling, and their displacement due to changing ocean chemistry leads to the possibility of positive feedbacks to the carbon cycle. In addition, other factors, such as nutrient pollution and resultant increased primary production (eutrophication), will likely work interactively with ocean acidification (Howarth et al., 2011; Duarte et al., 2013). For example, nearshore inputs of nutrients can fuel algal blooms. When these algal blooms senesce, microbial communities consume them and respire organic matter, which produces carbon dioxide and reduces oxygen concentrations. These types of biogeochemical processes influence the carbon budgets of coastal systems, affecting pCO$_2$ and pH in ways that can amplify the effects of ocean acidification (Howarth et al., 2011; Melzner et al., 2012).

All of these pursuits are challenging. An OA monitoring program must overcome these challenges by: (1) providing a network of shared data, enabling investigators to design and conduct experiments using environmentally relevant data; (2) standardizing techniques and practices, allowing investigators to share data and compare results; and (3) encouraging and facilitating development of causal models to reveal the influence of global versus local factors in changing ecosystem structure and function. Insights from such a monitoring program will be critical to forecasting the effects of ocean acidification not only on target species in one locale but also region-wide.

In terms of implementing a biological monitoring program, a nested sampling design with standardized, priority measurements conducted at all sites and secondary measurements collected

at a subset of sites is proposed, although the specific parameters that should be included are still under discussion (e.g., GOA-ON; Newton et al., 2014). Suggested priority biological measurements include: autonomous chlorophyll fluorescence, dissolved oxygen, and irradiance, as well as biomass of functional groups (phytoplankton, zooplankton, microbes, benthic animals, macroalgae, fungi, and vascular plants). Proposed secondary measurements include the community or species composition of functional groups and long-term field studies defining rates of key processes (e.g., growth and grazing rates at different life stages), and autonomous or discrete measurements of nutrient concentrations as well as nutrient loading from watersheds to coastal and estuarine waters.

Recommendation 5:
The monitoring network shall share data and make them accessible to a broad audience.

The primary goal of the monitoring network is to permit a comprehensive description of the status of acidification in US West Coast waters as well as enhanced understanding of acidification drivers and impacts. This requires cooperation of numerous entities because no single organization collects data over the range of geographies and conditions necessary to achieve this vision. A key measure of the network's success will be widespread

use of the data generated through its monitoring program. The goal is not only to provide chemical monitoring data for managers on current marine conditions but also to provide data required to design and conduct relevant laboratory and field experiments to understand the effects of ocean acidification on susceptible organisms, and to develop causative and pre-

> " The primary goal of the monitoring network is to permit a comprehensive description of the status of acidification in US West Coast waters as well as enhanced understanding of acidification drivers and impacts. "

dictive models for determining ecosystem response. If the data are to be useful for these purposes, they must be shared and reported in a consistent and reliable manner (Garcia et al., 2015, in this issue).

The IOOS Regional Associations already collect data critical to interpretation of ocean acidification effects and have infrastructure in place for parameters similar to those required for monitoring acidification. Thus, they have volunteered to serve as data managers and to preserve the data for a US West Coast OA monitoring network (http://www.nanoos.org). The regional associations have built upon existing capacity and capabilities to develop a Web portal that accepts data streams from all relevant data centers, provides visual and data link capabilities, and exhibits synthesis products for the US West Coast both as a whole and on the subregional scale. The Web portal will also allow tracking of all network participant data streams, serving as an inventory of ocean acidification monitoring assets for the West Coast and allowing determination

of spatial coverage and gaps in the network. It will incorporate both real-time and non-real-time data from monitoring units and observational studies, as well as experimental data. The required expansion of existing platform capacity to collate disparate data sources into an integrated network is being achieved via development of data input structures, metadata requirements, and data visualization and access tools.

CONCLUSIONS

A comprehensive OA monitoring network for the California Current System is a realistic and feasible goal. The foundation of such a network is already present through existing monitoring efforts and infrastructure. Integrating and building on existing monitoring efforts, infrastructure, and experience is key. Coordinating existing efforts adds value to all such efforts, not only through a linked data set but also through shared knowledge of new technologies and practices, standardization of protocols, and shared infrastructure and personnel. Chemical measurements can be added to existing biological monitoring efforts, biological monitoring can be added to existing chemical monitoring efforts, and long-term efforts can be prioritized for support into the future. While the core principles outlined here were designed to develop a cohesive network for the California Current System, these principles are broadly applicable to other OA monitoring efforts globally.

REFERENCES

Alin, S.R., R.E. Brainard, N.N. Price, J.A. Newton, A. Cohen, W.T. Peterson, E.H. DeCarlo, E.H. Shadwick, S. Noakes, and N. Bednaršek. 2015. Characterizing the natural system: Toward sustained, integrated coastal ocean acidification observing networks to facilitate resource management and decision support. *Oceanography* 28(2):92–107, http://dx.doi.org/10.5670/oceanog.2015.34.

Barton, A., B. Hales, G.G. Waldbusser, C. Langdon, and R.A. Feely. 2012. The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. *Limnology and Oceanography* 57:698–710, http://dx.doi.org/10.4319/lo.2012.57.3.0698.

Barton, A., G.G. Waldbusser, R.A. Feely, S.B. Weisberg, J.A. Newton, B. Hales, S. Cudd, B. Eudeline, C.J. Langdon, I. Jefferds, and others. 2015. Impacts of coastal acidification on the Pacific Northwest shellfish industry and adaptation strategies implemented in response. *Oceanography* 28(2):146–159, http://dx.doi.org/10.5670/oceanog.2015.38.

Bockmon, E.E., and A.G. Dickson. 2015. An interlaboratory comparison assessing the quality of seawater carbon dioxide measurements. *Marine Chemistry* 171:36–43, http://dx.doi.org/10.1016/j.marchem.2015.02.002.

Borges, A.V., and N. Gypens. 2010. Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification. *Limnology and Oceanography* 55:346–353, http://dx.doi.org/10.4319/lo.2010.55.1.0346.

Breitburg, D.L., J. Salisbury, J.M. Bernhard, W.-J. Cai, S. Dupont, S.C. Doney, K.J. Kroeker, L.A. Levin, W.C. Long, L.M. Milke, and others. 2015. And on top of all that… Coping with ocean acidification in the midst of many stressors. *Oceanography* 28(2):48–61, http://dx.doi.org/10.5670/oceanog.2015.31.

Bresnahan, P., T.R. Martz, Y. Takeshita, K.S. Johnson, and M. LaShomb. 2014. Best practices for autonomous measurement of seawater pH with the Honeywell Durafet. *Methods in Oceanography* 9:44–60, http://dx.doi.org/10.1016/j.mio.2014.08.003.

Cooley, S.R., H.L. Kite-Powell, and S.C. Doney. 2009. Ocean acidification's potential to alter global marine ecosystem services. *Oceanography* 22(4):172–181, http://dx.doi.org/10.5670/oceanog.2009.106.

Dawson, T.P., S.T. Jackson, J.I. House, I.C. Prentice, and G.M. Mace. 2011. Beyond predictions: Biodiversity conservation in a changing climate. *Science* 332:53–58, http://dx.doi.org/10.1126/science.1200303.

De Bièvre, P. 2008. Measurement uncertainty is not synonym of measurement repeatability or measurement reproducibility… *Accreditation and Quality Assurance* 13:61–62, http://dx.doi.org/10.1007/s00769-008-0371-0.

Dickson, A.G. 1990. Standard potential of the reaction AgCl(s) + .5H_2(g) = Ag(s) + HCl(aq) and the standard acidity constant of the ion HSO_4^- in synthetic sea water from 273.15 to 318.15 K. *The Journal of Chemical Thermodynamics* 22:13–127, http://dx.doi.org/10.1016/0021-9614(90)90074-z.

Dickson, A.G. 2010. The carbon dioxide system in seawater: Equilibrium chemistry and measurements. Pp. 17–40 in *Guide to Best Practices for Ocean Acidification Research and Data Reporting*. U. Riebesell, V.J. Fabry, L. Hansson, and J.-P. Gattuso, eds, Publications Office of the European Union, Luxembourg, http://www.iaea.org/ocean-acidification/download/7_Best practices/OA_guide_20110726.pdf.

Dickson, A.G., and J.P. Riley. 1978. The effect of analytical error on the evaluation of the components of the aquatic carbon-dioxide system. *Marine Chemistry* 8:77–85, http://dx.doi.org/10.1016/0304-4203(78)90008-7.

Dickson, A.G., C.L. Sabine, and J.R. Christian, eds. 2007. *Guide to Best Practices for Ocean CO₂ Measurements*. PICES Special Publication 3, 191 pp.

Doney, S.C., V.J. Fabry, R.A. Feely, and J.A. Kleypas. 2009. Ocean acidification: The other CO_2 problem. *Annual Review of Marine Science* 1:169–192, http://dx.doi.org/10.1146/annurev.marine.010908.163834.

Duarte, C.M., I.E. Hendriks, T.S. Moore, Y.S. Olsen, A. Steckbauer, L. Ramajo, J. Carstensen, J.A. Trotter, and M. McCulloch. 2013. Is ocean acidification an open-ocean syndrome? Understanding anthropogenic impacts on seawater pH. *Estuaries and Coasts* 36:221–236, http://dx.doi.org/10.1007/s12237-013-9594-3.

Fabry, V.J., B.A. Seibel, R.A. Feely, and J.C. Orr. 2008. Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65:414–432, http://dx.doi.org/10.1093/icesjms/fsn048.

Feely, R.A., V.J. Fabry, A.G. Dickson, J.P. Gattuso, J. Bijma, U. Riebesell, S. Doney, C. Turley, T. Saino, K. Lee, and others, eds. 2010. *An International Observational Network for Ocean Acidification*. ESA Publication WPP-306, Venice, Italy, September 21–25, 2009, http://dx.doi.org/10.5270/OceanObs09.cwp.29.

Feely, R.A., C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson, and B. Hales. 2008. Evidence for upwelling of corrosive "acidified" water onto the continental shelf. *Science* 320:1,490–1,492, http://dx.doi.org/10.1126/science.1155676.

Garcia, H.E., C. Cosca, A. Kozyr, E. Mayorga, C. Chandler, R.W. Thomas, K. O'Brien, W. Appeltans, S. Hankin, J.A. Newton, and others. 2015. Data management strategy to improve global use of ocean acidification data and information. *Oceanography* 28(2):226–228, http://dx.doi.org/10.5670/oceanog.2015.45.

Gruber, N., C. Hauri, Z. Lachkar, D. Loher, T.L. Frölicher, and G.-K. Plattner. 2012. Rapid progression of ocean acidification in the California Current System. *Science* 337:220–223, http://dx.doi.org/10.1126/science.1216773.

Hauri, C., N. Gruber, C.-K. Plattner, S. Alin, R.A. Feely, B. Hales, and P.A. Wheeler. 2009. Ocean acidification in the California Current System. *Oceanography* 22(4):60–71, http://dx.doi.org/10.5670/oceanog.2009.97.

Hoffmann, A.A., and C.M. Sgrò. 2011. Climate change and evolutionary adaptation. *Nature* 470:479–485, http://dx.doi.org/10.1038/nature09670.

Hofmann, G.E., J.P. Barry, P.J. Edmunds, R.D. Gates, D.A. Hutchins, T. Klinger, and M.A. Sewell. 2010. The effect of ocean acidification on calcifying organisms in marine ecosystems: An organism-to-ecosystem perspective. *Annual Review of Ecology, Evolution, and Systematics* 41:127–147, http://dx.doi.org/10.1146/annurev.ecolsys.110308.120227.

Hofmann, G.E., J.E. Smith, K.S. Johnson, U. Send, L.A. Levin, F. Micheli, A. Paytan, N.N. Price, B. Peterson, Y. Takeshita, and others. 2011. High-frequency dynamics of ocean pH: A multi-ecosystem comparison. *PLoS ONE* 6:e28983, http://dx.doi.org/10.1371/journal.pone.0028983.

Hoppe, C.J.M., G. Langer, S.D. Rokitta, D.A. Wolf-Gladrow, and B. Rost. 2012. Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies. *Biogeosciences* 9:2,401–2,405, http://dx.doi.org/10.5194/bg-9-2401-2012.

Howarth, R., F. Chan, D.J. Conley, J. Garnier, S.C. Doney, R. Marino, and G. Billen. 2011. Coupled biogeochemical cycles: Eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Frontiers in Ecology and the Environment* 9:18–26, http://dx.doi.org/10.1890/100008.

Ishimatsu, A., M. Hayashi, and T. Kikkawa. 2008. Fishes in high-CO_2, acidified oceans. *Marine Ecology Progress Series* 373:295–302, http://dx.doi.org/10.3354/meps07823.

Kroeker, K.J., F. Micheli, M.C. Gambi, and T.R. Martz. 2011. Divergent ecosystem responses within a benthic marine community to ocean acidification. *Proceedings of the National Academy of Sciences of the United States of America* 108:14,515–14,520, http://dx.doi.org/10.1073/pnas.1107789108.

Lee, K., F.J. Millero, R.A. Byrne, R.A. Feely, and R. Wanninkhof. 2000. The recommended dissociation constants for carbonic acid in seawater. *Geophysical Research Letters* 27:229–232, http://dx.doi.org/10.1029/1999GL002345.

Leinweber, A., and N. Gruber. 2013. Variability and trends of ocean acidification in the Southern California Current System: A time series from Santa Monica Bay. *Journal of Geophysical Research* 118:3,622–3,633, http://dx.doi.org/10.1002/jgrc.20259.

Lueker, T.J., A.G. Dickson, and C.D. Keeling. 2000. Ocean $p$$CO_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: Validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry* 70:105–119, http://dx.doi.org/10.1016/S0304-4203(00)00022-0.

McCulloch, M., J. Falter, J. Trotter, and P. Montagna. 2012. Coral resilience to ocean acidification and global warming through pH up-regulation. *Nature Climate Change* 2:623–633, http://dx.doi.org/10.1038/nclimate1473.

Melzner, F., J. Thomsen, W. Koeve, A. Oschlies, M.A. Gutowska, H.W. Bange, H.P. Hansen, A. Körtzinger. 2013. Future ocean acidification will be amplified by hypoxia in coastal habitats. *Marine Biology* 160:875–1888, http://dx.doi.org/10.1007/s00227-012-1954-1.

Mucci, A. 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere pressure. *American Journal of Science* 283:780–799, http://dx.doi.org/10.2475/ajs.283.7.780.

Newton, J.A., R.A. Feely, E.B. Jewett, P. Williamson, and J. Mathis. 2014. *Global Ocean Acidification Observing Network: Requirements and Governance Plan*. 60 pp., http://www.goa-on.org/docs/GOA-ON_plan_print.pdf.

Riebesell, U., V.J. Fabry, L. Hansson, and J.P. Gattuso, eds. 2010. *Guide to Best Practices for Ocean Acidification Research and Data Reporting*. Publications Office of the European Union, Luxembourg, 260 pp., http://www.iaea.org/ocean-acidification/download/7_Best practices/OA_guide_20110726.pdf.

Ries, J. 2011. Acid ocean cover up. *Nature Climate Change* 1:294–295, http://dx.doi.org/10.1038/nclimate1204.

Roleda, M.Y., P.W. Boyd, and C.L. Hurd. 2012. Before ocean acidification: Calcifier chemistry lessons. *Journal of Phycology* 48:840–843, http://dx.doi.org/10.1111/j.1529-8817.2012.01195.x.

Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97:7,373–7,382, http://dx.doi.org/10.1029/92JC00188.

Weiss, R.F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry* 2:203–215, http://dx.doi.org/10.1016/0304-4203(74)90015-2.

Weiss, R.F., and B.A Price. 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry*. 8:347–359, http://dx.doi.org/10.1016/0304-4203(80)90024-9.

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