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TECHNOLOGY FOR OCEAN ACIDIFICATION RESEARCH

Needs and Availability

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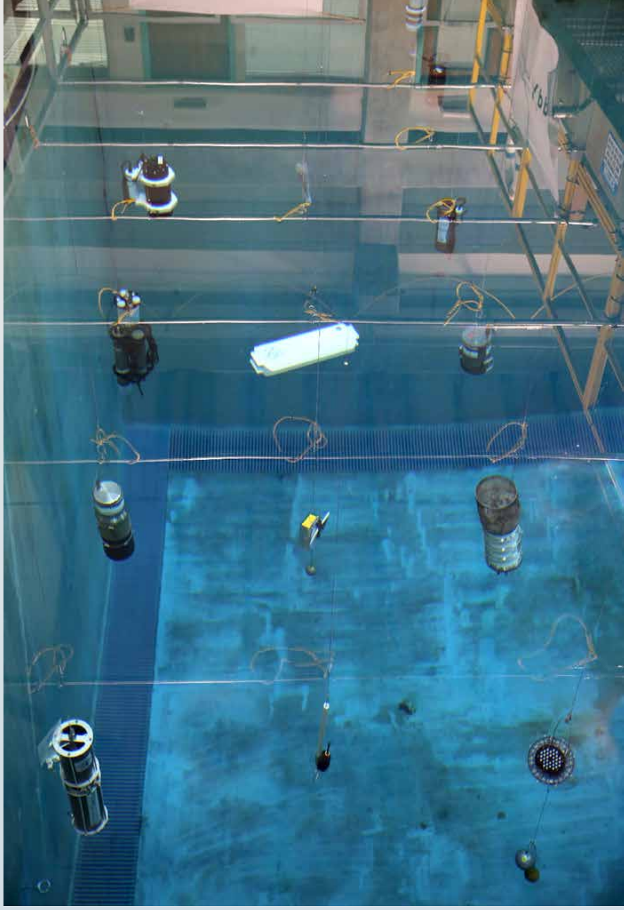

Autonomous pH sensors in the Monterey Bay Aquarium Research Institute test tank competing for the Wendy Schmidt Ocean Health XPRIZE. *Photo Credit: XPRIZE*

ABSTRACT. Diverse instruments, both custom built and commercially available, have been used to measure the properties of the aqueous CO_2 system in seawater at differing levels of autonomy (automated benchtop, continuous underway, autonomous in situ). In this review, we compare the capabilities of commercially available instruments with the needs of oceanographers in order to highlight major shortfalls in the state-of-the art instrumentation broadly available to the ocean acidification (OA) scientific community. In addition, we describe community surveys that identify needs for continued development and refinement of sensor and instrument technologies, expansion of programs that provide Certified Reference Materials, development of best practices documentation for autonomous sensors, and continued and expanded sensor intercomparison experiments.

INTRODUCTION

Understanding the changing chemistry of the ocean and the impacts of ocean acidification (OA) on marine ecosystems requires accurate characterization of carbonate chemistry. McLaughlin et al. (2015, in this issue) suggest that the core measurements for OA research should facilitate determination of aragonite saturation state (Ω_{arag}) with a maximum uncertainly of ±0.2 and provide a complete description of the carbonate system. Scientists working in the field of ocean acidification use a variety of instruments to characterize the aqueous CO_2 system. Some of these instruments are commercially available while others are custom built. Daly et al. (2004) described the state of commercially available and advanced prototype sensors for the CO_2 system, and a following review by Byrne et al. (2010) summarized in greater detail a limited selection of systems capable of in situ measurements. In the years since, new sensors have become commercially available, and descriptions of new prototype systems and developments have been published (Li et al., 2013; Liu et al., 2013; Spaulding et al., 2014; Wang et al., 2013). The Alliance for Coastal Technologies (ACT, http://www.act-us.info) and the International Ocean Carbon Coordination Project (IOCCP, http://www.ioccp.org) have begun to assemble online databases that track the advancing state of commercial ocean CO_2 instrument technology. In addition, ACT has organized performance verification exercises for pCO_2 (Tamburri et al., 2011) and pH sensors (Johengen et al., 2015). More recently, Byrne (2014) provided a broad overview of various measurement principles and instrumentation for the four CO_2 system master variables—pH, pCO_2, dissolved inorganic carbon (DIC), and total alkalinity (TA)—that included a discussion of the trade-offs among different measurement combinations and technologies. However, there is still a need for a comprehensive review article that contains an exhaustive list of the seawater CO_2 system instruments and sensors reported in the literature. Such a review is beyond the scope of this article, but it would certainly be useful to the oceanography community, as it would provide a much needed summary of the various techniques employed over the rich history of seawater CO_2 measurements, and it would remind the young generation of oceanographers of what has already been done, explain the limitations of various types of measurements, and potentially shed light on old ideas worth revisiting.

Although there are a number of commercially available sensors and instruments, the majority of systems described in the scientific literature are one-of-a-kind, not user-friendly, and not commercially available. For example, a spectrophotometer may be configured to measure pH by (1) performing automated benchtop analyses on discrete bottle samples collected by a ship rosette (Carter et al., 2013), (2) running continuous underway measurements on flowing seawater (Bellerby et al., 1995), or (3) operating autonomously in situ for extended periods (Martz et al., 2003). Such purpose-built instruments are intended for and generally restricted to specific, rather than universal, applications. Consequently, instrumentation for a given CO_2 master variable may not be readily available for a particular application. Furthermore, without formal training in the field of seawater CO_2 chemistry, scientists often find that replicating a system described in the literature is either untenably time consuming or completely intractable.

Estimating the potential impacts of ocean acidification in various habitats requires accurate characterization of carbonate chemistry. In addition to a multitude of laboratory OA studies (Kroeker et al., 2013), biological impacts of ocean acidification are being documented in coastal, nearshore, and estuarine organisms (Parker et al., 2009; Ries et al., 2009; Fangue et al., 2010; Yu et al., 2011). These studies include important ecosystem engineering involving, for example, coral reef ecosystems (Kuffner et al., 2008; Munday et al., 2009; Doropoulos et al., 2012; Ferrari et al., 2012) and economically important organisms, such as shellfish (Crim et al., 2011; Barton et al., 2012; Gobler and Talmage, 2013). Designing an observational plan for an OA experiment requires researchers to consider many factors, including the variability of the system or process, the necessary observational temporal frequency, spatial variability (horizontal and vertical), and the accuracy and precision of measurements.

In order to address the complex OA research questions and measurement requirements, the OA field has broadened to include scientists from a variety of disciplines with a need for CO_2 measurements but without backgrounds in the arcane techniques and technologies of the discipline (Dickson et al., 2007). Thus, the oceanography community faces the challenge of providing non-experts with access to cost-effective, high-quality CO_2 system measurements, as well as training opportunities and information on best practices. Community surveys are essential for identifying the current status and technology needs of the growing OA community. Such surveys include those carried out by ACT and the 2nd Ocean Acidification Principal Investigators' (OAPI) Meeting (Mathis et al., 2015, in this issue), sponsored by the US National Science Foundation (NSF), National Aeronautics and Space Administration (NASA), and National Oceanic and Atmospheric Administration (NOAA), through the Ocean Carbon and Biogeochemistry (OCB) program.

Here, we review the state of CO_2 measurement technology based on the results of a community survey and a breakout group discussion (led by the authors) during the 2nd OAPI Meeting, summarize the commercially available systems built specifically for seawater CO_2 system measurements, and point out areas where instrumentation is lacking. We also provide five recommendations, including a set of suggestions for "good practices," and outline basic steps for sensor operation. As such, the discussion is limited to "turnkey" instruments that, as of March 2015, have a presence in the form of a readily accessible website with ordering instructions. The mixture of expertise in our breakout group participants helped to shape the content of this summary, which contains information of value to instrument developers, users, companies, and funding agencies.

It is not the goal of this overview to endorse a specific technology or company. Accordingly, we avoid a summary of the various pros and cons of the different systems mentioned. Similarly, ACT and IOCCP strictly avoid promoting specific technologies. Potential users are encouraged to scrutinize the intercomparison exercises published by ACT along with the product literature of the instruments in order to draw their own conclusions about systems that best meet their research needs.

SURVEYS

OCB distributed a survey related to OA technology prior to the OAPI meeting. It was the second of two recent Web-based surveys that were developed with the goal of characterizing community needs and use patterns for CO_2 system instruments and sensors. The two surveys targeted similar yet not identical groups. The first survey was conducted in 2012 by ACT (2012b) and focused exclusively on autonomous pH sensors in advance of the ACT pH sensor performance verification (Johengen et al., 2015). The OCB survey encompassed both autonomous and benchtop instruments for all CO_2 parameters. All respondents were generally sensor users. The ACT survey was distributed to a select group of 173 nominees, while the OCB survey was distributed to the entire OCB listserv (>1,400 recipients total), including international users with a spectrum of backgrounds in benchtop and autonomous instrumentation. The ACT survey received 42 responses and the OCB survey 68 responses. ACT (2012b) presents the results of the ACT survey. The bullet points below summarize results of the OCB survey:

- >90% of respondents use benchtop systems for DIC and TA analyses.

- 50% of respondents use autonomous and underway pH and pCO$_2$ systems.
- Few respondents use autonomous and underway systems for DIC and TA.
- Periods of operation reported for autonomous and underway systems were distributed evenly from days to years.
- There is room for continued development to improve sensors and instruments. Although instrument failure rate was relatively low, the frequency with which unusable data were collected was relatively high. Responses in every category reflected user frustration. Many sensors and instruments present operational difficulties and/or don't work as well as people would prefer.
- It is critical to have continued access to Certified Reference Materials (CRMs). Many researchers rely on the use of CRMs for data quality control. The majority of all instrument and sensor users carry out some form of instrument calibration (e.g., routine measurement of CRMs on benchtop instruments) or field validation (e.g., comparison of sensor data with data obtained for bottle samples using benchtop instrumentation). Most respondents did not rely on factory calibrations.
- There was a general consensus that reference materials serve a critical need for identifying drift in all forms of instrumentation. Particular needs in this area include reference materials covering a broader range of CO$_2$ properties and salinity (e.g., for estuarine work), in addition to purified indicator dyes for spectrophotometric pH measurement.
- Biofouling of autonomous sensors is a pressing issue; all sensor designs need improvement.
- Intercomparison exercises such as those carried out for benchtop instruments (Bockmon and Dickson, 2015) should be extended to autonomous systems.

The ACT pH sensor survey obtained results that were similar to the OCB survey (refer to ACT [2012b] for figures and tables summarizing the full set of ACT survey results). Respondents used potentiometric, ISFET (ion-sensitive field-effect transistor), and spectrophotometric technologies in that order, primarily in estuarine, coastal, and blue water environments under a broad range of temperature, salinity, and turbidity conditions. Most participants reported their results using the total hydrogen ion pH scale (54.8%), followed by the NBS (9.5%), seawater scale (4.8%), and free scale (2.4%). A significant number reported they did not know which of these pH scales was used (28.6%). To calibrate pH sensors, respondents used buffers (67.5%), CO$_2$ chemistry of water samples (35%), CRM (22.5%), published information for properties of a pH indicator dye (17.5%), or manufacturer calibration (12.5%). Sensors deployed for long periods on moorings may be calibrated only once a year. It was uncertain from the survey results how often pH sensors need to be calibrated and how long they can last in the field and still yield meaningful data. Respondents reported that they required reproducibility of 0.1 (30.8%), 0.01 (41%), or ≤0.001 (28.2%). Similar to the OCB survey, most respondents would like to see improved pH sensors, especially for characteristics such as reliability, reproducibility, uncertainty, calibration life, and operational life.

The OAPI breakout group discussed the results of both of these surveys. There was general consensus that reference materials serve a critical need for identifying drift in all forms of instrumentation. Particular needs in this area include reference materials covering a broader range of CO$_2$ properties and salinity (e.g., for estuarine work), in addition to purified indicator dyes for spectrophotometric pH measurement. Biofouling of autonomous sensors continues to be a pressing issue, with all sensor designs needing improvements. In addition, intercomparison exercises, such as those carried out for benchtop instruments (Bockmon and Dickson, 2015), should be extended to autonomous systems.

INSTRUMENTS AND SENSORS

There is a significant disconnect between commercially available systems and those reported in the literature. Categorizing commercial instrumentation used for each of the four CO$_2$ system master variables by level of autonomy reveals that nearly half of the categories (five of 12) are unoccupied and five categories have only few (one to three) commercial sources (Table 1). Furthermore, Table 1 demonstrates that the available instrumentation is severely skewed toward pCO$_2$ measurement, with 13 of the 24 instruments listed being pCO$_2$ analyzers. Although examples may be found in the literature that are appropriate to every category of Table 1, due to complexity of design and low demand, most of these systems have not been commercialized. A number of instruments are beyond the prototype stage and are being replicated in small numbers, but only on an exclusive basis for select users. Examples include the underway pCO$_2$-DIC system built for NOAA by Burke Hales at Oregon State University (Bandstra et al., 2006; Barton et al., 2012), the SeapHOx sensor built by author Todd Martz (Bresnahan et al., 2014), and SEAS (spectrophotometric elemental analysis system) developed by author Robert Byrne (Liu et al., 2013). Table 1 is instructive because it exposes many significant gaps by limiting the systems listed to those that can be easily purchased by any researcher, rather than by the inner circle of ocean CO$_2$ specialists or those with information that would lead to inside contacts beyond a simple Web search.

An obvious omission to Table 1 is the glass electrode benchtop pH meter, ubiquitous in most chemistry labs. Although this device is commonly used by many labs to measure seawater pH, and has been automated to carry out all three types of measurements listed in Table 1, the glass electrode meters and sensors sold commercially do not qualify for Table 1 because the manufactures do not currently provide factory calibration or calibration guidance (including standard reference materials) for calibrating the electrodes on a pH scale appropriate to seawater. Thus, any lab using a simple pH meter to measure seawater pH must somehow gain access to certified buffers prepared in artificial seawater media and develop their own calibration calculations in house in order to report a pH value on the total hydrogen ion or seawater pH scales. This omission is exemplified by comparing the results of the ACT test (Johengen et al., 2015) with the benchmarks discussed by McLaughlin et al. (2015, in this issue). According to McLaughlin et al. "a maximum uncertainty of ±0.2 in the calculation of Ω_{arag} is required to adequately link changes in ocean chemistry to changes in ecosystem function." This requirement translates to a pH uncertainty of 0.02 to 0.05. ACT tested seven autonomous pH sensors, including four glass electrodes, one spectrophotometer, and two ISFET sensors. The tests included five different seawater deployments with accompanying bottle samples. If accuracy, relative to the bottle samples, is treated as representative of uncertainty as defined by McLaughlin et al., then out of the 20 tests involving glass electrodes (four devices in five deployments), 0 of 20 cases met the benchmark set by McLaughlin et al.

Progression of an instrument from proof-of-concept to commercial product may be deterred at many points along the path leading through progressive Technology Readiness Levels (TRL) (Waldmann et al., 2010). In the OA field, for better or worse, user-friendliness and cost often trump important factors such as accuracy, the prime example being the use of glass pH electrodes. Due to low cost and ease of operation, glass electrodes provide a simple means to obtain a pH measurement. In the absence of strict calibration protocols, pH errors associated with the use of glass electrodes have led to much criticism by marine CO_2 chemists for decades (Dickson, 1993). However, with care, high-quality pH measurements are possible with a simple and cheap benchtop pH meter (Easley and Byrne, 2012). In many cases, an inexpensive or lower-quality instrument may provide adequate service, depending on the accuracy required by the experimental design. Ultimately, it is the responsibility of the investigators to determine their measurement requirements and then select an instrument that meets their needs.

RECOMMENDATIONS

Here, we summarize the results of our breakout sessions by highlighting five recommendations broadly agreed upon in our discussions. It is not practical in this short report to provide a single set of instructions that definitively covers all aspects of an experimental design. Before selecting a system to purchase or construct, a researcher must first determine how frequently, accurately, and precisely a particular variable should be measured to address the process of interest; in many cases, there are multiple options that may perform adequately. Broadly speaking, short-term variability is usually easier to characterize than long-term trends, and the natural scales of variability associated with a study site should be given careful consideration when an observational plan is developed.

TABLE 1. Commercially available instruments designed to measure seawater CO_2 system variables, categorized by level of autonomy. Although custom systems have been developed for all cases shown, only commercially available instruments are displayed here, the criteria for inclusion being a manufacturer/vendor website with purchasing information as of December 2014.

	BENCHTOP[1]	UNDERWAY[2]	AUTONOMOUS[3]
DIC	VINDTA 3D/3C *Marianda* AIRICA *Marianda* AS-C3 *APOLLO SCITECH*		
TA	VINDTA 3S/3C *Marianda* AS-ALK2 *APOLLO SCITECH*	HydroFIA *Contros*	
pH		AFT-pH *Sunburst Sensors* SP200-SM *SensorLab*	SAMI-pH *Sunburst Sensors* SeaFET *Satlantic* SP101-LB *SensorLab*
pCO_2		GO 8050 *General Oceanics* MOG 701 *Kimoto* SuperCO_2 *Sunburst Sensors* OceanPack *SubCtech* AFT-CO_2 *Sunburst Sensors* AS-P2 *APOLLO SCITECH* SUNDANS *Marianda*	Seaology *Battelle* SAMI-CO_2 *Sunburst Sensors* HydroC *Contros* CO_2-PRO *Pro-Oceanus* OceanPack *SubCtech* C-Sense *Turner Designs*

[1]Benchtop: discrete bottle, auto-assisted. [2]Underway: flow-through, automated, externally powered. [3]Autonomous: automated, internally powered, in situ.

Recommendation 1: Establish Best Practices

Best practices in the form of standard operating procedures (SOPs) for benchtop CO_2 instruments were meticulously documented during the World Ocean Circulation Experiment/Joint Global Ocean Flux Study (WOCE/JGOFS) era in the late 1980s through the 1990s (Dickson et al., 2007). More recently, OA experts assembled a set of best practices for OA experiments (Riebesell et al., 2010). With the exception of underway pCO_2 systems (Pierrot et al., 2009), there are currently few best practices analogues for automated and autonomous systems. Most recently, Bresnahan et al. (2014) reported a set of best practices specific to ISFET pH sensors deployed for autonomous use in situ. Others have reported thorough assessments of in situ pCO_2 instruments that could likely be transformed into a set of best practices (Fietzek et al., 2013; Jiang et al., 2014). In a manner similar to the SOP developments for benchtop instrumentation and OA experimental design, it is anticipated that documentation of best practices for the automated and autonomous systems designated in Table 1 will require great care and specificity. Even within one of the 12 categories shown in Table 1, best practices can differ depending on measurement principle (e.g., coulometer-based DIC vs. nondispersive infrared [NDIR]-based DIC). While the user manuals associated with each device listed in Table 1 contain information on how to collect data with the instruments, it is unlikely that any of these manuals contain a set of directions that could be considered the equivalent of best practices or SOPs. To this end, we encourage experts in the community to develop and document instrument-specific best practices such as those recommended for underway pCO_2 and autonomous ISFET pH systems.

In addition to SOPs, many of our colleagues have pointed out a need to compile what might be considered "good practices" for sensor operation, somewhat analogous to the "recommendations for core monitoring principles" outlined by McLaughlin et al. (2015, in this issue). Some have even suggested that it may be useful to assemble a cautionary list of bad practices as advice on what not to do. In this article, we do not endeavor to list the numerous possibilities for bad practices, but instead suggest a noncomprehensive list of good practices discussed in our breakout sessions (Table 2).

TABLE 2. Good practices for sensor operation.

Measurements	• Always strive to measure at least two carbon system parameters in order to constrain the aqueous CO_2 system. • Consult the product literature and published results from intercomparison experiments to guide selection of instrumentation based on the needs of a specific experimental design.
Observational Design	• Pay careful attention to the advantages and disadvantages that surround choices of which CO_2 variable(s) will be measured and which will be calculated, and understand how error propagation will affect calculated parameters. • Consider the system and scientific question of interest. For example, the sampling frequency, required measurement accuracy, and measured variables often differ between highly variable coastal and highly stable open ocean systems. For coastal ecosystems, where carbonate chemistry may vary as much over the course of one day as what is expected in the open ocean over decades to centuries, a lower degree of precision may be adequate to assess many important aspects of the system, whereas open ocean CO_2 measurements typically require the highest possible level of accuracy and precision. A literature search for background information on the study site or similar sites is therefore recommended (Hofmann et al., 2011; Duarte et al., 2013). • Develop a strategy to address biofouling. Most commercial sensors include some form of fouling protection (e.g., Cu-Ni alloy, wipers, plumbed system involving a Sea-Bird CTD with tributyltin biocide, EP-1 paint). Because all anti-fouling measures function for a limited time, it is therefore important to discuss deployment environment and duration with instrument manufacturers or other qualified experts. Discrete samples are generally poisoned with $HgCl_2$ at the time of sample collection. • Seek guidance from experts familiar with systems similar to the study site in order to better understand the potential for local nuances that may affect measurement quality. For example, alkalinity measurements may be difficult to interpret in coastal environments due to interference by terrigenous output of salts, ions, nutrients, and organic acids. Mixing of seawater with freshwater flow may affect the derived $CaCO_3$ saturation state in ways independent of the CO_2 system via nonconservative behavior in calcium concentration and the portion of total alkalinity that is not attributable to carbonate alkalinity. It has also been suggested that preservation of low salinity samples with $HgCl_2$ may be problematic due to hydrolysis of the Hg(II).
Data Reporting	• When data are reported, metadata should include information on units (and pH scale), estimated uncertainties, thermodynamic constants used to compute modeled carbonate parameters, and the QC procedures applied to the data set. Explicit descriptions of the units of measurement, in situ and measurement temperature, and salinity are essential information for data evaluation and inter-comparison. • It is recommend that seawater pH measurements not be calibrated on the NBS scale due to the difficulties associated with converting from this low ionic strength buffer scale to the pH scales associated with seawater media (total hydrogen ion scale, seawater scale; Marion et al., 2011).

Recommendation 2: Conduct International Intercomparison Exercises

Previously, ACT reported on the performance of commercial pCO_2 sensors (Tamburri et al., 2011). This "performance verification" exercise provided a direct comparison of sensor data to reference samples collected alongside the sensors in different field settings. Individual research groups have conducted similar intercomparison exercises (Bates et al., 2000; Bresnahan et al., 2014). Experience gained during the pCO_2 sensor tests likely influenced the planning of the pH sensor tests (ACT, 2012a), the results of which became available during the revision of the present manuscript (Johengen et al., 2015). Likewise, combining the experience of the ACT Technical Advisory Committee with the expertise of others in the community who have performed similar tests will certainly prove useful in future large international intercomparisons, such as the ongoing Wendy Schmidt Ocean Health XPRIZE (see our opening photo on p. 40).

Recommendation 3: Enhance the CRM Program

Certified Reference Materials are critical for validating measurements listed in every category of Table 1. The CO_2 CRM program (Dickson, 2001) should be expanded to provide the oceanography community with (1) certified pH buffer solutions prepared in artificial seawater, (2) CRMs with a broader range of CO_2 system properties, (3) CRMs with a broader salinity range, and (4) access to purified indicator dyes for spectrophotometric pH measurements. For comparison, it is noteworthy that establishment of the CRM program reduced residual errors in DIC from ~14 μmol kg^{-1} during GEOSECS (Bradshaw et al., 1981) to ~3 μmol kg^{-1} (Lamb et al., 2001). Similarly, spectrophotometric pH measurement errors exceeding 0.1 have been reduced to ~0.0004 by purification of the indicator dye (Liu et al., 2011; Patsavas et al., 2013).

Recommendation 4: Expand Capabilities of CO_2 System Calculation Software to Include Error Propagation

A number of free software packages are available for performing thermodynamic calculations of seawater carbonate chemistry (Orr et al., 2014). Ideally, when a software package is used to compute modeled CO_2 parameters from measured parameters, the user could also enter errors associated with the measurements. The program would then calculate the uncertainty in the modeled parameters associated with both the measurement error and possibly additional uncertainties, such as those associated with the various equilibrium constants required to perform the calculations. A separate OAPI breakout group also suggests incorporating such error propagation features into the various software tools (McLaughlin et al., 2015, in this issue). On a similar note, it has been suggested that there is a need to revisit measurement of the CO_2 system equilibrium constants, especially at low salinity and high pressure.

Recommendation 5: Promote Availability of Instrumentation

One of the most common limitations faced by OA researchers is the lack of affordable and commercially available instruments for a given application (Table 1). Developing a commercial product for a small user base with low demand is one of the great challenges faced by the few academic researchers and the private companies that actively pursue technology development for CO_2 measurement applications. Shared instrument pools have been proposed, and while models for large-scale shared facilities (e.g., UNOLS) and smaller-scale instrument repositories (Ocean Bottom Seismometer Instrumentation Pool) exist, it is challenging to visualize how these models might apply to CO_2 instruments and sensors in terms of both startup funding and ongoing support. Is a shared instrument pool practical? How can the commercialization of needed CO_2 instrumentation be facilitated by funding agencies? Should academics be encouraged to replicate their prototype systems for use by the oceanography community at large? These questions should be considered as OA programs are developed and initiated.

CONCLUSION

Over the past decade, the OA field has matured rapidly, outpacing the development of CO_2 measurement technologies associated with OA research. Although progress has been made on many fronts in recent years, including the development of new CO_2 system sensors and methodologies, the relatively slow nature of chemical instrumentation development (e.g., commonly >10 years from concept to product) has led to several discussions, including the one highlighted here, regarding how best to address the current needs and move forward in terms of new development. Although it may be surprising to most OA researchers, the significant time required to reach TRL 9 (corresponding to a commercial product) is appreciated by those in the field of instrument development (Prien, 2007). With this in mind, it is useful to compare Table 3 of Daly et al. (2004) to our Table 1. Daly et al.'s Table 3 lists nine in situ CO_2 systems at various stages of development, with only one at TRL 9, compared to the nine systems at TRL 9 listed in column 3 of our Table 1. Based on these numbers, it would seem that much progress has been made over the past decade in terms of commercializing in situ CO_2 instruments. However, it is noteworthy that only two of the other eight systems listed in Daly et al.'s Table 3 advanced to TRL 9 over the past decade, indicating that the "ten-year rule" may represent a best-case scenario. On the other hand, it is also noteworthy that six of the nine sensors listed in Table 1 were not even recognized as TRL 1 in 2004, but advanced to TRL 9 in less than a decade. Of these apparent anomalies, two of the four systems (SeaFET and OceanPack) utilize sensors that were already at TRL 9 in 1994 (the Honeywell Durafet and Licor NDIR CO_2 analyzer, respectively), which greatly accelerated the development and commercialization process of the in situ systems based around these products. With the exception of recent work by Jiang et al. (2014), the developmental progress of the other three systems (HydroC, SP101, and CO2-PRO; C-Sense is the CO2-PRO, marketed by a different company) is not well documented in the peer-reviewed literature (presumably intentionally to preserve trade secrets). These systems are ostensibly based on technology modifications that were at an advanced state 10 years ago (Bellerby et al., 1995; McNeil et al., 1995) or that were made available through existing company expertise (Fietzek and Körtzinger, 2010). Nonetheless, these companies have clearly made impressive progress by developing complex equilibrator and detector systems in house and commercializing them in less than a decade. These final three sensors may therefore represent the closest exception to the ten-year rule of the systems listed in Table 1.

In addition to sensor development trajectories, the breakout group was also asked to discuss the possibility of developing or enhancing sensor networks, particularly with an eye toward coordination and intercomparison. Networks for observing, research, and collaboration exist (e.g., observing systems such as the NOAA OA mooring system, the Ocean Observatories Initiative, and Argo), as do data repositories (Biological and Chemical Oceanography Data Management Office, Carbon Dioxide Information Analysis Center) and coordinating organizations (OCB, IOCCP, California Current Acidification Network). It was noted that it is generally desirable to support and/or enhance existing entities rather than creating new ones. There has been some forward-looking discussion of shared-use analytical facilities and instrument repositories focused on CO$_2$ instrumentation.

There is a growing awareness that anthropogenic alteration of the ocean environment requires that interactive effects between changing environmental parameters (e.g., increasing temperatures, decreasing pH and oxygen) need to be addressed concurrently (Bockmon et al., 2013; Paganini et al., 2014). Suites of instruments need to be carefully co-located for long-term measurements, as sensors deployed even a few meters apart may not provide consistent information due to the vertical variability in physical, chemical, and biological processes. Additionally, researchers working in estuaries and coastal habitats characterized by large daily, tidal, or seasonal variation in carbonate chemistry should recognize that the precision required to characterize biologically relevant shifts in the carbonate system are quite different than what is required by oceanographers working in open-ocean systems. Such differences can be used in establishment of "good practices" for studies of such dynamic systems that could involve trade-offs in measurement precision for increased temporal and spatial resolution within the study system. Regular assessments of community planning, lessons learned, and best practices are needed to keep the OA community forward thinking and vibrant.

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