

# California Current Acidification Network (C-CAN)

## Core Principles for Development of a West Coast Network for Monitoring Marine Acidification and Its Linkage to Biological Effects in the Nearshore Environment



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This document was initiated by and developed under supervision of the California Current Acidification Network (C-CAN) Steering Committee.

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## PREFACE

The California Current Acidification Network (C-CAN) is a collaboration dedicated to advancing understanding of ocean acidification (OA) and its effects on biological resources of the U.S. West Coast. C-CAN first convened in 2010 in response to a growing realization that declines in shellfish hatchery production corresponded to coastal upwelling of low pH waters. The initial workshop brought together leading shellfish industry representatives, coastal managers, researchers, Sea Grant programs, and Integrated Ocean Observing Systems to increase collective understanding of OA effects on the nearshore environment. C-CAN has since expanded to include other ocean-dependent industries, environmental advocacy groups, regulatory agencies, and tribal groups.

The overarching goal of C-CAN is to coordinate and standardize OA measurement and data collection practices, ensuring data accessibility, utility, and application. C-CAN provides shared guidelines and support for participating groups in implementation of high quality, compatible monitoring programs. C-CAN also facilitates application of the network's data in developing tools that examine the causes of ecosystem impacts and predict future changes in ocean chemistry and biological communities. Finally, C-CAN communicates its findings to address management concerns about defining the ecological effects of OA for development of mitigation and adaptation strategies. Given the complexity of this emerging issue, and recognizing that advancing knowledge will require a concerted community effort, C-CAN is committed to serve as the region's source of reliable, vetted scientific information on ocean acidification.

## STATEMENT OF CORE MONITORING PRINCIPLES

The California Current Acidification Network (C-CAN) is a collaborative of interdisciplinary scientists, resource managers, industry, and others from local, state, and federal levels dedicated to advancing the understanding of ocean acidification and its effects on biological resources of the U.S. West Coast. A central component of C-CAN's mission is to coordinate and encourage development of an ocean acidification monitoring network for the US West Coast that incorporates the following core principles:

1. Core measurements should facilitate determination of aragonite saturation state ( $\Omega$ ) and a complete description of the carbonate system, including pH and  $p(\text{CO}_2)$ .
2. A  $\pm 0.2$  minimum uncertainty in the aragonite saturation state ( $\Omega$ ) calculation 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 engenders high frequency temporal data at fixed locations as well as spatial mapping across locations.
4. The monitoring network encourages linkage of physical and chemical oceanographic changes with changes in biological communities.
5. The monitoring network shall share data and make it accessible to a broad audience.

The complexity of ocean acidification requires a concerted community effort. C-CAN network participants share a vision for understanding the drivers and impacts of ocean acidification on the U.S. West Coast. By cooperating in the C-CAN network, participants agree to work together to collect and present reliable, comparable data for interested parties.

## CHAPTER 1 — INTRODUCTION AND MOTIVATION

Ocean acidification poses a threat to the health of the world's oceans and the significant beneficial uses they provide. Globally, one-quarter of carbon dioxide (CO<sub>2</sub>) released into the atmosphere by anthropogenic activities is being absorbed by the oceans (Doney et al. 2009). When CO<sub>2</sub> dissolves in seawater, it lowers pH and reduces the concentration of available carbonate ions, a process called ocean acidification (OA). Waters undersaturated with carbonate ions are corrosive to organisms that produce calcium carbonate exoskeletons, such as shellfish, corals, and some species of plankton that comprise the base of the marine food web (Feely et al. 2012).

The U.S. West Coast is particularly vulnerable to the effects of ocean acidification, potentially resulting in serious impacts to ecosystems and some recreationally and commercially important shellfish (Branch et al. 2013, Gruber et al. 2012). Deep ocean waters are naturally undersaturated with calcium carbonate and thus corrosive to shelled organisms. The Pacific coast's natural circulation patterns cause seasonal upwelling of these deep waters toward the ocean's surface. As ocean acidity increases on a global scale, corrosive waters rise closer to the surface and make their way into shallow coastal areas (Feely et al. 2009). For several years, the West Coast shellfish industry has been experiencing dramatic declines in hatchery production, which have been correlated with upwelling events that bring low-pH, corrosive waters to shore.

Determining the effects of ocean acidification on nearshore ecosystems, including coastal and estuarine waters, is fundamentally difficult. In the open ocean, decades of monitoring have culminated in development of ocean models that improve understanding of how ocean chemistry and oceanographic conditions in the deep sea may change due to rising atmospheric CO<sub>2</sub>. However, understanding the physical, chemical, and ecological impacts of ocean acidification in the nearshore environment is complicated by the interplay of numerous factors, such as freshwater inputs, tidal forcing, water stratification, nutrient overenrichment, algal blooms, and hypoxia (Fabry et al. 2008).

Furthermore, a disconnect between carbon chemistry data and biological effects data hampers development of models to understand the ecosystem effects of acidification in coastal environments. Most biological data are located inshore (e.g., at shellfish hatcheries), whereas most physical and chemical measurements are taken offshore, either on moorings or during ship-based sampling events. Nearshore OA sampling is also poorly coordinated, with a lack of uniformity among physical, chemical, and biological parameters.

Finally, the timescales over which data are integrated are fundamentally different. In the open ocean, the primary concern is predicting how large swaths of the ocean are changing over decadal scales; in the nearshore environment, stakeholders (e.g., shellfish harvesters, aquarium operators) need real-time data and predictive models that operate over a small segment of the coastline on daily to weekly timescales so they can adapt their operations to rapidly changing conditions.

Understanding the impacts of ocean acidification along the West Coast requires coordination of monitoring efforts to ensure intercomparable data collection regarding ocean acidification and its effects on nearshore ecosystems. However, the region lacks a well-developed consensus on monitoring approaches and a framework for sharing data with interested parties.

The California-Current Acidification Network (C-CAN) arose in part to address these issues. C-CAN is a collaborative that brings together diverse perspectives of scientists, resource managers, industry, and others from local, state, tribal, and federal levels. It aims to increase understanding about the acidification of coastal, estuarine, and offshore waters and acidification effects on biological resources. The overarching goal of C-CAN is to coordinate measurements, practices, and communication to define the effects of ocean acidification and develop strategies for adaptation. C-CAN has developed a vision that lowers barriers to implementing monitoring programs of sufficient quality to understand ecosystem effects of changing ocean chemistry.

C-CAN will provide explicit guidance as to how to take measurements (i.e., identify specific parameters, required precision, and suggested instrumentation) and will develop the necessary data infrastructure (in collaboration with Regional Associations of the US Integrated Ocean Observing System) for combining the various individual data sets into a coherent network. C-CAN also aims to facilitate use of network data in research to develop tools that help determine the causes of ecosystem declines, as well as tools to predict future changes in ocean chemistry and biological communities. Finally, C-CAN will communicate the findings of the monitoring network to address management questions and promote the data products and tools developed by C-CAN partners. More information on C-CAN's vision can be found in a companion document "Vision for Development of a West Coast Network for Monitoring Marine Acidification and Its Linkage to Biological Effects in the Nearshore Environment": <http://c-can.msi.ucsb.edu/c-can-documents/C-CAN%20%20Vision%20Document%20Final.pdf/view>.

The purpose of this document is to capture the core principles that C-CAN partners agree form the basis for a U.S. West Coast ocean acidification monitoring network:

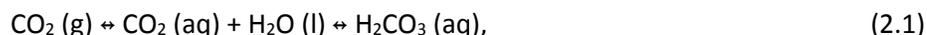
- Core measurements should facilitate determination of aragonite saturation state ( $\Omega$ ) and a complete description of the carbonate system, including pH and  $p(\text{CO}_2)$  (Chapter 2 – Core Measurements);
- A  $\pm 0.2$  minimum uncertainty in the aragonite saturation state ( $\Omega$ ) calculation is required to adequately link changes in ocean chemistry to changes in ecosystem function (Chapter 3 – Precision Requirements);
- Inclusion of a variety of monitoring platforms and levels of effort in the network engenders high frequency temporal data at fixed locations as well as spatial mapping across locations (Chapter 4 – Types of Chemistry Monitoring Systems);
- The monitoring network encourages linkage of physical and chemical oceanographic changes with changes in biological communities (Chapter 5 – Linkage to Biological Effects Data);
- The monitoring network shall share data and make it accessible to a broad audience (Chapter 6 – Data Sharing).

## CHAPTER 2 — CORE MEASUREMENTS

Ocean acidification (OA) refers to the reduction in seawater pH associated with the global oceanic uptake of atmospheric carbon dioxide (CO<sub>2</sub>) and other chemical additions to, or subtractions from, the ocean (Doney et al. 2009). When CO<sub>2</sub> dissolves in seawater, a new equilibrium is established that influences the concentration of other key molecules: hydrogen ion (H<sup>+</sup>) and bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) concentrations increase, the carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentration decreases, and the saturation state of biologically important forms of calcium carbonate (CaCO<sub>3</sub>) declines. These changes in seawater chemistry have negative effects on a wide range of physiological processes in marine organisms, particularly among calcifying (shell-forming) species (Feely et al., 2012). Several experiments have shown a variety of organisms depend on the saturation state of the calcium carbonate polymorph called aragonite ( $\Omega_{arag}$ ). This was particularly true for the viability and development of oyster larvae (Barton et al., 2012). These findings have led to widespread agreement that  $\Omega_{arag}$  is a key indicator of ocean acidification effects. However, because some species respond more strongly to other carbonate system parameters, it is desirable to obtain a complete description of the seawater CO<sub>2</sub> system, including  $p(\text{CO}_2)$  and pH (Doney et al. 2009). Thus, C-CAN's objective is to produce measurements that enable determination of  $\Omega_{arag}$  as well as a complete description of the seawater CO<sub>2</sub> system. In this way, even if the actual seawater CO<sub>2</sub> parameter that affects an individual organism is not  $\Omega_{arag}$ , complete description of the seawater CO<sub>2</sub> system enables derivation of the necessary information.

### Reactions When CO<sub>2</sub> Dissolves In Seawater<sup>1</sup>

When CO<sub>2</sub> dissolves in seawater, it reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>):



where the notations (g), (l), (aq) refer to the states of gas, liquid, and aqueous solution respectively.

Carbonic acid then dissociates to form hydrogen ion and bicarbonate ion:



In seawater, most of the hydrogen ions formed by this dissociation react with carbonate ions to form bicarbonate:



The equilibrium relationships can be simplified to:

$$K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p} \quad (2.4)$$

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<sup>1</sup> Text adapted from Dickson et al. (2007) Guide to Best Practices for Ocean CO<sub>2</sub> Measurements.

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (2.5)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (2.6)$$

where  $[CO_2]$ ,  $[HCO_3^-]$ ,  $[CO_3^{2-}]$ , and  $[H^+]$  are the molar concentrations of carbon dioxide, bicarbonate, carbonate, and hydrogen ions in seawater respectively<sup>2</sup>,  $x(CO_2)$  is the mole fraction of carbon dioxide,  $p$  is the equilibration pressure, and  $K_0$ ,  $K_1$ , and  $K_2$  are the equilibrium constants for reactions, which are dependent on temperature and pressure.

When the system is at equilibrium, the state of the  $CO_2$  system is described by the partial pressure of carbon dioxide in the gas phase ( $p(CO_2)$ ) and the molar concentrations of  $[CO_2]$ ,  $[HCO_3^-]$ ,  $[CO_3^{2-}]$ , and  $[H^+]$  in seawater and the three equilibrium relationships between these concentrations ( $K_0$ ,  $K_1$ , and  $K_2$ ), which leaves only two degrees of freedom. Thus, complete characterization of the seawater  $CO_2$  system requires independent measurements of two carbon system parameters.

### Definition Of Aragonite Saturation State<sup>3</sup>

The solubility of calcium carbonate can be represented by the following equilibrium:



and equilibrium expression:

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \quad (2.8)$$

where  $[CO_3^{2-}]$ , and  $[Ca^{2+}]$  are the molar concentrations of carbonate ions and calcium ions, (s) and (aq) refer to the state of the species, solid and aqueous respectively. The value of the equilibrium constant,  $K_{sp}$ , depends on the form of calcium carbonate of interest, for example, aragonite.

The saturation state of a seawater sample with respect to aragonite,  $\Omega_{arag}$ , is defined as

$$\Omega_{arag} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}(arag)} \quad (2.9)$$

The saturation state is the ratio between the product of calcium ions  $[Ca^{2+}]$  and carbonate ions  $[CO_3^{2-}]$  estimated for the seawater sample and the value the concentration product would have if the seawater were at equilibrium with aragonite (i.e., the stoichiometric solubility product for aragonite).

In equation 2.9, the concentration of calcium ion in seawater,  $[Ca^{2+}]$ , is usually assumed to be a simple function of salinity:

$$[Ca^{2+}] = 0.01028S / 35, \quad (2.10)$$

<sup>2</sup> Brackets are used here to indicate total concentrations in moles per kilogram of seawater.

<sup>3</sup> Text adapted from Dickson et al. (2007) Guide to Best Practices for Ocean  $CO_2$  Measurements.

and the solubility product of aragonite,  $K_{sp}(\text{arag})$ , at a pressure of one atmosphere is a function of temperature and salinity (Mucci, 1983):

$$\begin{aligned} \lg K_{sp}(\text{arag}) = & -171.945 - 0.077993T + 2903.293/T + 71.595 \lg T \\ & + (-0.068393 + 0.0017276T + 88.135/T)S^{0.5} \\ & - 0.10018S + 0.0059415S^{1.5} . \end{aligned} \quad (2.11)$$

A value for the saturation state of a seawater sample with respect to aragonite ( $\Omega_{\text{arag}}$ ) can thus be estimated for a seawater sample, provided the carbonate ion concentration,  $[\text{CO}_3^{2-}]$ , is known for the water sample in question.

### Estimation Of Carbonate Ion Concentration

Many alternative combinations of measurements can be used to determine the carbonate ion concentration and thus characterize the aragonite saturation state. There are various recognized methods (a brief review is provided by Dickson, 2010) for the measurement of these parameters. Seawater pH, a measure of the hydrogen ion concentration in seawater:

$$pH = -\log[H^+] \quad (2.12)$$

can be measured on discrete bottle samples collected from a Niskin or similar water sampler using spectroscopy (e.g., Carter et al. 2013) or autonomously using ion sensitive field effect transistor (ISFET) sensors or submersible sensors that utilize reagent-based colorimetry. The partial pressure of carbon dioxide in air in equilibrium with seawater  $p(\text{CO}_2)$ :

$$p(\text{CO}_2) = x(\text{CO}_2)p = \frac{[\text{CO}_2]}{K_0} \quad (2.13)$$

can be measured autonomously using an infrared analyzer or on bottle samples using a pH-based titration system. Total dissolved inorganic carbon ( $C_T$  or  $\text{TCO}_2$ ), the sum of the dissolved inorganic carbon species in seawater:

$$C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (2.14)$$

can be measured on bottle samples using an infrared analyzer or coulometry, and a prototype system is available using an autonomous infrared analyzer. Total alkalinity ( $A_T$ ) is a mass balance equation representing a solution's ability to neutralize an acid, effectively the stoichiometric sum of bases minus acids in solution:

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \dots \quad (2.15)$$

where the ellipses stand for additional minor acids or base species that are present in such small amounts that they may be safely neglected in many environments. Total alkalinity can be measured on discrete bottle samples using open cell or closed cell titration.

A complete description of the seawater CO<sub>2</sub> system requires that you know at least two of the parameters: pH,  $p(\text{CO}_2)$ ,  $C_T$  together with the equilibrium constants for the CO<sub>2</sub> system:  $K_0$ ,  $K_1$ ,  $K_2$ . To use total alkalinity, either as a measured or as a calculated parameter, requires additional knowledge of the total concentration and equilibrium constant(s) of any other significant acid-base system in seawater. For open-ocean surface seawater, this usually only involves the borate and water systems; coastal environments with restricted exchange with the open ocean may have significant amounts of other acid-base systems, such as phosphate.

A publicly available computer program, such as CO2SYS, CO2calc, or Seacarb, is typically used to calculate carbonate ion concentration from measured data.<sup>4</sup> For a review of the relevant calculations, see Dickson et al. (2007).

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<sup>4</sup> All of these programs are available from CDIAC: <http://cdiac.ornl.gov/oceans/pubs.html> in the section on CO<sub>2</sub> system calculation programs.

## CHAPTER 3 — UNCERTAINTY REQUIREMENTS

### Biologically Significant Measurements

C-CAN's chemical monitoring system should be of sufficient quality to inform co-located studies of biological response (see Chapter 5). Small changes in ocean chemistry may represent the difference between life and death for some marine species; thus, aragonite saturation measurements must meet a minimum uncertainty level that is both achievable by available technology and biologically meaningful. To achieve that, a core principle of the C-CAN monitoring network is to enable the calculation of the aragonite saturation state with an overall uncertainty of  $\pm 0.2$ .

Calcifying organisms exert a variable degree of control over biomineralization. As such, the degree of sensitivity to reduced aragonite saturation state varies across taxa (Doney et al. 2009). Reduced calcification rates are observed for a variety of calcareous organisms following acidification, even when the aragonite or calcite  $\Omega > 1.0$  (Doney et al. 2009, Barton et al. 2012). However, research on biologically important thresholds, in terms of aragonite saturation state, is lacking for a number of target species (Hofmann et al. 2010), complicating definition of a biologically meaningful threshold for measures of aragonite saturation state.

One threshold that will affect marine organisms is when surface waters become undersaturated with respect to their shell mineralogy (Doney et al. 2009). The calcification thresholds for many organisms does not necessarily coincide with the chemical threshold where saturation state  $\Omega = 1$ , 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), and oyster larvae have been shown to have severe mortalities at aragonite saturation states less than 1.8 (Barton et al. 2012). Given these limited data, C-CAN members agreed that a minimum uncertainty of  $\pm 0.2$  was both technologically achievable and biologically meaningful to biological thresholds between  $\Omega = 1$  and  $\Omega = 2$ .

As discussed in Chapter 2, any two (or more) CO<sub>2</sub> 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. These uncertainties can propagate through the calculations resulting in uncertainties in the calculated values (e.g.,  $\Omega_{arag}$ ). In addition to uncertainties in the measured parameters, there are also uncertainties in the various equilibrium constants. For total alkalinity, there are additional uncertainties in the total concentrations of other acid-base systems (such as boron and phosphate, etc.).

### Technological Limitations

Currently, available technology is sufficient for achieving measurements that enable the determination of aragonite saturation state with an overall uncertainty of  $\pm 0.2$ . Table 1 provides estimated uncertainties for the available technology for monitoring each CO<sub>2</sub> system parameter, depending on the platform. Table 2 provides a demonstration (using “dummy” estimates for each parameter that

approximate typical seawater conditions) of the maximum allowable uncertainty in each measurement that still enables calculation of aragonite saturation state with an overall uncertainty of  $\pm 0.2$ .

**Table 1. Estimated uncertainties in CO<sub>2</sub> system parameters associated with use of current, commercially-available technologies. All uncertainties assume proper calibration to suitable reference materials.**

Parameter	Laboratory	At Sea	Other Techniques
pH	$\pm 0.010$	$\pm 0.015$	$\pm 0.01-0.03$
$p(\text{CO}_2)$	$\pm 1.0 \mu\text{atm}$	$\pm 2 \mu\text{atm}$	$\pm 5-10 \mu\text{atm}$
$C_T$	$\pm 1.0 \mu\text{mol kg}^{-1}$	$\pm 2 \mu\text{mol kg}^{-1}$	$\pm 4-10 \mu\text{mol kg}^{-1}$
$A_T$	$\pm 1.2 \mu\text{mol kg}^{-1}$	$\pm 2 \mu\text{mol kg}^{-1}$	$\pm 4-10 \mu\text{mol kg}^{-1}$

**Table 2. Allowable uncertainty in each CO<sub>2</sub> system parameter that enables calculation of specified aragonite saturation state within  $\pm 0.2$ . Two scenarios are presented, one for determination of  $\Omega_{\text{arag}} = 2.2$  and one for  $\Omega_{\text{arag}} = 1.0$ . All calculations assume temperature is 15°C and salinity is 35 ppt.**

Parameter	Calculation of $\Omega_{\text{arag}} = 2.2$		Calculation of $\Omega_{\text{arag}} = 1.0$	
	“dummy” value	Allowable uncertainty	“dummy” value	Allowable uncertainty
pH	8.00	$\pm 0.04$	7.62	$\pm 0.07$
$p(\text{CO}_2)$	450 $\mu\text{atm}$	$\pm 60$	1200 $\mu\text{atm}$	$\pm 100$
$C_T$	2100 $\mu\text{mol kg}^{-1}$	$\pm 20$	2250 $\mu\text{mol kg}^{-1}$	$\pm 25$
$A_T$	2300 $\mu\text{mol kg}^{-1}$	$\pm 20$	2300 $\mu\text{mol kg}^{-1}$	$\pm 25$

## CHAPTER 4 — CHEMICAL MONITORING PLATFORMS AND LEVELS OF EFFORT

### Diverse Data Sets From Different Monitoring Platforms

Chemical monitoring in the nearshore environment can be conducted from several types of platforms, each providing different types of data. A core principle of C-CAN is to support monitoring of chemical parameters that enable calculation of aragonite saturation state and the complete characterization of carbonate chemistry at a  $\pm 0.2$  precision for each platform. This support includes provision of guidance manuals for each monitoring system, training, and assistance in setting up monitoring equipment, as well as ongoing support in the form of a regional expert who can provide technical assistance as necessary.

Two primary types of data sets will be incorporated into the C-CAN network: 1) continuous, high frequency data at a fixed location from one or more depths; and 2) high spatial coverage maps and vertical profiles. High frequency data can provide information on short-term changes and cycles in ocean acidification parameters (tidal, diurnal, etc.). However, collection of high frequency data is resource intensive. As a result, 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.

### Which Parameters Should Be Measured?

C-CAN's recommendations for which carbonate system parameter to measure are driven by available technology and reference materials. Recommendations may vary depending on the monitoring platform and level of effort. Specific recommendations for each platform will be described in more detail in the "How-To" manuals. For most C-CAN participants, commercially available technology is recommended for monitoring. For those with time and expertise, cutting-edge technology options exist. For autonomous measurements and remote deployments, pH and  $p(\text{CO}_2)$  are the recommended parameters. For discrete bottle samples, pH,  $C_T$ , and  $A_T$  are the recommended parameters.

The environment in which monitoring is conducted should also be considered when selecting parameters. There are differences between high salinity ocean samples and brackish estuarine waters that affect data interpretation. Presently, pH measurements cannot be well calibrated for brackish water environments (salinity range of 5 to 20 ppt), which affects the interpretation of these data in estuarine environments. In addition, in coastal environments, there may be other acid/base systems that significantly affect the total alkalinity and must be taken into account.

### Level Of Effort May Vary

C-CAN recognizes that not all organizations possess equal levels of technical expertise and financial capability, but limited funding should not preclude participation in the network. A core principle of C-CAN is to be inclusive, developing a nested sampling design to ensure all sites are collecting a minimum

set of priority measurements. Secondary measurements can be added for those with additional resources. There are three levels of operation:

- 1) **Principal Mode:** This is the primary mode of operation for most C-CAN participants. 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<sub>2</sub> system. This mode is recommended for those with a basic level of technical experience collecting continuous data and utilizes relatively reliable, commercially available, and supported materials;
- 2) **Economy Mode:** This mode provides a less expensive option for partners who lack resources to support the principal mode, but still allows for meaningful data that can contribute to the C-CAN network. Priority measurements include temperature, salinity, dissolved oxygen, and one of the carbonate system parameters (pH or  $p(\text{CO}_2)$ ) that allow for modeling of aragonite saturation state (though not a complete description of the seawater CO<sub>2</sub> system). This mode is recommended for those with limited resources or a minimal level of technical experience who can collect continuous data on at least one carbonate chemistry parameter using reliable, commercially available, and supported materials. Whenever possible, C-CAN will assist participants in the economy mode search for support to upgrade to the principal mode.
- 3) **Cutting-Edge Mode:** This mode pertains to those with a high level of technical expertise working with prototype materials at the leading edge of technology. Priority measurements include temperature, salinity, dissolved oxygen, and three carbonate chemistry parameters, allowing for direct calculation of aragonite saturation state with redundancy of a third parameter to add reliability and precision. This mode is recommended for those with time and willingness to work with prototype technology that will require considerably more maintenance (and maintenance cost) as well as technical expertise. This mode is considered critical for a subset of partners as this it is expected to improve monitoring in the long term and may be commercially adopted in the future for use in the principle mode.

Because developing linkages between changes in ocean chemistry and biological response is another core principle of C-CAN, participants in all modes are encouraged to collect monitoring data on biological parameters such as measures of larval recruitment/settling on plates or brushes and measures of primary productivity (chlorophyll fluorescence and concentration) (see Chapter 5).

Participants in the principal and cutting edge modes may also elect to collect secondary measurements as resources allow. Secondary measurements include: current speed and direction, meteorology (air temperature, wind speed and direction, solar irradiance, etc.), atmospheric  $p\text{CO}_2$ , photosynthetically available radiation (PAR), nutrient concentrations, trace metal concentrations, particulate organic carbon, particulate inorganic carbon, export production, stable isotopic measures for nutrient and carbon source tracking ( $\delta^{18}\text{O}$  of water,  $\delta^{13}\text{C}$  of particulate organic matter,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  of dissolved nitrate,  $\delta^{15}\text{N}$  of dissolved ammonia, etc.), and measures of rates of nutrient and carbon cycling (nutrient uptake kinetics, nitrification, denitrification, nitrogen fixation, primary production and respiration, net

ecosystem metabolism, etc.). These measurements are important for parameterization of coupled biogeochemical and physical models.

### **Quality Assurance Program**

Regardless of which parameters C-CAN participants choose to use for determining aragonite saturation state, all participants are expected to implement a quality assurance and quality control (QA/QC) program to ensure data integrity. Sensors can fail or drift, and deployment in a seawater environment is hard on even the most robust instruments. Part of C-CAN's mission is to provide a QA/QC program and technical support to ensure data collected in the monitoring network meet the highest possible data quality standards. The C-CAN QA/QC program includes standardized protocols for regular calibration using approved reference materials as well as routine intercalibration with partner laboratories. Bottle samples for analyzing pH,  $C_T$ , and  $A_T$  should be used to ground truth sensors and improve data quality by correcting for drift for all autonomous measurements. Bottle samples for intercalibration should be collected and run in-house and at a series of partner laboratories four times per year to ensure precision and comparability of network monitoring stations. The QA/QC program also includes support for setting up new monitoring systems and training for instrument operation and calibration, as well as ongoing technical support to aid in troubleshooting when problems arise.

Specifics on setting up monitoring systems for each type of platform will be detailed in a series of "How-To" manuals that C-CAN is producing. These manuals will provide recommended equipment and standards for each type of platform, provide estimates for start-up costs as well as ongoing costs for each type of platform and each level of effort, and a description of the quality assurance protocols required to produce the high quality data needed by the C-CAN network. Because monitoring technology is expected to improve and evolve over time, these manuals will be "living" documents. C-CAN will produce new versions, distribute them to C-CAN network participants, and post them on the C-CAN website as needed.

Participants in the C-CAN network will have access to a training program for new participants to help install monitoring systems and ensure data generated for the C-CAN network meet the highest quality standards practical at the time. A C-CAN expert will instruct new participants in the protocols for taking the required chemical measurements and meeting QA/QC and intercalibration requirements. They will also be trained to conduct routine maintenance on the equipment and troubleshoot basic problems; however, participants are not expected to have the technical expertise to troubleshoot complex instrument problems. The regional C-CAN experts will provide ongoing technical support for these types of issues and inform participants of newly available technologies as they evolve.

## CHAPTER 5 — LINKAGE TO BIOLOGICAL SYSTEMS

The biology, chemistry, and physics of coastal waters are intertwined. Changing ocean chemistry has direct effects on biological communities, which, in turn, influence ocean chemistry (Duarte et al. 2013). Understanding these ecological interactions and feedbacks is critical to characterizing the impacts and drivers of ocean acidification in the nearshore environment. Both observational measurements and field and laboratory studies are required to address this issue. C-CAN's core principles encourages linking data to understand how changing ocean chemistry affects biological communities and how biological communities influence ocean chemistry.

### **Data To Understand How Changing Ocean Chemistry Affects Biological Communities**

Increasing ocean CO<sub>2</sub> concentrations can have adverse effects on organisms, including reduced tolerance to temperature increases, impaired reproduction, inefficient cell function, impaired growth, larval shell dissolution, disease susceptibility, and higher mortality rates at early life stages (Hofmann et al. 2010). Generally, there is a higher “cost of living” for organisms subjected to a high-CO<sub>2</sub> marine environment, but different organisms have different sensitivities to ocean acidification. Furthermore, the same organism may have different sensitivities at varying life stages. The timing of acute acidification events can have implications for organism reproductive success; impacts during early life stages can carry over effects into adulthood (Hettinger et al. 2012). Thus, C-CAN aims to collect data to understand the effects and implications of changing ocean chemistry on individual species and biological communities.

The first way to address this principle is by co-locating seawater monitoring sensors with biological measurements to document how organisms respond to *in situ* changes in ocean chemistry (Hofmann et al. 2011). These measurements range from assessments of biodiversity (abundance and distribution of species) to tests of physiological capacity of species or the population biology and genetics of key species. C-CAN participants adding complementary parameters to existing monitoring programs can help clarify causes and effects and can be used to develop correlations between chemical parameters and biological response. These effects can then be further be tested in the laboratory to more clearly define the relationships.

The second way to address this principle is by implementing experiments that allow understanding of animal's adaptive capacity (*sensu* Dawson et al. 2011) in the face 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 (Hofmann and Sgro 2011).

Both of these pursuits are challenging. C-CAN will work to 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 allowing investigators to share data and compare results; and 3) encouraging and facilitating investigators in examining organismal performance relative to

population differences. Regarding the third area, recent studies have shown significant genetic differences in populations of marine organisms, indicating that scientists cannot use one population to describe the results for the entire species (Pespeni et al. 2013, Kelly et al. 2013, Collins et al. 2013). Further, these studies strongly argue that some organisms have the genetic capacity to adapt to future acidification. Revealing these types of insights is critical to forecasting the effects of ocean acidification on target species.

In terms of implementing a biological monitoring program, C-CAN proposes a nested sampling design with standardized, priority measurements conducted at all sites and secondary measurements collected at a subset of sites, although the specific parameters that should be included are still under discussion. Suggested priority biological measurements include: fluorescence, irradiance, biomass of functional groups (phytoplankton, zooplankton, microbes, benthic animals, macroalgae, fungi, and vascular plants). Proposed secondary measurements include speciation of functional groups and long-term field studies defining rates of key processes (e.g., growth and grazing rates at different life stages).

C-CAN will prioritize installation and maintenance of chemical monitoring equipment at shellfish hatcheries and other locations where long-term biological monitoring programs exist. These sites have long histories of biological community response that may be linked to changing ocean chemistry and are a natural fit for incorporation into the C-CAN monitoring network. In the short term, larval settling collectors (TUFFY or scrub brushes), which target species at their vulnerable early life stages, should also be placed on existing and planned mooring buoys and pier monitoring stations to expand the spatial extent of biological monitoring. These collectors can be analyzed for biomass of specific taxa including crabs, urchins, brittle stars, clams, snails. They are also cost effective and sustainable (given the operators receive suitable training), executable over a wide geographic range, complimentary to laboratory experiments, and capable of detecting the episodic nature of settling for a wide range of organisms that may respond differently to changing ocean chemistry.

### **Data To Understand How Biological Communities Influence Ocean Chemistry**

As acidification alters biological community structures, species shifts may result in changes in carbon and nutrient cycling. Many nearshore pelagic and benthic calcified organisms are integral parts of marine food webs, and ecological consequences will potentially follow loss of foundational species. Filter feeders in particular play key roles in nutrient cycling, and their displacement due to changing ocean chemistry leads to the possibility for negative feedbacks to the carbon cycle. In addition, other factors, such as nutrient pollution and resultant increased primary production (eutrophication), will likely have synergistic effects with ocean acidification (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  $p\text{CO}_2$  and pH in ways that are synergistic with the effects of ocean acidification.

Causal modeling can reveal the relative influence on nearshore ocean chemistry of global factors versus local changes in biological communities. However, parameterizing the models requires two types of

data. First, calibrating and validating the models necessitates that synoptic, regional monitoring surveys collect discrete OA parameters. Second, models require information from comparison studies that look at differences in key rates and processes at “control” versus “affected” sites influenced by a terrestrial source of either acidification or nutrient enrichment. Three principle “types” of influenced systems will be targeted: 1) areas with significant freshwater flow, such as the Columbia River mouth, 2) areas with significant anthropogenic nutrient inputs through point source outfalls, like the Southern California Bight, and 3) large estuarine systems, such as the Puget Sound. Rates and processes measured near these influenced areas using standardized protocols should be compared to “control” or “reference” type areas in the same region.

Here as well, C-CAN proposes a nested sampling design. Priority measurements include autonomous chlorophyll and dissolved oxygen measurements for use in understanding development of algal blooms and hypoxia and their linkage with changing ocean chemistry over different timescales (daily, monthly, seasonally, interannually). Secondary measurements include autonomous or discrete measurements of nutrient concentrations as well as nutrient loading from watersheds to coastal and estuarine waters. These parameters could aid in understanding the role of nutrient enrichment in development of eutrophication and its effects on ocean chemistry. Special studies might include field studies targeted at understanding nutrient uptake kinetics and changes in microbial nutrient cycling (nitrification, denitrification, etc.) to characterize biological and chemical interactions in the coastal zone and fill out carbon budgets for the nearshore environment. These measurements and studies close the loop between understanding how ocean chemistry affects biology and, in turn, how biology affects ocean chemistry.

## CHAPTER 6 — DATA SHARING

C-CAN's vision is to develop a monitoring network that allows for a comprehensive description of the status of acidification in U.S. 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. C-CAN has as a core principle that its monitoring network participants agree to share their data and that they will use the west coast regional observing systems to house and serve that data. This chapter expands on those two key principles.

### **C-CAN Members Agree To Share Data**

Multiple researchers, organizations, and agencies currently collect data using their own data management strategies. This lack of coordination impedes effective use of these data to characterize the region's status with respect to ocean acidification, identify trends in changing ocean chemistry, and support modeling efforts to understand the impacts and drivers of acidification. To overcome this challenge, data management must be collaborative. Essential principles for collaborative data management have been articulated in the "Declaration of Interdependence of Ocean Acidification Data Management Activities in the US," resulting from the first Ocean Acidification Data Management Workshop in March 2012 and draft Integrated Management Plan. C-CAN participants agree in principle with the concepts outlined in the "Declaration of Interdependence" as this document describes the effective relationship among C-CAN partners working as a network toward a unifying vision with a single strategy (text of the Declaration of Interdependence is provided in Appendix 1).

While C-CAN participants have agreed to share their data, they also recognize that different types of data or different users necessitate flexible data sharing strategies. For instance, some users need near-real time data to make short-term operational decisions, while the typical researcher does not have that temporal urgency and would prefer to receive data that have undergone a higher level of quality assurance, allowing them to conduct comparative or retrospective analyses. C-CAN participants have agreed to share their data to meet both of these data needs. Participants will post raw data to the network in near-real time, or at minimum provide a picture or graphic of their data in near-real time, to support the first user need. They will then provide data that has undergone a standardized QA/QC protocol within six months of collection to support the second user need.

A second data sharing consideration is the difference between observational and experimental data. Where C-CAN seeks to standardize collection of observational data to accommodate comparison across space and time, most experimental data will be related to the specific experiment. As such, C-CAN will develop standardized data templates for the observational data, while relying on the addition of metadata to capture core information from the experiments.

One challenge in data sharing is ensuring that people receive appropriate credit for their data collection efforts, as data and their publication are the lifeblood of scientific researchers. C-CAN participants have

agreed not to publish data from the network, or findings based on those data, without permission of the data originator. Though many C-CAN participants whose data are collected with public funds intend to make the information freely available for use by all, C-CAN sees consultation with data originators as a courtesy that should be extended in all cases. This guideline protects the interests of the data originator, and serve data users by ensuring they understand any idiosyncrasies associated with the data.

### **The Integrated Ocean Observing System (IOOS) Is The Repository For C-CAN Data**

The IOOS Regional Associations<sup>5</sup> will act as the primary data repositories, collators, and sharing portals for the C-CAN network. Development of synthesis and modeling tools for understanding ocean acidification drivers and predicting impacts is impossible without a unified, easily accessible, and sustainable data management framework. The 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 are ideally situated to serve this function for C-CAN. The Regional Associations will build upon existing capacity and capabilities to develop a web portal that will accept data streams from all relevant data centers, provide visual and data link capabilities, and exhibit synthesis products for the U.S. West Coast as a whole as well as the sub-regional scale.

The web portal, by tracking all C-CAN participant data streams, will also serve as an inventory of ocean acidification monitoring assets for the West Coast, allowing determination of spatial coverage and gaps in the network. It will incorporate both real-time and non-real-time data from C-CAN monitoring units and observational studies, as well as experimental data. This will require expansion of the existing platform capacity to collate disparate data sources into an integrated network, achieved via development of data input structures, metadata requirements, and data visualization and access tools.

The new IOOS web portal will be set up to accept and share three types of data: sensor data, observational monitoring data, and experimental data. Acidification data collected via sensor technology is the first priority. The existing IOOS platform is set up to accept multiple types of sensor data collected in conjunction with ocean acidification parameters (e.g., temperature, salinity, dissolved oxygen, chlorophyll). Thus, building out capacity for additional sensor parameters (pH and  $p(\text{CO}_2)$ ) is a logical first step. The second priority will be observational monitoring data, specifically discrete bottle samples for acidification parameters (pH,  $p(\text{CO}_2)$ ,  $C_T$ ,  $A_T$ ), bottle samples for ancillary measurements (nutrients, chlorophyll  $a$ , etc.), and observational biological monitoring data (field surveys or settling plate counts of functional groups or species). The final data priority results from laboratory experiments: determination of critical biological and biogeochemical rates and processes associated with changing ocean conditions, and determination of biological response to elevated  $p(\text{CO}_2)$  and pH. While the first two priority data types entail numerical data (field data collected by sensor, bottle sample, or observation), the third type of data will consist only of links to published work.

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<sup>5</sup> West Coast IOOS regional associations:

[Pacific Northwest](#) (NANOOS)

[Central and Northern California](#) (CeNCOOS)

[Southern California](#) (SCCOOS)

The IOOS Regional Associations will standardize data management for all C-CAN participants. C-CAN participants benefit by not having to invest in developing their own data management program. The IOOS web portal will provide universal access to data in standardized formats, integrating ocean acidification data with other relevant measurements (temperature, salinity, dissolved oxygen, etc.). It will also ensure the data meet standardized quality assurance requirements, including: 1) uncertainty estimates in measured, estimated, and calculated parameters, regardless of quality level; 2) instrument calibration data and notation of reference materials used for this purpose; and 3) results from intercalibrations conducted with partner laboratories. The web portal will ensure data are version-controlled, citable through globally unique identifiers, and properly documented with metadata. Finally, the data management framework will be well organized, searchable, and easy to use for submission, discovery, retrieval, and access to data through a small number of standardized programming interfaces.

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## **APPENDIX 1: “DECLARATION OF INTERDEPENDENCE OF OCEAN ACIDIFICATION DATA MANAGEMENT ACTIVITIES IN THE US”**

Whereas Ocean Acidification (OA) is one of the most significant threats to the ocean ecosystem with strong implications for economic, cultural, and natural resources of the world;

Whereas our understanding of OA and our ability to: 1. inform decision makers of status, trends, and impacts, and 2. research mitigation/adaptation strategies, requires access to data from observations, experiments, and model results spanning physical, chemical, and biological research;

Whereas the various agencies, research programs and Principal Investigators that collect the data essential to understanding OA often pursue disparate, uncoordinated data management strategies that collectively impede effective use of this data for synthesis maps and other data products;

Whereas an easily accessible and sustainable data management framework is required that: i) provides unified access to OA data for humans and machines; ii) ensures data are version-controlled and citable through globally unique identifiers; iii) documents and communicates understood measures of data and metadata quality; iv) is easy to use for submission, discovery, retrieval, and access to the data through a small number of standardized programming interfaces;

Whereas urgency requires that short-term actions be taken to improve data integration, while building towards higher levels of success, and noting that immediate value can be found in the creation of a cross-agency data discovery catalog of past and present OA-related data sets of a defined quality, including lists of parameters, access to detailed documentation, and access to data via file transfer services and programming interfaces;

Whereas this integration will also benefit other users of data for a diverse array of investigations;

Therefore, be it resolved that the 31 participants of an OA Data Management workshop in Seattle, WA on 13–15 March 2012 established themselves as the Consortium for the Integrated Management of Ocean Acidification Data (CIMOAD) and identified three necessary steps forward to achieve this vision:

1. The endorsement of agency program directors and managers for collective use of machine-to-machine cataloging and data retrieval protocols (including THREDDS/OPeNDAP) by each agency data center to provide synergistic, consolidated mechanisms for scientists to locate and acquire oceanographic data;
2. The commitment of the scientific community to establish best practices for OA data collection and metadata production, and the leadership to provide a means of gaining this consensus; and
3. The endorsement of agency program directors and managers to direct data managers to collaborate to develop the system articulated above and contribute to a single national web portal to provide an access point and visualization products for OA.

We, the undersigned, request your attention to this matter and commitment to bringing this vision to reality in the next five years for the benefit of our nation and contribution to the global understanding.

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