California Current Acidification Network (C-CAN)

Guidance Manual for Establishing a Land-Based Station for Measurement of Ocean Acidification Parameters



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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.

CHAPTER 1 — INTRODUCTION AND MOTIVATION

Ocean acidification poses a threat to the health of the world's oceans and to the significant beneficial uses they provide. Globally, a quarter of carbon dioxide (CO_2) released into the atmosphere by anthropogenic activities is absorbed by the oceans (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). 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 marine food webs (Feely et al. 2012).

The U.S. West Coast is particularly vulnerable to the effects of OA, potentially causing 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 respect to calcium carbonate and thus corrosive to shelled organisms. The Pacific Coast has natural upwelling circulation patterns that draw these deep waters towards the ocean's surface, with seasonally modulated intensity and in some cases reaching the surface (Feely et al. 2009). As OA increases, the corrosive effect of these waters is intensified, and the instances of exposure to harmful conditions become more frequent, intense, and persistent. The West Coast shellfish industry has recently experienced dramatic declines in hatchery production; these declines have been correlated with upwelling events that bring low-pH, corrosive waters to shore (Barton et al. 2012).

Determining the effects of OA on nearshore ecosystems, including coastal and estuarine waters, is difficult. In the open ocean, relatively low-variability, natural conditions allow for easier resolution in how ocean chemistry and oceanographic conditions change due to rising atmospheric CO_2. However, understanding the physical, chemical and ecological impacts of OA in the nearshore coastal environment is complicated by the interplay of numerous additional factors, such as freshwater inputs, tidal forcing, water stratification, nutrient over-enrichment, algal blooms, and hypoxia (Fabry et al. 2008). Furthermore, development of models to understand ecosystem effects of OA in coastal environments is hampered by a disconnect between carbon chemistry data and biological effects data. 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. Nearshore OA sampling is also poorly coordinated, with a lack of uniformity in the measured physical, chemical and biological parameters among programs. 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 timescales, so they can adapt their operations to rapidly changing conditions.

Changes in the degree to which seawater is favorable to carbonate mineral ($CaCO_3$) formation (measured as calcium carbonate mineral saturation state, denoted as Ω) are considered the best measure for inferring the effects of OA. When CO_2 dissolves in seawater, new equilibria are established that influence the concentrations of other key chemical species: hydrogen (H^+) and bicarbonate (HCO_3^-) ion concentrations increase, carbonate ion (CO_3^{2-}) concentration decreases, and saturation state of biologically important forms of calcium carbonate ($CaCO_3$) declines. These changes in the chemistry of seawater can have negative effects for a wide range of physiological processes in marine organisms, particularly among calcifying (shell-forming) species (Feely et al. 2012).

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. Several experiments have shown that many organisms are dependent on the saturation state of aragonite, and that this was particularly true for the viability and development of oyster larvae (Barton et al. 2012). This has led to widespread adoption of aragonite saturation state as a key indicator for OA effects. There is no method for direct measure of Ω, which is most commonly calculated from concurrent determination of at least two other parameters. In the process of determining Ω, the entire seawater CO_2 system is constrained, which makes Ω an ideal indicator for understanding the effects of OA. A number of indices for evaluation of biological effects of changing ocean chemistry can be inferred using the same data collected for calculation of Ω (Doney et al. 2009).

Understanding the impacts of OA in the coastal environment requires coordination of monitoring efforts to ensure that intercomparable data on OA and its effects on nearshore ecosystems are collected. However, there is currently no well-developed, consensual approach for making these measurements, nor is there a framework for sharing these data with interested parties. The California Current Acidification Network (C-CAN) was initiated, in part, to address these issues. C-CAN has developed a vision that lowers barriers to making seawater CO_2 measurements of sufficient quality, paving the way to understand ecosystem effects of changing ocean chemistry[1]. A central component of this vision is to coordinate and encourage development of an OA monitoring network for the U.S. West Coast that incorporates the following core principles[2]:

1. Core measurements should facilitate determination of aragonite saturation state (Ω) and a complete description of the carbonate system.
2. A combination of core measurements and methodology that leads to better than ± 0.2 uncertainty in the aragonite saturation state (Ω) calculation is required to adequately link changes in ocean chemistry to changes in ecosystem function.
3. A variety of monitoring platforms and levels of effort should be included in the network to engender high-frequency data at fixed locations as well as spatial mapping across locations.
4. The monitoring network encourages linkage of physical and chemical oceanographic measurements with observations of biological communities.
5. The monitoring network shall share data and make them accessible to a broad audience.

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[1] More information on C-CAN's vision can be found in a companion document available at: http://c-can.msi.ucsb.edu/c-can-documents/C-CAN%20%20Vision%20Document%20Final.pdf/view)

[2] More information on C-CAN's core monitoring principles can be found in a companion document available at: http://c-can.msi.ucsb.edu/c-can-documents/C-CAN%20Core%20Monitoring%20Principles%20Final.pdf/view)

The purpose of this document is to provide guidance for practitioners at land-based sites, such as those at shellfish hatcheries, aquaria, and coastal research laboratories, who wish to collect data for the determination of aragonite saturation state using continuous measurement systems. These sites are critical to the C-CAN network due to their location in the extreme nearshore environment as well as their direct linkage to biological data. The aim of this document is to provide explicit guidance on how best to make carbonate chemistry measurements (i.e., identify specific parameters, required precision, and suggested instrumentation) that will be intercomparable with other sites in the C-CAN network. This document will:

- Describe the recommended measurement parameters for the determination of aragonite saturation state with an overall uncertainty of ± 0.2 or less at three levels of effort: the core recommendation, a less-expensive option, and the cutting-edge option (Chapter 2 – Measurement Options);
- Define the core monitoring recommendation: continuous, autonomous, real-time measurement of temperature, salinity, dissolved oxygen, p(CO_2), and pH (Chapter 3 – Principal Recommendation);
- Provide a recommendation for a less expensive monitoring option: continuous, autonomous, real-time measurement of temperature, salinity, dissolved oxygen, and either p(CO_2) or pH (Chapter 3 – Economy Recommendation);
- Provide a recommendation for a cutting-edge monitoring option: continuous, autonomous, real-time measurement of temperature, salinity, dissolved oxygen, p(CO_2) or pH, and TCO_2 (Chapter 4 – Cutting-Edge Recommendation);
- Describe the resources that are available for training and setup of monitoring systems as well as for maintenance and troubleshooting of established monitoring systems (Chapter 5 – Resources).

C-CAN was established as an enabling body with its efforts centered on standardizing protocols to collect data of sufficient quality to meet the prescribed core principles. This document is one in a series defining those protocols for land-based systems. Other manuals for ship-based and mooring-based monitoring will also be made available. Because technology is rapidly evolving, these manuals are expected to be "living" documents and, as such, will be periodically updated as advancements are made.

While C-CAN is pleased to provide these guidance documents, readers should recognize that characterizing the state of a particular seawater sample's carbonate chemistry and assigning a well-constrained measurement uncertainty is not straightforward. Investigators who wish to do high-quality work in ocean acidification, but who have little previous experience in seawater CO_2 measurements, would do well to collaborate with a scientist with experience in this area who has access to a laboratory that can perform the necessary measurements to the required quality standard.

CHAPTER 2 — MEASUREMENT OPTIONS

Possible Measurements to Characterize Aragonite Saturation State

One of C-CAN's core principles is to monitor chemical parameters that allow for determination of aragonite saturation state (Ω) with a maximum uncertainty of ± 0.2 and a complete description of the seawater carbonate system. This core principle defines the types of parameters that can be measured and the uncertainty required in each parameter. The parameters that can be measured to meet this objective are defined by the equilibria established through a series of reactions when CO_2 dissolves in seawater[3]:

CO_2 gas dissolves in and reacts with water to form a mixture of aqueous carbon dioxide ($CO_{2\,(aq)}$) and carbonic acid (H_2CO_3)[4] that is dominated by $CO_{2\,(aq)}$:

$$CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow H_2CO_{3\,(aq)} + CO_{2\,(aq)} + H_2O_{\,(l)} \tag{2.1}$$

Carbonic acid dissociates and aqueous carbon dioxide reacts with water to form hydrogen ion and bicarbonate ion:

$$H_2CO_{3\,(aq)} + CO_{2\,(aq)} + H_2O_{\,(l)} \leftrightarrow H^+_{\,(aq)} + HCO_3^-{}_{\,(aq)}, \tag{2.2}$$

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

$$H^+_{\,(aq)} + CO_3^{2-}{}_{\,(aq)} \leftrightarrow HCO_3^-{}_{\,(aq)}. \tag{2.3}$$

The sum of the reactions is sometimes more conceptually approachable:

$$CO_{2\,(g)} + H_2O_{\,(l)} + CO_3^{2-}{}_{(aq)} \leftrightarrow 2HCO_3^-{}_{\,(aq)}, \tag{2.4}$$

as this shows the interaction between $CO_{2\,(g)}$ and $CO_3^{2-}{}_{\,(aq),}$ whereby additions of CO_2 to seawater lead to decreases in carbonate ion concentration and aragonite saturation state.

The above reactions are all essentially in instantaneous thermodynamic equilibrium, and the relationships between the concentrations of these species can be simplified to:

$$K_H = \frac{[CO_2]}{x(CO_2)*P} \tag{2.5}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{2.6}$$

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[3] Text adapted from Dickson et al. (2007) Guide to Best Practices for Ocean CO_2 Measurements.

[4] The notations (g), (l), (aq) refer to the state of the species, gas, liquid, and aqueous solution respectively.

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{2.7}$$

where $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$, and $[Ca^{2+}]$ are the molar concentrations of the aqueous species carbon dioxide, bicarbonate, carbonate, hydrogen, and calcium ions in seawater respectively[5]; $x(CO_2)$ 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[6]:

$$CaCO_{3\ arag\ (s)} \leftrightarrow Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}, \tag{2.4}$$

is almost never in thermodynamic equilibrium, so the abundance of calcium and carbonate ions is usually related to the thermodynamic solubility product, $K_{sp\ (arag)}$ (a known function of temperature, salinity, and pressure), through a term called the saturation state. The saturation state of a seawater sample with respect to aragonite, Ω_{arag}, is defined as the ratio between the product of aqueous calcium $[Ca^{2+}]$ and carbonate ions $[CO_3^{2-}]$ estimated for that seawater sample and the solubility product:

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

A saturation state greater than 1 means the water is over-saturated with respect to aragonite and net precipitation from seawater is thermodynamically possible; a saturation state less than 1 means the water sample is under-saturated with respect to aragonite and spontaneous net dissolution is thermodynamically possible. 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 simple function of salinity (S):

$$[Ca^{2+}] = \frac{0.01028 * S}{35} \tag{2.10}$$

However, users should note that this relationship is parameterized for the open ocean and may not work well in low-salinity waters.

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, $[CO_3^{2-}]$, 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.

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[5] Brackets are used here to indicate total concentrations in moles per kilogram of seawater.

[6] There are different polymorphs of calcium carbonate; we focus here on aragonite, though it should be noted that this reaction is also relevant for calcite if a different equilibrium constant were applied in place of K_{arag} to describe the equilibrium.

Recommended Parameters and Rationale

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

$$\mathrm{pH} = -\log[\mathrm{H}^+] \qquad (2.11)$$

There are a number of pH scales that can be used for seawater applications. C-CAN recommends use of the total scale, often denoted as $\mathrm{pH_T}$. The total scale is defined using a medium containing sulfate ions. These ions experience protonation:

$$\mathrm{H^+}_{(aq)} + \mathrm{SO_4}^{2-}{}_{(aq)} \rightleftharpoons \mathrm{HSO_4}^-{}_{(aq)} \qquad (2.12)$$

such that the total scale includes the effect of both protons (free hydrogen ions, $[\mathrm{H}^+]_F$) and hydrogen sulfate ions ($[\mathrm{HSO_4}^-]$):

$$[\mathrm{H}^+]_T = [\mathrm{H}^+]_F + [\mathrm{HSO_4}^-] \qquad (2.13)$$

The pH of a sample 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 [$p(\mathrm{CO_2})$] of a small gaseous headspace in equilibrium with seawater (by rearranging equation 2.5):

$$p(\mathrm{CO_2}) = \mathrm{x}(\mathrm{CO_2}) * \mathrm{P} = \frac{[\mathrm{CO_2}]}{\mathrm{K_H}} \qquad (2.12)$$

can be measured autonomously or on bottle samples.

Total dissolved inorganic carbon (C_T or $\mathrm{TCO_2}$), the sum of the dissolved inorganic carbon species in seawater:

$$\mathrm{TCO_2} = [\mathrm{CO_2}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \qquad (2.13)$$

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

$$\mathrm{A_T} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \ldots \qquad (2.14)$$

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. Total alkalinity can be measured on discrete bottle samples using open-cell or closed-cell titration.

Calculation of the carbonate ion concentration requires knowledge of at least two of the parameters (pH, $p(CO_2)$, TCO_2, or A_T), together with the equilibrium constants for the CO_2 system (K_H, K_1, 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 typically 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.

A publicly available computer program, such as CO2SYS, CO2calc or Seacarb, is typically used to calculate carbonate ion concentration from measured data.[7] For a detailed review of the relevant calculations, see Dickson et al. (2007).

Sources of Uncertainty

A key goal for any observing network is to ensure that the measurements made are of appropriate quality for their intended purpose and that they are comparable with one another, even though they are made at different times, in different places, and in many cases by different instruments and maintained by different groups. C-CAN prescribes that aragonite saturation state should be calculated with an overall uncertainty of ± 0.2 or less. However, because aragonite saturation state, Ω_{arag}, is a calculated parameter, it depends not only on the independent measurements of chosen pairs of pH, $p(CO_2)$, TCO_2, or A_T, but also on the thermodynamic constants that determine the relationships of the carbonate species to one 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 of 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 if perfect (zero uncertainty) measurements of pH, $p(CO_2)$, TCO_2, or A_T are attained, calculation of Ω_{arag}, will have an associated uncertainty nevertheless. Furthermore, the magnitude of this uncertainty will depend on the pair of analytical parameters chosen for the calculation. It is beyond the scope of most C-CAN end-users' objectives to undertake efforts to constrain these terms, or even to perform analysis of the propagated calculation errors associated with these uncertainties. However, intercomparisons among C-CAN user groups will be meaningless if calculations were performed with different assumed sets of thermodynamic constants; as such, C-CAN strongly encourages all participants to rely on a common set

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[7] All of these programs are available from CDIAC: http://cdiac.ornl.gov/oceans/pubs.html in the section on CO_2 system calculation programs.

of thermodynamic constants based on the total pH scale. Recommendations for equilibrium constants for use at salinities greater than 20 ppt are:

1. Lueker et al. (2000) for the temperature and salinity-dependent constants for first and second dissociation constants of carbonic acid, K1 and K2 on the total pH scale;
2. Lee et al. (2010) for relationship between boron and total alkalinity;
3. Dickson (1990) for the dissociation constant for hydrogen sulfide ion;
4. 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. C-CAN will maintain awareness of ongoing research in these fields, and, if sufficient resolution is made regarding improvement of thermodynamic parameters, recommendations and calculation tools will be updated accordingly. C-CAN participants are encouraged to retain detailed records of primary chemical measurements, as well as information on equilibrium constants and quality control data. This will allow straightforward and consistent community-wide recalculation should it be deemed necessary.

Considerations for Selecting a Monitoring System

C-CAN has developed recommendations for which parameters to measure, driven largely by available technology and reference materials. There are four considerations a user must take into account before investing in a monitoring system:

1. Availability of appropriate instrumentation;
2. Physical environment in which the instrument will be deployed;
3. Total cost of the investment, including equipment, supplies, and labor;
4. Level of expertise required.

However, it should be noted that high-quality data cannot be achieved without proper training and continuing experience with selected instrumentation. While this document may focus on selection of parameters and instrumentation, operator error in deploying and recovering instruments can render the data useless. One of C-CAN's goals is to foster relationships between experienced and non-specialist operators. For more information on finding collaborators, please refer to Chapter 6 – Resources.

Availability of Appropriate Instrumentation

For most C-CAN participants, commercially available technology is recommended for monitoring, although for those with access to the resources and expertise, more cutting-edge technology exists. Commercial systems are available for continuous, autonomous measurement of pH and $p(CO_2)$, although users should be advised that using $p(CO_2)$ and pH as the two carbon-system parameters for determination of aragonite saturation state is non-ideal, given that they co-vary strongly. Equipment can be purchased for discrete measurement of pH, TCO_2, $p(CO_2)$, and A_T on preserved bottle samples; however, C-CAN does not recommend that non-specialists attempt TCO_2 and $p(CO_2)$ measurements in their laboratories without expert assistance. Table 1 presents the advantages and disadvantages of each parameter. It should be noted that, while commercial options are available for instrumentation, they are often not particularly well-supported, and as such, C-CAN recommends collaboration with a research lab that has extensive experience with these measurements for assistance with set-up and trouble-shooting.

Table 1. Advantages and disadvantages of different parameters that can be measured to calculate carbonate ion concentration and aragonite saturation state.

Parameter	Advantages	Disadvantages
TCO_2	• Temperature- and pressure-independent	• Need care with sample handling • Automated measurements available only through a prototype system that is not commercially available • Discrete measurement requires expensive instrumentation and skilled operators that are typically beyond stakeholder capabilities
pH	• Commercially available and supported continuous, autonomous sensors available • Discrete spectrophotometric methods available to independently ground-truth continuous measurements	• Function of temperature and pressure • Lack of reference materials for brackish water salinities (5-20 on the practical salinity scale)
$p(CO_2)$	• Commercially available and supported continuous, autonomous sensors available	• Function of temperature and pressure • Discrete measurement requires expensive instrumentation and skilled operators that are typically beyond stakeholder capabilities
A_T	• Temperature and pressure independent	• Hard to interpret in some coastal systems if other significant acids/bases are present • Determined manually by titration; no autonomous systems are available

In selecting an instrument, users should pay particular attention to the uncertainty they can expect in the measurement of different parameters. C-CAN prescribes that aragonite saturation state should be calculated with an overall uncertainty of ± 0.2 or less, which sets a limit for the allowable uncertainty in each carbonate parameter. Because there are four possible parameters but only two are needed to calculate Ω_{arag}, there are a variety of combinations that can be used. Mathematically, all choices should be equivalent, but in practice it is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations, resulting in uncertainties in the calculated values. As discussed above, in addition to uncertainties in the measured CO_2 parameters, there are also uncertainties in the various equilibrium constants, in the total concentrations of other acid-base systems such as boron, in the completeness of the expression for total alkalinity, etc. Therefore, it is essential to state the desired uncertainty for each of the measured and/or calculated parameters reported in coastal ocean acidification studies.

Table 2 provides an expectation for achievable uncertainties in measureable carbonate system parameters, as well as the uncertainties associated with the thermodynamic constants, that could result in an overall uncertainty of ± 0.2 or less in Ω_{arag}. Tables 3 and 4 demonstrate the effect of these uncertainties and the choice that each pair of carbonate system parameters has on the calculated value of Ω_{arag}.

Table 2. Expectation for achievable uncertainties in measurable carbonate system parameters and uncertainties associated with thermodynamic constants (95% confidence).

Parameter	**Absolute Uncertainty *u*(x)**	**Parameter**	**Relative Uncertainty *u*(x)/x**
TCO_2	10 µmol kg^{-1}	**$u(TCO_2)/TCO_2$**	0.5%
pH	0.02	**$u(pH^+)/(pH^+)$**	0.5%
$p(CO_2)$	12 µatm (at 400 µatm)	**$u(p(CO_2))/p(CO_2)$**	3%
A_T	10 µmol kg^{-1}	**$u(A_T)/A_T$**	0.5%
pK_0	0.004		
pK_1	0.015		
pK_2	0.030		

Table 3. Calculated combined relative uncertainties for a seawater sample with a pH ~ 8.1 and Ω_{arag} ~ 2.5. 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**	**A_T**	**$p(CO_2)$**	**Ω_{arag}**
pH + TCO_2	**0.3%**	**0.5%**	1%	6%	8%
pH + $p(CO_2)$	**0.3%**	7%	7%	**3%**	13%
TCO_2 + A_T	0.6%	**0.5%**	**0.5%**	12%	14%
TCO_2 + $p(CO_2)$	0.3%	**0.5%**	1%	**3%**	7%

Table 4. Calculated combined relative uncertainties for a seawater sample with a pH ~ 8.1 and Ω_{arag} ~ 1.0. 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	A_T	$p(CO_2)$	Ω_{arag}
pH + TCO_2	**0.3%**	**0.5%**	1%	6%	9%
pH + $p(CO_2)$	**0.3%**	7%	7%	**3%**	13%
TCO_2 + A_T	0.7%	**0.5%**	**0.5%**	14%	15%
TCO_2 + $p(CO_2)$	0.3%	**0.5%**	1%	**3%**	8%

Physical Environment of Deployment

When selecting technology for monitoring, it is important to consider the local physical environment in which the monitoring will take place. While there are considerable advantages to land-based monitoring systems (including ease of access for servicing and removal of biofouling, increased instrument stability, and less restrictive weight/size considerations that are intrinsic to deployed systems), the physical environment is inherently more dynamic than open-ocean settings, with large swings in temperature and salinity that can take place on tidal timescales. It is also subject to terrestrial pressures such as sediment, organic matter, freshwater runoff, and nutrient loads, which can create coastal algal blooms and affect the concentration of dissolved oxygen, carbon dioxide, and pH. These differences can have implications for how the different carbon system parameters are measured and interpreted and, as a result, what technology is most appropriate to make the required measurements. For example, pH measurements cannot be accurately calibrated for brackish-water environments (salinity range of 5 to 20), which affects the interpretation of these data in estuarine environments. In addition, the effect of other acid/base systems on total alkalinity must be accounted for in coastal environments.

It is also worth noting that in some nearshore environments, an overall uncertainty of ± 0.2 in Ω aragonite may not be possible. In coastal waters where salinity is greater than 30, an overall uncertainty of ± 0.2 is achievable with appropriate equipment and practices; however, it is probably not realistic in estuaries, given the uncertainties in equilibrium constants and pH measurements.

Total Cost of Investment

Investment in a monitoring system that enables generation of high-quality data for understanding the effects of OA on the nearshore environment goes well beyond the initial capital cost of purchasing an instrument. Choosing a system based on acquisition cost alone is ill-advised. C-CAN recommends that the full costs, including the personnel costs for training, operation and maintenance of the equipment (which will typically be the largest fraction of the total) in addition to the acquisition and operating costs, be considered. For example, the capital costs of continuous, autonomous sensors are typically high, but can be small compared to the alternative of the many person-hours required to collect and analyze discrete samples at a high enough frequency to be useful for understanding tidal scale changes in ocean chemistry.

For the non-specialist, the learning curve in taking high-quality seawater CO_2 measurements is steep and, as such, extensive training may be required before new users can expect to produce high-quality data. New users should rely on local experts for developing their monitoring systems as much as possible. The initial investment in personnel to competently operate the instruments and interpret the data can be high, but is not easily quantified given the different levels of experience of potential users. As a result, this document focuses primarily on the much less significant costs of capital equipment, supplies, and sample analysis for quality assurance. As users gain experience with the equipment, operating costs may be reduced over time. Wherever possible, some expectation of personnel hours required for set-up and maintenance are provided, but users should expect that the most significant cost for monitoring will be the ongoing maintenance and troubleshooting of the equipment.

Three Levels of Operation

C-CAN recognizes that while not all organizations possess equal levels of technical expertise and financial capability, 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 that all sites are collecting a minimum set of priority measurements, with secondary measurements that can be added for those with additional resources. C-CAN provides recommendations for monitoring at three levels of operation:

1) **Principal Recommendation**: The core recommendation of operation recommended for most C-CAN participants, priority measurements include continuous measurements of temperature, salinity, dissolved oxygen and two out of the four carbonate system parameters, allowing for direct calculation of aragonite saturation state and a full characterization of the seawater CO_2 system. Participants may choose to include secondary measurements as resources allow (see below). 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 Recommendation**: This recommendation provides a less expensive option for partners who lack resources to support the Principal Recommendation, 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 $p(CO_2)$) that allow for modeling of aragonite saturation state and collection of discrete bottle samples to verify modeling results. This mode is recommended for those with limited resources or a minimal level of technical experience that can collect continuous data on at least one carbonate chemistry parameter using reliable, commercially available, and supported materials.
3) **Cutting-Edge Recommendation**: This recommendation is for 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 adding reliability and precision. Participants may choose to include secondary measurements as resources allow. 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 recommendation is considered critical for a subset of partners, as it is expected to improve monitoring in the long term and may be commercially adopted in the future for use in the Principal Recommendation.

Participants at all levels are encouraged to collect monitoring data on biological parameters such as measures of larval recruitment/settling on plates or brushes (e.g., Barton et al. 2012) and measures of primary productivity (chlorophyll fluorescence and concentration), because developing linkages between changes in ocean chemistry and biological response is another core principle of C-CAN.

Participants 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 $p(CO_2)$; photosynthetically available radiation (PAR); nutrient concentrations; trace metal concentrations; particulate organic carbon; particulate inorganic carbon; export production; stable isotopic measures for nutrients, carbon, and water ($\delta^{18}O$ 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, 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.

Data Quality Assurance and Quality Control

The objective of C-CAN is to create a network of monitoring stations that generate an intercomparable data set that can track changes in ocean chemistry and can be related to biological responses along the U.S. West Coast. This will require a rigorous quality assurance and quality control plan to ensure data quality and intercomparability. C-CAN's quality assurance plan has four components:

1) All monitoring stations in the C-CAN network will collect data using standard operating procedures as outlined in the Guide to Best Practices for Ocean CO_2 Measurements (Dickson et al. 2007);
2) All sensors will be routinely calibrated with certified reference materials and maintained according to established best practices. Error estimates associated with sensor drift and fouling must be reported. The frequency of sensor calibration will depend upon the instruments in question;
3) Ideally duplicate sensors should be co-located in areas where continuous data are critical to build confidence in the continuous dataset;
4) Discrete bottle measures should be used to validate sensor measurements and identify if a sensor has failed; these samples may either be run at the monitoring station by the network participant or by a C-CAN-recommended analytical facility (see Appendix 2). Check samples

must be run for salinity, pH, and A_T. Users should record suspected spatial and temporal mismatch of validation samples, which may account for discrepancies between sensor and discrete measurements.

5) A subset of discrete bottle measurements should be collected in triplicate for intercalibration. Duplicate samples must be sent to a shared analytical facility to ensure intercomparability between monitoring stations, with a third sample held as a backup (Appendix 2). These samples should be analyzed for salinity, pH, TCO_2 and A_T. These intercomparison samples must be treated with mercuric chloride to prevent biological alteration of the samples. This poison may be added off-site (within an hour) at hatcheries. Samples are stable for several months after treatment with mercuric chloride.

CHAPTER 3 — PRINCIPAL MEASUREMENT RECOMMENDATION

The Principal Recommendation aims to collect continuous, autonomous, real-time, high-quality data on aragonite saturation state with a maximum uncertainty of ± 0.2. C-CAN recognizes that hatcheries and aquaria require high-quality data to safeguard their operations and that there is a significant cost to collecting poor-quality data. Inadequate ocean acidification measurements can do more harm than good, particularly if the measurements suggest that waters are "safe" (i.e., non-corrosive) when, in fact, they are not. Furthermore, a number of existing off-the-shelf instruments can have errors that could spell life or death for sensitive organisms. Recommendations for measurement equipment and data collection in the Principal Recommendation are designed to ensure collection of data of sufficient quality, so that hatcheries and aquaria can be confident in their estimations of aragonite saturation state and its effects on their operations. It should also be noted that insufficient calibration and maintenance of recommended technology can result in erroneous estimates of aragonite saturation state. Thus, not only is it important to purchase equipment that can adequately measure the parameters of interest, but it is also critical to adhere to the QA/QC program to ensure that measurements are sufficiently accurate. Participants should also be aware that the stated uncertainty in measurements is often "better" than the uncertainty in the measurements in practice, and that only through continued operation will any given user adequately understand the uncertainty inherent in any of these measurements and the resultant calculation of aragonite saturation state.

The Principal Recommendation incorporates continuous, autonomous, real-time measurements of temperature, salinity, dissolved oxygen, $p(CO_2)$, and pH. The rationale for selecting $p(CO_2)$ and pH as the carbon system parameters of interest is driven largely by the desire for continuous data sets, though C-CAN recognizes that this is a non-ideal pairing given that $p(CO_2)$ and pH co-vary strongly. Presently, there are no commercial systems for continuous, autonomous measurements of TCO_2 and A_T, although prototype units are available for TCO_2. In the Principal Recommendation, aragonite saturation state is determined from: (1) carbonate ion concentration, calculated from $p(CO_2)$ and pH, (2) calcium ion concentration, estimated from seawater salinity measurements, and (3) the apparent solubility product, $K_{sp\text{-arag}}$, calculated from temperature and salinity. Continuous measurements should be routinely checked against discrete bottle measurements of salinity, pH, $p(CO_2)$, TCO_2 and/or A_T. Additionally, C-CAN recommends that monitoring stations periodically (approximately quarterly) check the calcium ion/salinity relationship against direct measurements of $[Ca^{2+}]$ and salinity (see Appendix 2).

In brackish water environments such as near large river mouths or within estuaries, pH may not be an appropriate parameter to use for calculation of aragonite saturation state, because there are presently no reference materials to properly calibrate the probes within the salinity range of 5 to 20 on the practical salinity scale. In these cases, C-CAN still recommends deployment of ISFET pH sensors in anticipation that a correction may be applied at a future date. In the interim, for a number of coastal locations, there is a strong correlation between salinity and alkalinity. Consequently, continuous data sets for alkalinity can be generated from temperature and salinity data, and thus, a continuous record of aragonite saturation state can be modeled from these measurements in combination with continuous measurements of $p(CO_2)$. However, characterization of the relationship between alkalinity and salinity requires an initial period of data collection to derive the appropriate algorithms. This calibration period requires regular collection of bottle samples that are analyzed for A_T. This period should ideally be defined by the system variability, which includes a statistically robust regression analysis of the relationship between total alkalinity, temperature, and salinity [$A_T = f(Sal, T)$]. To achieve a 95% confidence, the required sample size is given by $n = \left(\frac{s \times t_{n-1,0.5}}{95\%CI}\right)^2$ where *n* is the sample size, $t_{n-1,0.5}$ is a t-value and *s* is the standard deviation estimated from previous studies or determined by a pilot study. Individual participants are recommended to consult with an expert to generate a calibration program appropriate for their area. From this data set, relationships can be derived between temperature, salinity, and alkalinity, which can be used to estimate the aragonite saturation state with an uncertainty within requisite ± 0.2 (See Box 1, Chapter 4). This will be the preferred reporting for aragonite saturation state in brackish water salinities, where there are challenges in calibrating pH sensors. However, users are strongly cautioned that this protocol may not work in all environments. Alternatively, if expertise is available, C-CAN participants in brackish water systems could deploy or develop a prototype unit for continuous, autonomous TCO_2 measurements and couple these measurements with $p(CO_2)$ to calculate aragonite saturation state directly (see “Cutting-Edge Measurement Recommendation” in Chapter 5).

This chapter describes the general specifications that instruments should achieve for use in the C-CAN network. Specific suppliers and short reviews of existing technology are given in Appendix 1. Desired specifications will be given for the following:

1. **Accuracy**: The expected degree of closeness between the measurement and a reference value;
2. **Precision**: Reproducibility or the degree to which repeated measurements under unchanged conditions show the same result;
3. **Stability**: The expected drift of sensors within a given deployment period;
4. **Response time**: Minimum time between measurements. All instruments must possess an internal clock that must be routinely checked against GMT, as all data sets must be synchronized.

Temperature, Salinity and Dissolved Oxygen

The accurate measurement of both temperature and salinity is central to determination of aragonite saturation state. Seawater salinity can be calculated from measured values of conductivity and temperature. Combination temperature and conductivity probes are available from a variety of suppliers and are typically stable and reliable. The temperature sensor is typically calibrated by the manufacturer. C-CAN participants should plan to check the calibration and stability of the temperature sensor a minimum of once per month, by placing the probe in a temperature-controlled water bath and comparing the probe reading to a reference thermometer. The conductivity sensor should be calibrated a minimum of once per month using a certified standard, unless otherwise directed by best practices. Conductivity standards are sold at a range of specific conductance values. Participants should choose standards that encompass the expected salinity of the environment in which the sensor is deployed. The calibration of the conductivity sensor will be compared against discrete bottle measurements of salinity of intercalibration samples, as described below.

Dissolved oxygen can be considered a “check variable” in that it typically co-varies with pH and $p(CO_2)$; thus, deviations from dissolved oxygen may be the first indication that the seawater CO_2 monitoring system requires maintenance. C-CAN recommends use of optical dissolved oxygen sensors due to their increased stability and resistance to drift compared to membrane probes. Sensors calibration should be checked a minimum of once per month, but preferably every week, followed by an offset/slope applied to the calibration according to vendor specifications.

Temperature, salinity, and dissolved oxygen probes are supplied by a variety of vendors, and options are available that allow for integration with seawater systems that also measure either $p(CO_2)$ or pH. Integrated data sondes that measure temperature, salinity, and dissolved oxygen (independent of pH or $p(CO_2)$ instrumentation) can be purchased commercially and are relatively stable and reliable if properly maintained.

Minimum Specifications for Temperature Sensors

Allowable Uncertainty (95% confidence): < 0.01 ˚C

Stability: System should not experience appreciable drift over the deployment period if routinely cleaned of biofouling

Response Time: <3 seconds

Minimum Specifications for Conductivity Sensors

Allowable Uncertainty (95% confidence): < 0.018 mS/cm

Stability: System should not experience appreciable drift over the deployment period if routinely cleaned of biofouling

Response Time: < 3 seconds

Minimum Specifications for Dissolved Oxygen Sensor

Allowable Uncertainty (95% confidence): < 0.3 mg/L

Stability: System should not experience appreciable drift over the deployment period if routinely cleaned of biofouling

Response Time: < 25 seconds

Partial Pressure of Carbon Dioxide in Coastal Water Samples

The partial pressure of carbon dioxide [$p(CO_2)$] of coastal water is the first of the two carbon-system parameters that C-CAN is recommending for the Principal Recommendation. Instruments equilibrate a fixed volume of air with a continuous stream of seawater. As the volume of seawater that flows through the equilibrator is essentially infinite compared to the volume of air, the CO_2 content of the air adjusts to equilibrium with the seawater without altering the CO_2 content of the seawater appreciably. The equilibrated air is circulated through a non-dispersive infrared analyzer to measure its CO_2 content. The standard operating procedure for determination of $p(CO_2)$ in seawater is described in Guide to Best Practices for Ocean CO_2 Measurements (Dickson et al. 2007) SOP 5. The analyzer should be routinely calibrated (as specified by instrument supplier; typically every few hours) using gases of known CO_2 concentration.

Seawater $p(CO_2)$ measurements must have a maximum uncertainty of ± 12 µatm. Instruments are notoriously finicky, and non-specialists will require a long period of time to become adept with the technology. Manufacturer support varies, and users are encouraged to collaborate with local laboratories that have experience with the technology.

Minimum Specifications

Allowable Uncertainty (95% confidence): 3% (~12 µatm)

Stability: System should not experience appreciable drift over the deployment period if routinely cleaned of biofouling

Response Time: < 30 seconds

pH

The pH of coastal water is the second of the two carbon-system parameters that C-CAN is recommending for the Principal Recommendation. There are two continuous types of systems for measurement of pH with the required accuracy and precision: a non-glass, Ion Sensitive Field Effect Transistor (ISFET)-based pH sensor or spectrometric (indicator-dye-based) instruments. Glass potentiometric probes are not recommended by C-CAN.

As noted above, pH should be used with caution in brackish salinity environments (5-20 on the practical salinity scale). Efforts are underway to understand how the probes function in the mid-salinity range, and protocols will be improved to incorporate calibration practices and newly developed standards for these environments. In order to develop appropriate protocols and data correction methods, stations in brackish environments that incorporate pH must collect data on pH using ISFET technology. These pioneering efforts will allow for development of data corrections and new standards that will benefit the network overall.

Minimum Specifications

Allowable Uncertainty (95% confidence): 0.02 (~5% in relative hydrogen ion concentration)

Stability: System should not experience appreciable drift over the deployment period if routinely cleaned of biofouling

Response Time: < 30 seconds

Bottle Measurements

As a part of the QA/QC program recommended by C-CAN, bottle measurements should be collected and compared to continuous data to determine if the instruments are operating according to specifications. There are two types of bottle measurements required: (1) check samples to confirm proper calibration and maintenance of continuous monitoring instruments, and (2) intercalibration samples to ensure data comparability across network stations. Water samples must be collected in glass or Pyrex bottles in a manner that minimizes gas exchange with the atmosphere. Samples should be treated with mercuric chloride solution to prevent biological alteration of chemical parameters and sealed to prevent exchange of carbon dioxide or water vapor with the atmosphere. The standard operating procedure for sample collection is described in Guide to Best Practices for Ocean CO_2 Measurements (Dickson et al. 2007) SOP 1.

Bottle measurements that serve as check samples may be run either in-house by the C-CAN participant or at a partner laboratory. Bottle measurements for check samples must be collected a minimum of twice per month and analyzed for salinity, pH (SOP 6b), and A_T (SOP 3a or 3b). Bottle samples for intercalibration must be analyzed for salinity, pH, TCO_2, and A_T by a C-CAN-recommended laboratory (Appendix 2) a minimum of once per month. If the participant is running check samples in-house, duplicates of the same sample should be sent to the intercalibration laboratory. Bottle samples to check the calcium ion/salinity relationship must be run quarterly by an analytical laboratory.

Minimum Specifications

Allowable Uncertainty in Total Alkalinity (95% confidence): 0.5% (~10 µmol kg^{-1})

Allowable Uncertainty in Total Inorganic Carbon (95% confidence): 0.5% (~10 µmol kg^{-1})

CHAPTER 4 — ECONOMY MEASUREMENT RECOMMENDATION

The economy measurement recommendation is designed for organizations that would like to contribute information on OA to the C-CAN network, but lack the resources to fully support the Principal Recommendation. In particular, this recommendation is anticipated to be used by organizations that are already collecting water quality or biological data and would like to supplement those data sets with OA data, consistent with C-CAN's goals of understanding relationships between changes in biological communities with changing ocean chemistry and broadening the scope of the network along the U.S. West Coast. This option supports these goals by providing a less expensive option (in terms of capital expenditures), enabling the recruitment of a larger number of partners to the network.

Priority measurements include temperature, salinity, dissolved oxygen, and one of the carbonate-system parameters (pH or $p(CO_2)$). Generally, pH is the recommended carbonate-system parameter because, of the two parameters, it has the more stable, user-friendly, and robustly available technology. However, as noted in the previous chapter, pH cannot presently be calibrated in brackish water salinities (between 5 and 20 on the practical salinity scale), and in these situations, $p(CO_2)$ is the recommended parameter. Descriptions of the available technology to measure temperature, salinity, and dissolved oxygen, pH and $p(CO_2)$ are all described in Chapter 3.

Because data on only one carbonate parameter are collected in this mode, a complete description of the seawater CO_2 system in a continuous fashion is not possible. Consequently, this mode is not recommended for operations that are dependent on continuous, accurate determination of seawater aragonite saturation state (such as shellfish hatcheries). However, in some coastal settings, total alkalinity is closely and consistently correlated with salinity, and as a result, a continuous record of alkalinity can be modeled from salinity data. This allows for determination of continuous aragonite saturation state from continuous pH or $p(CO_2)$ and from modeled alkalinity; however, this will require an initial period of data collection to calibrate the model (see Box 1 for an example). This calibration period requires collection of continuous, autonomous, real-time temperature, salinity, dissolved oxygen, and pH or $p(CO_2)$, plus bottle measurements of A_T two times per day (with tides) a minimum of once per week, with additional samples that encapsulate the range of freshwater input volumes and resulting salinity variability. This calibration period should last approximately 1 year, although individual participants are recommended to consult with an expert to generate a calibration program appropriate for their area. After this, the model should be checked with bottle samples a minimum of once per month.

BOX 1: Use of Models to Estimate Components of the Carbonate System

The measurement of any two of the four commonly measured parameters of the aqueous seawater CO_2 system – A_T, TCO_2, $p(CO_2)$, and pH – allows for the calculation of the remaining carbonate system parameters and Ω. In lieu of direct measurement, proxies have been utilized to model carbonate parameters and constrain Ω within the level of uncertainty established by C-CAN (± 0.2). Estimating Ω from commonly available hydrographic parameters (temperature, salinity, and dissolved oxygen) is a key advantage for two reasons: (1) Because the technology for monitoring these parameters is lower cost and significantly more user-friendly for the non-specialist, it can provide a low-cost means of evaluating natural variability in carbon chemistry at higher spatial and temporal resolution than would be possible if determination of the more complex carbon chemistry parameters was required. (2) It provides the capability to hindcast Ω from historical datasets to explore relationships with previously documented ecological/physical observations, provided that corrections for reduced anthropogenic CO_2 in prior data, if significant, can be taken into account.

Recently, several such studies have demonstrated this approach:

- Using hydrographic surveys of the Northeastern Pacific region, Juranek et al. (2011, 2009) developed empirical regional algorithms to predict pH and Ω using temperature, salinity, and dissolved oxygen data, a typical dataset collected from any standard CTD package. As described in Chapter 1, Ω is a function of temperature, salinity, pressure, $[Ca^{2+}]$, and $[CO_3^{2-}]$. Because changes in $[Ca^{2+}]$ are proportionally small in seawater, variations in Ω are largely determined by changes in carbonate ions, which can be predicted from observations of TCO_2 and A_T. Robust predictive relationships were developed to model these TCO_2 and A_T from the CTD data.
- Lee et al. (2006) developed region-specific algorithms to enable the estimation of the global distribution of A_T from sea surface salinity (SSS) and temperature (SST) data. This analysis indicated that the distribution of surface A_T can be derived by dividing the global ocean into five regimes with corresponding equations relating A_T to SSS and SST. To establish their algorithms, they used 5,692 surface A_T measurements that were carefully quality-controlled to determine the relationships of A_T with SSS and SST for different ocean regimes. However, the Lee et al. relationships only apply to the surface, not to samples collected at depth, and users are likely to find an offset between the Lee et al. estimates of A_T and those generated with relationships developed to reflect more localized conditions, as there are different water masses present at the surface nearshore compared to in the open North Pacific Ocean.
- Alin et al. (2012) developed empirical equations for estimating pH, Ω, TCO_2, A_T, and $[CO_3^{2-}]$ from dissolved oxygen, temperature, salinity, and other hydrographic proxy data to reconstruct the state of the carbonate system within the southern California Current System on sub-decadal time scales. The calibration data included high-quality measurements of carbon-system parameters and hydrographic data, collected during a cruise from British Columbia to Baja California from May 2007 to June 2007 (Feely et al. 2008).
- At the University of New Hampshire's Coastal Marine Lab, Salisbury and co-investigators have

measured $p(CO_2)$ since December 2010. For proposed OA monitoring work in Maine and New Hampshire, they will use A_T, which is modeled from local salinity–A_T relationships (Hunt et al. 2011). The UNH group presently has a database of more than 1,000 determinations from diverse locations in the coastal Gulf of Maine. Using this data, the group infers changes in Ω with an accuracy of ± 0.2.

Caveats

The examples summarized above required extensive calibration to ensure that the empirical relationships for estimating carbonate-system parameters are robust and constrained by the geographical regions where they were validated. No model is an ideal substitute for direct observations of the carbon system using direct observations of $p(CO_2)$, TCO_2, A_T, or pH (Juranek et al. 2011). In describing the multiple linear regression approach to generate empirical models using dissolved oxygen, temperature, salinity, and other variables to reconstruct Ω and other seawater CO_2 parameters, Alin et al. (2012) wrote that "river-dominated continental margins such as the U.S. East Coast may present a greater challenge to developing the types of empirical relationships described" because riverine inputs may be localized and individual rivers may have different chemical signatures. In studying the relative proportions of carbonate and non-carbonate alkalinity measured in 15 river systems located in northern New England (USA) and New Brunswick (Canada), Hunt et al. (2011) showed that estimates of $p(CO_2)$ derived from A_T and pH measurements were 13% to 66% higher than $p(CO_2)$ estimates derived from TCO_2 and pH, likely due to the presence of significant non-carbonate alkalinity.

CHAPTER 5 — CUTTING-EDGE MEASUREMENT SYSTEMS

The Cutting-Edge Recommendation is designed for research groups, or those working closely with research groups, who possess a high level of technical expertise in OA monitoring and are willing to work with prototype materials at the leading edge of technology. Like the Principal Recommendation, the aim is to collect continuous, autonomous, real-time, high-quality data on aragonite saturation state with a maximum uncertainty of ± 0.2. Priority measurements include temperature, salinity, dissolved oxygen, and three carbonate chemistry parameters (pH, $p(CO_2)$, and TCO_2) allowing for direct calculation of aragonite saturation state with redundancy of a third parameter adding reliability and reducing uncertainty. Furthermore, because pH and $p(CO_2)$ are known to co-vary so strongly, addition of TCO_2 as a continuous parameter further reduces the uncertainty of the aragonite saturation state calculation. Consequently, this mode is ideal for shellfish hatcheries and other organizations for which complete and accurate real-time knowledge of aragonite saturation state is critical for the health and security of the operation. Thus, partnerships between research labs that can support these types of systems in hatcheries are ideal (see Barton et al. 2012).

As with all monitoring recommendations, participants using the Cutting-Edge Recommendation are expected to adhere to the QA/QC program to ensure that measurements are as accurate as possible. This includes routine calibration of monitoring instruments with certified reference materials, as well as collection of bottle samples for validation of continuous measurements and intercalibration among laboratories (Chapters 2 and 3).

Descriptions of commercially available technology for measurement of pH and $p(CO_2)$ are given in Appendix 1. These can be incorporated into a cutting-edge monitoring system with addition of measurement of total dissolved carbon (TCO_2). Presently, no commercially available technology is available for continuous, autonomous measurement of TCO_2, and operators in the cutting-edge mode would have to build a unit based on an existing prototype or design their own system. Description of an existing custom system is given in Appendix 1. It is expected that this type of system may eventually be made commercially available, as most of the existing commercial technology is based upon prototypes designed and tested by research groups. This technology transfer between research groups and commercial suppliers make the Cutting-Edge Recommendation critically important, because it catalyzes advancement of technology for the entire network in the future.

CHAPTER 6 – RESOURCES

All participants in the C-CAN network will have some measure of support over the long-term for conducting ocean acidification measurements. Most participants in the network (those operating in the Principal or Economy recommendations) are expected to be working with commercially supported technology; in these cases, they may be able to contact their supplier for assistance with troubleshooting. However, C-CAN encourages non-specialists to consult with an expert early in their planning process to ensure that their monitoring needs will be met. C-CAN is also partnering with other monitoring programs to develop an online wiki and listserv for monitoring participants to learn and exchange ideas.

Resources include:

Finding a collaborator: Whenever possible, C-CAN recommends that non-specialists seek expert advice in designing a monitoring program that is appropriate for their needs and is sustainable given their available resources. A number of expert laboratories have volunteered for this purpose, and new network participants should contact Stephen Weisberg, the C-CAN chair, at stevew@sccwrp.org for assistance and direction in establishing an appropriate collaboration.

Using best-practices manuals: C-CAN is facilitating the development of a series of best practices documents for deploying continuous sensors for monitoring. The first set of documents in this series will include a best practices manual for ISFET sensors and an intercomparison study of deployed ISFET sensors. The series may continue as funds allow. All documents will be posted to C-CAN's website.

Taking part in technology evaluations and workshops: The Alliance for Coastal Technologies (ACT) is a collaborative partnership of academic institutions, state and federal resource managers, and private-sector companies dedicated to fostering the development and adoption of effective and reliable sensors and sensor platforms for environmental monitoring and long-term stewardship of coastal and ocean resources. Fundamental ACT activities include: (a) verification and validation of sensors and platforms for coastal and ocean observing systems through technology evaluations in different environments, utilizing both field experiments and laboratories to recreate environmental conditions; (b) capacity-building through technology workshops that involve researchers, manufacturers, users, regulators, and facilitators; and (c) knowledge exchange through an Information Clearinghouse and Technology Database that connects users with technology suppliers worldwide, presenting a forum to explore instrumentation options, and ultimately to share knowledge and experience, and exchange best practices. In particular, ACT has held several technology evaluations (with test protocols) and technology workshops, and has a comprehensive list of instruments in the technology database addressing the various parameters of interest to the C-CAN network, all of which are available at www.act-us.info.

Turning to online resources: An international wiki and listserv will be established to increase communications with other users who monitor ocean acidification parameters internationally. Users can post publications and documents that describe advancements in ocean acidification monitoring, so that the community can remain informed of the latest technology. These resources also will provide a forum for users to post questions and get answers to their monitoring-related questions, allowing the user community to continue to learn and exchange ideas. Users will be able to browse previous question-and-answer sessions to see how others have addressed problems that may be similar to those that they themselves are currently experiencing.

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APPENDIX 1 – AVAILABLE TECHNOLOGY FOR MAKING SEAWATER CO_2 MEASUREMENTS

This appendix only includes instruments expected to meet the data quality needs of the C-CAN network. It is not a comprehensive listing and will be updated as the body of experience with emerging technologies grows.

Systems for Measuring Temperature, Salinity, and Dissolved Oxygen

<u>YSI EXO 1 or EXO2</u>

The EXO1 multiparameter water quality sonde collects data with up to four user-replaceable smart sensors, including temperature, conductivity (salinity), and dissolved oxygen at user-programmable intervals. These sensors are developed for extended deployments in the field, but can be adapted for collection of continuous measurements in a flow-through system. Data can be stored on the sonde or relayed in real time to either a PC or to the EXO handheld unit.

<u>SBE 37 MicroCAT</u>

The SBE 37 MicroCAT utilizes high-accuracy sensors with field-proven long-term stability to measure and record conductivity, temperature, pressure, and optical dissolved oxygen at user-programmable intervals. It is ideally suited for extended deployments in remote, biologically rich environments, but can be adapted for laboratory flow-through systems. Depending on the application, the MicroCAT can collect high-quality data for several months to a year between calibrations. Excellent bio-fouling protection is provided by EPA-approved anti-foulant devices, an integral pump, and a unique internal flow path, which minimizes flow between samples and allows anti-foul concentration to build up inside the cell. Data can be logged internally or transmitted in real time.

Cost: $10K to 15K

Review of Sondes: Continuous monitoring probes have been on the market for several decades and have been utilized in a variety of environments. Factory calibrations are provided, and probes are easy to replace. User offsets in slope and gain are relatively straightforward to apply to the sensor output. Some CO_2 systems can be equipped with integrated temperature, salinity, and dissolved oxygen units, which would also solve the problem. Temperature and conductivity probes are known to produce reliable data in the field with minimal drift if calibrated routinely, though efforts should be made to prevent biofouling to the greatest extent possible, because probes are sensitive to fouling. Optical probes for dissolved oxygen are less susceptible to drift compared to membrane probes and are thus preferred for use in the network. Probes are relatively durable, although the optical sensing element may require replacement after > 1 year of continuous deployment. It is recommended that conductivity sondes and optical sensors alike are sent to the manufacturer on a regularly scheduled interval for factory overhaul and recalibration. This approach of "preventative maintenance" is essential to minimize the total number of instrument failures and system down-time. Projected costs of the project should account for replacements on this time frame. Probe failures, while relatively rare, are possible; thus, it is recommended to have spare conductivity and temperature probes on hand. Data sonde systems are very well-supported. Technicians are available for troubleshooting by phone during normal business hours. Warranties are available for a fee. Sondes can be sent in for maintenance and service for a fee at any time regardless of warranty. Turnaround time for service and delivery of replacement parts is variable.

Systems for Measuring Seawater *p*(CO_2)

Sunburst Sensors AFT-CO_2:

Sunburst Sensors autonomous flow-through (AFT) instrument is a compact, fully autonomous instrument for the measurement of pCO2 in marine and freshwater environments with a precision < ± 1 µatm. It uses the same technology as Sunburst Sensors' remote mooring technology, which is sold under the name *SAMI* (Submersible Autonomous Moored Instrument). It is relatively compact (26 x 28 x 14 cm) and requires 2-4 liters/minute flow through the unit. It is designed for underway or bench-top use, and when connected to a laptop, it can provide real-time measurements, but can also log data download. The *p*(CO_2) of intake water is measured using a colorimetric method. The AFT can take up to 17,000 measurements per reagent bag, with a precision of approximately 1 µatm and an accuracy of approximately ± 3 µatm. Measurements can be made a maximum of every 5 minutes. AFT sensors are not sold as an integrated system and must be coupled with sensors for salinity. The AFT internally logs each measurement and supports up to 3 external instruments with power and data logging. It can support 0-5V, RS232 or light-sensing instruments such as a PAR. New client software allows updating of firmware in the field, as well as graphing of real-time or downloaded data.

The AFT-CO2 uses calibrated reagent-based colorimetry to measure a change in the pH of the indicator, bromothymol blue (BTB). The BTB is contained in a gas-permeable membrane that is exposed to the environment. The pH change is driven by the diffusion of CO_2 across the membrane. Long-term drift-free performance is obtained by renewing the BTB reagent for each measurement, by recording the indicator absorbance at two wavelengths corresponding to the peak absorption of the acid/base forms of BTB, and by periodically measuring blank (indicator-free) water in the optical cell. Changes in the light intensity between blank measurements are corrected with reference detectors that monitor the light output. Fouling protection is provided by a copper mesh cage covering the membrane.

http://www.sunburstsensors.com/

Sunburst Sensors flow-through p(CO_2) system.

Review of Sunburst AFT-CO2:
Installation in a laboratory setting can be relatively straightforward and fast (on the order of hours if the right physical infrastructure is pre-existing – i.e. power, water circulation pumps/tank, etc.), including setting up standard cylinders (small ones). The unit plugs into a seawater line and wall power like any standard underway equipment. All shipboard instruments need access to flowing seawater, and this system is no different. The systems are designed to run autonomously once set up and will require minimal attention when all is working well, but can require a high level of technical expertise to troubleshoot and/or repair when a system component malfunctions, is flooded, or experiences other technical difficulty. Post-processing the data can be a little complicated for deployed units because at the start of the deployment, the instrument is calibrated at the expected median temperature and range of pCO_2. A primary standard (NOAA CMDL) CO_2-calibrated NDIR instrument (e.g. Licor 840) is used to measure CO_2 during calibration. Post-deployment, the raw SAMI data are corrected for the difference between the calibration and measurement temperature using an accurately known temperature coefficient. Testing of the SAMI instrument has shown that the system can provide robust readings with no changes in the differences between instrument and reference measurements during testing, indicating that biofouling and instrument drift did not affect measurement performance over the duration of the test.

Approximate cost: $12K

Sunburst Sensors SuperCO$_2$ System:

The SuperCO_2 system is an automated system for measuring pCO_2 as well as atmospheric CO_2. Built around the Licor 840A NDIR system, it can sample at rates of up to 1 Hz. The system equilibrates a fluid stream flowing at 2-4 lpm, with an air stream using either a showerhead equilibrator or a membrane contactor. It allows the user to use up to 4 gas standards (user-supplied) for automated periodic calibration of the system. Using a separate air pump, it can also periodically sample atmospheric CO_2. The system can be configured to support other instruments, such as a thermosalinograph. Custom software will display and log the data in real time on an integrated touchscreen tablet running Windows 8.

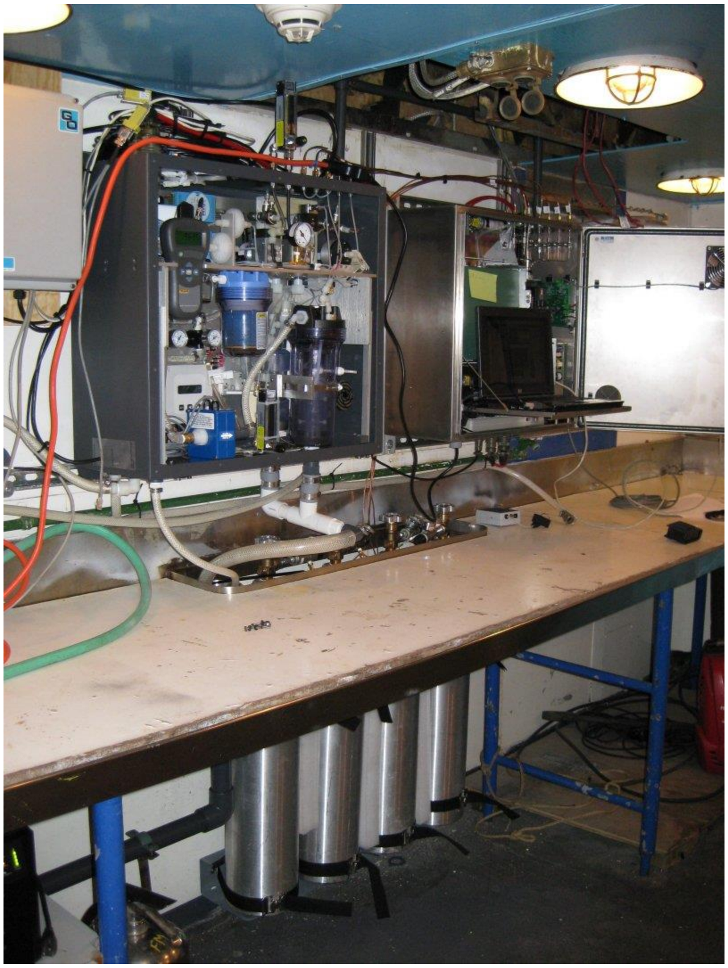
Sunburst Sensors SuperCO2 NDIR-based shipboard system (equilibrator and calibration gas cylinders not shown). The system footprint is approximately 2' x 2' x 1'.

Approximate cost: $25K

General Oceanics GO p(CO_2) Model 8050:

General Oceanics Inc. offers an autonomous analytical system for measuring the partial pressure of carbon dioxide in oceanic surface water and air. The system is based on an instrument package developed by Craig Neill, based on earlier prototypes by Rik Wanninkhof and Richard Feely. The system is designed for ship-based underway measurements and can also readily be used for laboratory-based measurements. It is relatively large and can provide real-time measurements, which are also logged on the computer. Users must supply the CO_2 infrared analyzer (Licor 6262 or 7000 or similar).

http://www.generaloceanics.com



GO Model 8050 flow-through p(CO$_2$*) system, showing all components of a typical ship-based installation, including the wet and dry boxes that together comprise the GO8050 system (the two large boxes of equipment mounted above the counter), plumbing and drainage lines, and four gas standard tanks (below the counter). The footprint would be similar for a laboratory-based installation, where a sink or other outflow to handle waste water was available so that a separate reservoir and pump system would not be required to get rid of water after p(CO*$_2$*) measurement. (Photo credit: Cathy Cosca)*

Review of GO8050:

While there are quite a few GO8050 pCO$_2$ systems in use within the ocean carbon community, operating and maintaining them to obtain the highest-quality results require quite a bit of expertise and attention. Their best applications will be in settings where maintenance attention can be regular (e.g. on a seawater intake, a tank setting, or attended shipboard survey). The level of precision and accuracy that can be attained with this system is on the order of <1-2 µatm pCO$_2$ with proper operation and calibration. Care must be taken to ensure that gas standards fully bracket the expected range of pCO$_2$ values to be encountered during a deployment, and up to five gas standards can be used with the system to generate calibration curves. Installation in a laboratory setting can be relatively straightforward and fast (on the order of hours to days if the right physical infrastructure is pre-existing – i.e. power, Unistrut or similar physical framework for supporting the system, water circulation pumps/tank, etc.), but installation on a ship-based platform might require work to modify seawater plumbing, power supplies, and other engineering support, and may need to be done over weeks or longer. The systems are designed to run autonomously once set up and will require minimal attention when all is working well, but can require a high level of technical expertise to troubleshoot and/or repair when a system component malfunctions, is flooded, or experiences other technical difficulty. Although processing the underway pCO_2 data from GO8050 systems takes a significant amount of time, there is a well-formed community of scientists making underway pCO_2 measurements (www.socat.info) and an established protocol for data processing (Pierrot et al., 2009).

Approximate cost: $80K for GO Unit plus Licor CO_2 analyzer; does not include incidentals needed to install and plumb the system, ancillary sensors (e.g. in situ temperature, salinity, and others), or labor.

Battelle Seaology CO_2 System

Developed in partnership with NOAA's Pacific Marine Environmental Lab (PMEL), Battelle offers a CO_2 system that measures the fraction of CO_2 (XCO_2 as ppm) in surface seawater and marine boundary air as part of the Seaology® platform, which is related to the partial pressure of CO_2:

$$pCO_2 = XCO2 * P$$

where P is the partial pressure. The standard configuration of the CO_2 sensor system includes three separate watertight cases containing the electronics, a reference gas and a D-Cell battery pack. The system also includes a bubble-type equilibrator and an atmospheric inlet device (air block). The electronics case (tube diameter: 7.4", height with connectors: 42", weight: 39 lbs.) contains the detector, gas-handling systems and computer control. The data collected by the system are recorded internally on a compact flash card, but an optional component included in both of the systems tested was an Iridium satellite data transmission component that allows remote operation of the system and automatically sends data and diagnostic information back to the laboratory once per day. The reference gas case (tube diameter: 8.6", height with connectors: 42", weight: 52 lbs.) contains a Luxfer aluminum N60 type gas cylinder filled with calibrated CO_2 in air at a nominal pressure of 2000 psi. With each sampling sequence, the NDIR undergoes a two-point calibration with a zero CO_2 gas (air with the CO_2 stripped by soda lime) and a high CO_2 standard span gas (typically around 500 ppm). The battery case (tube diameter: 7.4", height with connectors: 36", weight: 72 pounds, including batteries for satellite transmissions) produces a nominal voltage of 10 V (7 V to 14.5 V) with 2.43 kWh (approximately 243 A-hr) for system operation. The transmitter power source is nominally 9 V (8.5 V to 9.0 V) with 252 Wh. The system is nominally designed to take readings every 3 hours with daily data transmissions for 400 days, but systems have operated continuously in the field for well over 1.5 years.

The standard measurement cycle takes approximately 20 minutes, with the water reading occurring at about 17 minutes followed by the air reading. The only component that touches water is the equilibrator, which is primarily made of a copper-nickel alloy to prevent bio-fouling. A number of ancillary measurement devices (e.g. SeaBird CTD sensors and SAMI-pH system) can be controlled, logged, and transmitted by the MAPCO2 system. Operating temperature is 0°C to 40°C. Typical precision is better than 1 ppm. Estimated accuracy is better than 5 ppm for seawater within the nominal operating range of 100-600 ppm, and better than 2 ppm for air readings.

While this system is primarily constructed for remote deployments, the system can be adapted for a flow-through setting using a PVC or similar chamber, in which the sensor can be placed and submerged in water from the flow-through system. The system can be connected to a laptop for real-time visualization of data, and the unit also logs data internally.

http://www.battelle.org/

Review of Batelle Seaology:

In operation since 2003, PMEL currently maintains pCO_2 systems at 22 mooring locations around the globe. Battelle calibrates each system prior to delivery to the customer, but many scientists who use these systems spend a few days in the lab testing, setting up, and verifying calibrations before deploying a system, which requires an independent pCO_2 system for comparison. The *in situ* calibration system guarantees data integrity and comparability between instruments. Systems are returned to the manufacturer for refurbishment between deployments ($5K-$10K, depending on whether span gas and battery packs are included in the refurbishment, and not including any required repairs). Typical deployments have been 12 to 18 months, with a sampling interval of 3 hours (changeable through the firmware). Span gas concentration should be targeted to bracket the top end of the pCO_2 range anticipated during the deployment. Based on laboratory tests and field intercomparisons at various institutions, estimates of uncertainty for air and seawater pCO_2 measurements are better than 3 and 4 µatm, respectively, with proper operation. The firmware can integrate data from auxiliary sensors into the Seaology data stream and is pre-designed to integrate SeaBird CTD data (which, in turn, integrates other sensor data attached to it, such fluorometer or optode data), along with SAMI-pH or SeaFET pH data. Telemetering the data in real-time or near real-time is straightforward, as the Seaology system includes a SIM card; however, Iridium contracts to transmit the data by satellite must be purchased separately ($1K-2K per year). Optimal configuration of the system as well as data processing and quality control require moderate experience and skill with *in situ* sensors and data processing.

Additional deployment considerations*:* The Seaology systems were designed for deployment on free-floating surface moorings. The equilibrator system cannot be affixed to a stationary platform that does not move freely with the surface of the water, such as a pier piling. The system cannot be deployed at depth. The analytical Seaology package works optimally when deployed through the body of a moored buoy, such that the cylinder extends into the water, protecting the analytical instruments from wide temperature swings that may occur above the water surface. This would also be true in a laboratory or hatchery setting, where temperature variation is not excessive.

Approximate cost: \$50K-60K, including the pCO_2 measurement package, a battery pack, and one span gas. Ancillary sensors that are frequently deployed in conjunction with a Seaology pCO_2 system include a SeaBird CTD system (SBE16, \$10K-15K, depending on whether an external pump is needed for additional sensors), optodes (\$5K each), fluorescence/backscatter for chlorophyll and turbidity (\$6-7K), and a SeaFET (~\$11K with cable) or SAMI-pH (\$18K). No labor is included in the above estimates.

ProOceanus PSI CO2-Pro

The PSI CO2-Pro is a compact, lightweight, plug-n-play pCO_2 sensor designed for use on moorings, on drifters and profilers, in under-way mode, and in the laboratory. The PSI CO2-Pro is fitted with a non-dispersive, infrared gas analyzer and a patented PSI pump-driven fast-transfer interface. This pumped interface provides an equilibrated gas sample to the detector and is configured to inhibit bio-fouling. The PSI CO2-Pro is factory-calibrated from 0 to 600 ppm (other ranges available by special order) with calibration burned into EPROM. The analyzer features onboard sensors that are used to compensate for pressure, temperature and humidity. To maintain accuracy, the detector module has a power interruption or contact-closure-initiated automatic zero-point calibration (AZPC). When the AZPC is initiated, the gas stream is routed through a pCO_2 absorbent to provide a zero-ppm pCO_2 measurement. The pCO_2 AZPC measurement compensates for changes in optical cell performance and significant changes in environmental parameters such as gas stream temperature. The AZPC is used in determinations of ppm pCO_2 until a new AZPC is performed (recommended: a minimum of once per day, more often where possible and especially where conditions such as water temperature change significantly).

The data stream includes a time stamp (if fitted with the optional logger/controller), digitized optical transmission at the last automatic-zero measurement, current digitized optical cell transmission, calculated ppm pCO_2, optical cell temperature, gas stream humidity (mb), humidity cell temperature, and gas stream pressure (mb). The pCO_2 in micro-atmospheres is obtained by multiplying ppm pCO_2 by the pressure reading.

The CO2-Pro is contained in an anodized, aluminum housing with end-cap secured by a mason-jar closure. If the instrument is not fitted with the data logger/controller, data is transmitted through the RS-232 communications link at 0.6 hertz. If fitted with the logger controller, the data rate is 0.3 hertz. The new PSI logger/controller was developed in-house and features 2 gigabytes of memory for program and data storage, real-time onboard clock, programmable measurement schedule and capability of operating in “power-saving” mode, which cycles the interface pump while placing the instrument in a state of sleep between measurements. To further save energy, the detector board is available in 30°, 40°, and 55° detector-temperature set points, with the choice typically at least 15 degrees above the highest-anticipated ambient water temperature.

Averaging has been applied to pCO_2 measurement to improve resolution and reduce fluctuations. An exponential running average algorithm is applied with a time response to a step change of 5.6 seconds to 66% of final value, and of 26.4 seconds to 99% of final value. If a new CO_2 reading differs from the current running average by more than about 1.8 ppm, a new running average is started. Thus, when the CO_2 concentration is changing rapidly, the averaging is eliminated and the instrument can track changes at the basic instrument data rate.

The pumped gas transfer interface is typically supplied with water from a Sea Bird 5T pump (3000 RPM). As configured, the time constant for sample gas equilibration is about 2½ minutes at low hydrostatic pressures and somewhat longer at higher pressures. Maintenance of the instrument involves rinsing the housing and interface with distilled water immediately on recovery. If the instrument is to be stored, the interface should be dried by passing clean, dry gas through the interface housing. Further cleaning of the interface is done using protocols provided by Pro-Oceanus. Periodically and depending on the frequency of AZPCs, the pCO_2 absorbent used in the AZPC loop will need to be replaced.

Review of ProOceanus PSI CO2-Pro:

Installation in a laboratory setting can be relatively straightforward and fast. The systems are designed to run autonomously once set up and will require minimal attention when all is working well, but can require a high level of technical expertise to troubleshoot and/or repair when a system component malfunctions. Testing of the instrument has shown that the system can provide robust readings with no changes in the differences between instrument and reference measurements during testing, indicating that biofouling and instrument drift did not affect measurement performance over the duration of the test.

Approximate cost: $30K

Contros HydroC™/CO2

The HydroC™/CO_2 is an optical, headspace-based underwater sensor for the measurement of the partial pressure of carbon dioxide (pCO_2). It is available for different operating depths with a maximum of 6000-m and 2000-m depth capability by default. The standard measuring range is 200 to 1000 ppm (µmol/mol) for CO_2 in the gas phase, but other ranges are available as well depending on user requirements (200 to 3000 ppm, 200 to 5000 ppm). Its titanium housing has a cylindrical shape with a diameter of 90 mm and a length of 500 mm. Due to its small size and weight (5.9 kg in air and 2.6 kg in water), an integration of the instrument into various static (i.e. buoys, moorings) as well as moving platforms (i.e. research vessels, ships of opportunity, ROVs, AUVs) can be easily achieved.

Within the HydroC™, a headspace is realized in the form of an equilibrated gas stream in which the CO_2 concentration is measured optically by means of non-dispersive infrared (NDIR) absorption spectrometry. The air within the gas stream is continuously pumped and circulates between the membrane equilibrator in the sensor head and the NDIR-detector. A flat silicone membrane with an effective layer thickness of around 10 µm is used within the equilibrator as a semi-permeable phase boundary between the water and internal gas circuit. The entire two-beam NDIR unit is temperature-stabilized as well as temperature-calibrated. Furthermore, the gas within the circuit passes a heater to stabilize the measuring conditions. Additional sensors for temperature, relative humidity and pressure at different positions within the gas stream are included. Their data are used for both a proper correction of the NDIR-unit output and as an indicator for conditions differing largely from calibration conditions. The whole system is managed by a micro-controller. A data logger can be incorporated into the sensor, or the data can be transmitted via cable connection (RS-232, RS-485, analog) either in auto-transmission mode or by command-driven data request.

A temperature probe at the back of the sensor for the measurement of the water temperature is optional. Its data can be used to derive the actual amount of dissolved CO_2 if necessary, rather than just the partial pressure by assuming a constant salinity.

Every HydroC™ is calibrated individually and *in situ* within a special insulated water tank in which the pH value is altered to set up different amounts of dissolved CO_2 ($CO_{2,aq}$). The pCO_2 of the tank water is permanently monitored during calibration by means of a proven under-way instrument. By calibrating the sensors *in situ* under conditions close to the deployment conditions, the entire instrument is calibrated, and possible sources of error are minimized, e.g. varying equilibration properties of the membrane or effects caused by changing temperature and humidity conditions. Regarding drift-correction tools, the HydroC™ features a repeated zero-point calibration beside the two-beam design of the NDIR unit. The zero-point calibration is carried out regularly at discrete intervals during long-term deployments. During the time of such a zeroing, the CO_2 within the gas stream passing the NDIR unit is chemically removed from the sample gas.

In operation, the HydroC™ continuously runs through different intervals. It starts with a warm-up interval followed by a zeroing. After that, the data are associated with a flush interval. Finally, the sensor remains within the measuring interval. The duration of all intervals, the sampling and logging frequency, and the calculation of mean values can be configured by the user. The data recorded during the zeroing and flush interval is specifically flagged. Online as well as archived data viewing, and changes to the sensor settings, are realized by means of special software.

The HydroC™ can be provided between 11 V and 24 V. The warmup time of the instrument largely depends on the water temperature as well as the applied voltage, and varies from approximately 2 to 27 minutes. A typical warmup time is approximately 8 min for a water temperature of 20°C and a voltage of 12 V. The power consumption averages 3-4 W during operation, and less than 10 W during warmup for voltages around 12 V.

The response time of the sensor depends of the water flow in front of the membrane, the water temperature and the pressure/depth. The actual response time as well as its change during a long-term deployment – which might be evoked by fouling – can be determined by looking at the data recorded during the flush interval after a zeroing. As a mechanical protection of the membrane and a basic anti-fouling measure, a copper grating is mounted in front of the membrane. The response time is typically around 6 min ($t_{63\%}$) and 15 min ($t_{90\%}$), respectively, for water temperatures around 20°C, which is sufficiently fast for applications like buoy installations. It increases with decreasing water temperature and increasing pressure. If necessary for the application, the response time can be largely improved by using a pump and a flow-head with the HydroC™; response times of around 90 sec ($t_{63\%}$) and 210 sec ($t_{90\%}$), respectively, are achieved. The overall accuracy of the sensor, i.e. the sum of all errors, is given as 1% of the upper measuring value.

> **Review of HydroC:**
>
> Installation in a laboratory setting can be relatively straightforward and fast. The systems are designed to run autonomously once set up and will require minimal attention when all is working well, but can require a high level of technical expertise to troubleshoot and/or repair when a system component malfunctions. Testing of the instrument has shown that the system can provide robust readings with no changes in the differences between instrument and reference measurements during testing, indicating that biofouling and instrument drift did not affect measurement performance over the duration of the test.
>
> ***Approximate cost***: $30K

Custom System for Measurement of $p(CO_2)$: Bubbalator

This system, designed by Coastal Carbon Group at the University of New Hampshire, measures $p(CO_2)$ using custom-engineered equipment that provides accurate pCO_2 measurements with automated calibrations. The instrument has been deployed at the UNH Coastal Marine Lab and is known colloquially as the "Bubbalator." The custom-engineered system provides accurate measurements and automated calibrations, and measures pCO_2 as follows: seawater is pumped at a rate of 5-10 L min^{-1} into a spray head equilibrator (based on a design by T. Newberger, NOAA), whose function is similar to that described by Wanninkhof and Thoning (1993). Sample air is dried with a Nafion® dryer supplied with N_2 carrier gas and then pumped into a non-dispersive infrared Li-cor Li-840A gas analyzer. The system is computerized and typically performs a 2-, 3- or 4-point calibration each hour using a set of switching valves that monitor Scott Marrin UltraPure™ calibration gases. Corrections of the data for water vapor pressure and sea surface temperature will be carried out according to DOE protocols (1994). The switching mechanisms can also be set up to allow periodic sampling of the atmosphere. During the present deployments, data are collected at 1Hz. The time and costs for parts, assembly, and installation will depend on monitoring needs and the degree of UNH collaboration.

> ***Approximate cost***: $20K

Left, an inside view of the Licor^{TM} *based* pCO_2 *monitoring system built by University of New Hampshire's Coastal Carbon Group. Right, the shower head equilibrator built into a small commercial Bubba*^{TM} *cooler.*

Instruments for Measuring Seawater pH

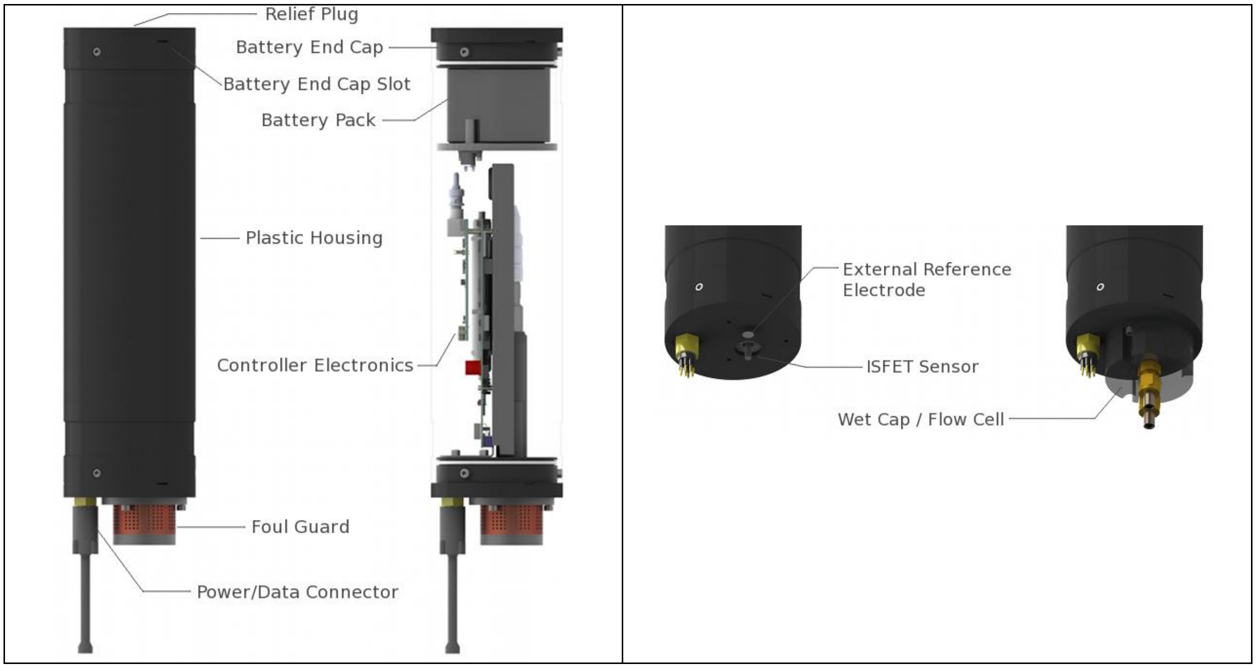
Ion-Sensitive Field-Effect Transistor (ISFET)

ISFET-based, solid-state pH sensors are stable for long deployments, eliminating the need for frequent calibrations. ISFET pH sensors are manufactured by Honeywell (DuraFET) and can be assembled with components purchased directly from Honeywell. Alternately, Satlantic (SeaFET) sells a self-contained pH system based on a Honeywell DuraFET, packaged with an external reference cell, battery pack, and internal data logging capability; the system is capable of being deployed on a mooring, but requires salinity as a separate measurement. Honeywell's reported precision of pH measurements (total hydrogen scale) for DuraFET sensors is 0.001, with an accuracy on the order of 0.01. ISFET sensors can be plumbed to a pump for continuous flow-through measurements. Measurements can be made every 3 seconds. Honeywell provides instructions for calibrating its ISFET sensors, and sells kits to replace the internal reference electrode gel. However, there is considerable ongoing work to adapt the original industrial uses of Honeywell DuraFET components to various seawater applications, so these systems are still best used in partnership with research groups or other experienced users with significant expertise in DuraFET-based pH systems. In contrast, Satlantic calibrates the SeaFET systems it sells, and SeaFET must be returned to the manufacturer annually for re-calibration and refurbishment.

C-CAN recommends that the accuracy of the ISFET calibration be compared to measurements made by the unit when placed in a standard under temperature-controlled conditions as well as against check samples taken with bottle measurements. It is important to check the ISFET probe against pH standards;

information on the determination of pH in seawater is described in Guide to Best Practices for Ocean CO_2 Measurements (Dickson et al. 2007) SOP 6a. Honeywell and Satlantic pH sensors can be integrated with other sensor packages (temperature, salinity, and dissolved oxygen).

http://www.honeywellprocess.com
http://satlantic.com



ISFET sensor (Satlantic)

Review of ISFET Sensors:

When making a choice between using a Honeywell DuraFET versus a Satlantic SeaFET, the user should be aware of the tradeoffs between equipment and labor costs associated with using the two different systems. It is possible to buy components to assemble a DuraFET-based pH system for a laboratory or hatchery application for on the order of $1K; however, it can be difficult and time-consuming to get the components to interface with computer systems and other sensors. Thus, labor costs, including some programming needs and electronics capabilities, can be significant. Such a system is not easily adapted for a moored deployment. Honeywell's technical staff is largely geared toward a more industrial customer base, and is thus not well-suited to assisting with technical troubleshooting in the aquatic observing community. In contrast, the Satlantic systems, which cost more off the shelf, are intended to be more self-contained and are appropriate for either a lab or field setting. They cost more initially ($10-15K), but should require significantly less labor to install. Their operation should also be straightforward in terms of deployment and data-logging.

It is recommended to operate each ISFET-based sensor in a non-fouling tank setting for one week before deployment, with discrete pH samples measured spectrophotometrically throughout this conditioning period to assess when the sensor's pH readings have stabilized. A single-point calibration in tris buffer is currently recommended after the conditioning period and before deployment. Collection of 10 to 20 check samples during the deployment, or ideally on a regular basis (e.g. weekly) if in a laboratory, is recommended to assess stability of the sensor over time. The use of ISFET-based systems to monitor seawater pH is still a relatively recent development, and preferred methods for calibration and validation of sensors, as well as development of improved systems for various applications, are rapidly evolving. It is thus advisable to establish connections with experienced users or research groups to ensure that routine operation and maintenance practices continue to stay in lockstep with the current best thinking.

Approximate cost: $10K to $15K for a Satlantic SeaFET system

Sunburst Sensors- AFT pH

Sunburst Sensors also offers an autonomous flow-through (AFT) instrument for pH, which uses the same technology as Sunburst Sensors remote mooring technology sold under the name *SAMI* (Submersible Autonomous Moored Instrument). It is relatively compact (26 x 28 x 14 cm) and requires 2-4 liters/minute flow through the unit when connected to a seawater line. It can also be used for discrete samples (down to 5 mL). It can provide real time measurements, but can also log data for later download. The pH of intake water is measured spectrophotometrically, using meta-cresol purple as the indicator. The AFT operates in the salinity range of 25-40 and can take up to 10,000 measurements per reagent bag with a precision of 0.001 pH units (total hydrogen scale) and an accuracy of ± 0.003 pH units. The instruments can be configured to periodically measure tris buffer for QA/QC. Measurements can be made every 3 minutes. AFT sensors are not sold as an integrated system and must be coupled with measurements of salinity.

http://www.sunburstsensors.com/

The Sunburst Sensors flow-through pH system.

Review of Sunburst AFT:
The technology uses pH indicators and the recommended method for oceanic pH measurements, and has accuracy and precision similar to the benchtop method. The software is easy to use, and the plumbing and electronics are readily accessible for maintenance and troubleshooting.

Approximate cost: $12K

Systems for Measuring Seawater TCO_2

Custom System for Measurement of TCO_2 and $p(CO_2)$: "Burkilator Deluxe"

Burke Hales and co-investigators at Oregon State University have developed instruments for the measurement of TCO_2 in seawater with state-of-the-art precision and order-of-magnitude or better increases in the frequency of analysis. The system allows for near-continuous calculation of aragonite saturation state using temperature, salinity, and $p(CO_2)$, and TCO_2 data at *in situ* conditions (Barton et al. 2012, Croswell et al. 2012). The TCO_2 and $p(CO_2)$ components of the system are based on equilibration of a CO_2-free carrier gas stream with aqueous carbon dioxide in a flowing seawater sample stream using a Licor CO_2 analyzer that employs the NDIR technology. Seawater remains unacidified for analysis of $p(CO_2)$ and is acidified for analysis of TCO_2. The $p(CO_2)$-only version of this instrument is colloquially known as the "Burkilator" (now available commercially by Sunburst Sensors as AFT-CO_2), while the version of the instrument that measures $p(CO_2)$ and TCO_2 is known as the "Burkilator Deluxe." The $p(CO_2)$ in the showerhead equilibration chamber is determined by re-circulating a carrier gas at a flow of approximately 1000 sccm through the equilibrator and sending a small split (30 sccm) to a nondispersive infrared (NDIR) absorbance detection analyzer (Licor LI-840; modified from Hales et al. 2004) (Croswell 2012). A key advantage to using this system is the opportunity it affords to calculate Ω aragonite using the $p(CO_2)$ and TCO_2 carbonate pair (Hales et al. 2004). A set of reference standards (cylinders of known CO_2 content) is employed for regular, automated calibration of the Licor's nonlinear absorbance signal (Hales et al. 2004).

Approximate cost: $50K

APPENDIX 2 – ANALYTICAL LABORATORIES

C-CAN recommends selecting an analytical laboratory with a demonstrated ability to produce reliable and comparable results for carbon chemistry parameters. Laboratories have participated to varying degrees in intercalibration exercises and have reported accuracy and precision for carbon chemistry parameters that would meet the needs of a monitoring program.

Please note that the laboratories on this list have variable capacity to run external, fee-for-service samples. Users should contact each laboratory in advance of the start of a monitoring program to establish a contract for analysis of samples. All laboratories should agree to run standard seawater as reference for each batch of submitted samples and to report uncertainties in measurements with the results.

List of Analytical Laboratories Running Carbon Chemistry Parameters

Dr. Andrew Dickson's Laboratory at Scripps Institution of Oceanography

Contact:	Andrew Dickson
Phone:	1-858-822-2990
Email:	adickson@ucsd.edu
Address:	Marine Physical Laboratory Scripps Institution of Oceanography UC San Diego 9500 Gilman Drive # 0244 La Jolla CA, 92093-0244

NOAA Pacific Marine Environmental Laboratory Carbon Group

Contact:	Richard Feely
Phone:	206-526-6214
Contact:	Simone Alin
Phone:	206-526-6819
Email:	co2.samples@noaa.gov
Website:	http://www.pmel.noaa.gov/co2/story/Laboratory+analysis+details http://www.pmel.noaa.gov/co2/story/Contact+Us
Address:	NOAA Pacific Marine Environmental Laboratory 7600 Sand Point Way NE Building 3 Seattle, WA 98115-6349

NOAA Atlantic Oceanographic and Meteorological Laboratory

Contact:	Rik Wanninkhof
Phone:	1-305-361-4379

Email: Rik.Wanninkhof@noaa.gov
Website: http://www.aoml.noaa.gov/ocd/gcc/co2research/
Address: NOAA/AOML
4301 Rickenbacker Causeway
Miami, FL 33149

Dr. Burke Hales' Laboratory at Oregon State University

Contact: Burke Hales
Phone: 1-541-737-8121
Email: bhales@coas.oregonstate.edu
Website: http://ceoas.oregonstate.edu/profile/hales/
Address: College of Earth, Ocean, and Atmospheric Sciences
Oregon State University
104 CEOAS Administration Building
Corvallis, OR 97331-5503

Dr. Frank Millero's Laboratory at the University of Miami

Contact: Frank Millero
Phone: 1-305-421-4707
Email: fmillero@rsmas.miami.edu
Website: http://www.rsmas.miami.edu/people/faculty-index/?p=frank-millero
Address: Rosenstiel School of Marine and Atmospheric Science
University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149

Dr. Joseph Salisbury's Laboratory at the University of New Hampshire
Contact: Joe Salisbury
Phone: 1-603-862-0849
Email: joe.salisbury@unh.edu
Website: http://www.eos.unh.edu/Faculty/joe
Address: Ocean Processes Analysis Laboratory
University of New Hampshire
Durham, NH 03824

Dr. Zhaohui 'Aleck' Wang's Laboratory at the Woods Hole Oceanographic Institution
Contact: Aleck Wang
Phone: 1-508-289-3676
Email: zawang@whoi.edu
Website: http://www.whoi.edu/profile.do?id=zawang
Address: Woods Hole Oceanographic Institution
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Woods Hole, MA 02543-1050