Alliance for Coastal Technologies: Advancing Moored pCO$_2$ Instruments in Coastal Waters

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Introduction

The Alliance for Coastal Technologies (ACT; www.act-us.info) is a world leader in the evaluation of commercial-ready and emerging open-ocean, coastal, and freshwater sensing technologies, engaging nationally prominent ocean science and technology institutions and experts to provide credible per-

ABSTRACT

The Alliance for Coastal Technologies (ACT) has been established to support innovation and to provide the information required to select the most appropriate tools for studying and monitoring coastal and ocean environments. ACT is a consortium of nationally prominent ocean science and technology institutions and experts who provide credible performance data of these technologies through third-party, objective testing. ACT technology verifications include laboratory and field tests over short- and long-term deployments of commercial technologies in diverse environments to provide unequivocal, unbiased confirmation that technologies meet key performance requirements. ACT demonstrations of new technologies validate the technology concept and help eliminate performance problems before operational introduction. ACT's most recent demonstration of pCO$_2$ sensors is an example of how ACT advances the evolution of ocean observing technologies, in this case to address the critical issue of ocean acidification, and promotes more informed decision making on technology capabilities and choices.
Keywords: emerging technology, sensors, ocean observing, pCO$_2$, ocean acidification

formance data of these technologies through third-party, objective testing. ACT was established by the National Oceanic and Atmospheric Administration (NOAA) in 2001 to bring about fundamental changes to innovation and engineering practices in marine technology. It arose at a time when the United States began moving toward the development and implementation of a sustained national Integrated Ocean Observing System (IOOS®). During this period, the U.S. Commission on Ocean Policy (2004) found and concluded in its final report, *An Ocean Blueprint for the 21st Century*, that the process for instrument innovation and development by federal agencies and academic research institutions offered little hope of rapid and continuous integration of new technologies into operational coastal observing systems. More recently, the final recommendations of the Interagency Ocean Policy Task Force (2010) has also emphasized the importance of ocean, coastal, and great lakes observations, mapping, and infrastructure and has called for the strengthening and integration of federal and nonfederal ocean observing systems, sensors, and data collection platforms into a national system. ACT's goals are to facilitate the creation and application of knowledge on current and emerging coastal- and ocean-observing and research technologies, to improve the capabilities of existing observations, and to deliver innovative solutions to specific emerging global environmental issues and operational ocean-observing challenges that address the priorities of the Commission and the Task Force. ACT's independent, rigorous, and quality-assured data on the performance characteristics of environmental monitoring technologies (tested under

true operational conditions) provide IOOS and other users with relevant assessments of instrument capabilities and operational readiness while assisting instrument developers and manufacturers in technology maturation and transfer.

Independent validation and verification are considered within any technology industry as "best practice," which provides visibility, accountability, and fact-based decision making for technology initiatives. ACT Technology Verifications focus on classes of commercially-available instruments to provide unequivocal confirmation that a given technology meets performance specifications and/or provide verified data on those operational capabilities that stakeholders claim must be known in order to make a use decision. Testing is carried out under reproducible, well-understood conditions that allow manufacturers to assess and improve different components, configurations, and designs as necessary until desired performance is achieved. ACT Demonstrations help technology developers and manufacturers to identify and address limitations of new instrumentation, to explore instrument performance under diverse applications and environmental conditions, and to build user community awareness of emerging technologies.

Since 2004, ACT has evaluated 40 sensors from 24 international companies. In total, ACT has conducted 226 instrument performance tests in the laboratory and in the field, under a wide range of environmental conditions and different deployment applications on a variety of sensor classes, including salinity, dissolved oxygen, turbidity, chlorophyll fluorometry, nutrients, and pCO_2. More than 200,000 technology verification/

demonstration reports have been downloaded from ACT's Website (www.act-us.info). Selection of a technology for an ACT evaluation involves broad community input and strives to address critical environmental concerns.

The continual production of anthropogenic carbon dioxide from the burning of fossil fuels is increasing CO_2 gas in the atmosphere and, by absorption to the ocean, acidifying surface waters around the world. Ocean acidification has become one of the most significant and urgent issues facing ocean resource harvesters and managers (Doney et al., 2009). Monitoring the open ocean and the coastal oceans for CO_2 levels will become paramount in assessing impacts and developing regulatory criteria, both nationally and internationally. In 2005, ACT held a workshop focused on measurements of Dissolved Inorganic Carbon (DIC) parameters to spur the use of pCO_2 sensors for coastal applications (ACT, 2005).

There are three important reasons for sustained, *in situ* measurements of pCO_2 from coastal moorings. The first is to evaluate whether coastal areas are functioning as a source or sink of atmospheric CO_2. Coastal areas are expected to be vulnerable to climate change, and this potential impact has direct consequence on managing CO_2 as a pollutant in the 21st century. High-frequency temporal and spatial measurements of pCO_2 will provide some understanding of the fluxes and their variability and forcing parameters. The second reason for continuously monitoring pCO_2 is to understand changes in saturation state of the water with respect to carbonate minerals and its impact on the health of calcifying organisms and communities (e.g., planktonic fo-

raminifera, coral reefs, and oyster reefs). Surface pCO_2 measurements in conjunction with direct measurements of one other parameter of the marine CO_2 system (pH, total alkalinity [TA], or total dissolved inorganic carbon) can be used to calculate saturation state (for calcite and aragonite). The third important use of continuous monitoring is the direct measurement of net community production in shallow waters, which provides further understanding of how the carbon cycle is affected by climate change parameters such as temperature and pH. Changes in pCO_2 can occur on time scales ranging from hourly to seasonal and interannual. All of these parameters are potentially being altered by CO_2 fluxes and progressive ocean acidification. Thus, it is vital to further promote, develop, and improve measurement capabilities for seawater pCO_2.

Most of the sophisticated instrumentation for the analysis of marine carbon biogeochemistry has been used onboard ships (Schuster et al., 2009). However, recent technological developments have led to instruments that can be deployed on surface moorings and buoys, allowing high-frequency, time-series measurements of pCO_2 in the coastal ocean. Some of the challenges to long-term deployment of *in situ* pCO_2 sensors (or analyzers) in coastal environments, as with most sensors, include accuracy and precision, reliability and drift, response time and frequency of measurements, sensitivity to biofouling, ruggedness, size and weight, power requirements, and ease of use and maintenance (ACT, 2005; Schuster et al., 2009). The general objectives of the ACT Demonstration of pCO_2 sensors were: (1) to highlight the potential capabilities of *in situ* pCO_2 analyzers by

demonstrating their utility in two different coastal environments, a vertically stratified sound and a shallow coral reef; (2) to increase awareness of this emerging technology in the scientific and management community responsible for monitoring coastal environments; and (3) to work with instrument manufacturers that are presently developing new or improved sensor systems by providing real-world quality assured tests to support technology advancement and adoption. This pCO_2 sensor evaluation focused on collecting data on instrument accuracy, precision, and stability. There were four instruments evaluated: three instruments using infrared detection in a gas stream and one using a change in pH indicator dye.

Methods

As with all ACT Technology Evaluations, test protocols are developed under the guidance of an expert Technical Advisory Committee, in partnership with the participating manufacturers (ACT, 2009). Perhaps the most important step in protocol development is the establishment of an agreed-to standard to measure instrument performance. Commonly, this comparison involves the collection of water samples adjacent to the test instruments, followed by detailed laboratory analysis.

Reference Standards and Analytical Procedures

Reference samples or measurements are either prepared standards or measurements made by a method that is agreed as a standard. In the pCO_2 sensor evaluation, reference pCO_2 concentrations were determined in two ways: (1) from pH, TA titrations performed on discrete water samples collected near the instruments and (2) direct measurements of pCO_2 on discrete water samples using a flow-through pCO_2 analyzer developed by Burke Hales (Oregon State University).

For the titration analysis, pH was measured using the dye technique (Dickson et al., 2007). Total alkalinity was measured using bromocresol green dye method as an endpoint pH indicator (Yao and Byrne 1998; Dickson et al., 2007) and calibrated directly to Certified Reference Materials in DIC and TA. Final pCO_2 concentrations were then calculated using the standard CO2sys program with dissociation constants (Millero et al., 2006; Pierrot et al., 2006). Water samples analyzed in the laboratory had four replicates for both pH and for TA. All pH measurements were calibrated directly to Dickson buffers on the total hydrogen seawater scale and pH for two batches of Certified Reference Materials (Dickson batch nos. 82 and 96). Normality of the added acid for the TA measurements was adjusted to calibrate all alkalinities to Dickson seawater standards (Batch nos. 82 and 96).

For the flow-through pCO_2 analyzer reference, the instrument sampled an aliquot of water that had been pumped into a cooler, spanning the time at which all test instruments were making measurements. Results were averaged from readings collected over a 5-min time period, approximately 10 min into the sampling cycle, when the system was well equilibrated. The reference sample analyzer was calibrated each day with known gas concentrations immediately before going into the field to collect the reference sample.

Field Tests

Moored field tests were conducted at two coastal sites, one in the Hood Canal, a temperate stratified estuary adjacent to Puget Sound, Washington, (Figure 1A; http://orca.ocean.washington.edu/mooringDesign.html), and the second at a subtropical coral reef in Kaneohe Bay,

FIGURE 1

(A) Field test site located in the Hood Canal east of Union, Washington; the PMEL-MAPPS instrument is in the buoy and the other test instruments are mounted about 1 meter below the surface. (B) Field test site located in Kaneohe Bay, northeast side of Oahu, Hawaii; the PMEL-MAPPS instrument is on the buoy and the other test instruments are mounted about 1 m below the surface.

(A)

(B)
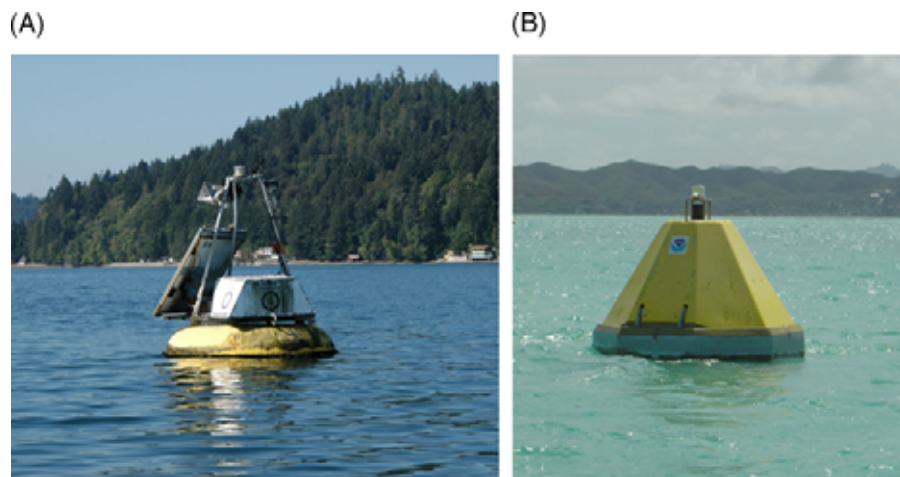
Hawaii (Figure 1B; http://www.pmel.noaa.gov/co2/coastal/HI/). Both locations were very challenging environments for measuring pCO_2 due to large ranges and rapid changes in pCO_2 and temperature. Another factor in the site selection was that both sites have moored buoy systems, which not only provided platforms to mount the test instruments but were also already equipped with the NOAA Pacific Marine Environmental Laboratory MapCO2 analyzer. The sites were also contrasting, with different water temperature regimes and with different kinds of biofouling pressures.

Test instruments were deployed for approximately four weeks at each site. ACT personnel worked with the instrument manufacturer to design an appropriate deployment arrangement on the buoy at each of the field test sites. The test instruments were mounted on the buoys in a manner that field reference water samples were collected no more than 0.5-m from the sampling inlet of all instruments. All instruments were deployed at a fixed depth, approximately 1 m below the water surface. A calibrated CTD package was attached to the mooring and programmed to provide an independent record of conductivity and temperature at time intervals to match any of the test instruments. In addition, two calibrated RBR 1060 logging thermometers were deployed at depths immediately surrounding the instrument (20–30 cm above and below) to characterize any fine scale temperature variation near the sampling depth.

Before deployment, each instrument was set up and calibrated by a manufacturer representative with assistance from ACT staff. The instrument was programmed to record data on the basis of a sampling time of the reference sample and the best use of power. Internal clocks were set to local time and synchronized against the time standard provided by www.time.gov. To provide a qualitative estimate of biofouling during the field tests, photographs of the instrument and mooring rack were taken just before deployment and just after recovery.

A predeployment, laboratory-based, tank test was conducted before the instruments were moored in the field. The instrument was placed in a well-mixed, tank filled with ambient seawater and equilibrated for at least an hour. Independent reference sample measurements were taken at least two to three times over the next hour and matched against corresponding time points of instrument readings. Reference samples collected to determine *in situ* pCO_2 concentrations during the exposure were processed and analyzed using the same procedures as for field reference samples, defined below. At the end of field deployment, the tank exposure test was repeated under conditions as similar as possible. Instruments were cleaned to remove biofouling before the post-deployment tank test to help differentiate between biofouling effects on performance and instrument drift characteristics.

The collection of reference water samples in the field was structured to examine changes in pCO_2 concentrations over hourly to weekly time scales. Twice each week, we conducted an intensive sampling event that consisted of four consecutive samples spaced at 1- to 2-h intervals. For the remaining two sampling days of the week, we sampled twice per day. The specific timing of pCO_2 water sampling was determined on site, but with the goal to measure the maximum variation in concentration. All sampling times were recorded on log sheets and entered into a database for final data comparisons.

For the field tests conducted at Hood Canal, a 20-L cooler was brought to thermal equilibrium with seawater by repeated flushing for 10 min before water sampling. Water was then pumped from near the inlets of the pCO_2 instruments mounted on the buoy to the cooler. The cooler acted as a reservoir with a running 3-min integrated water sample. The integrated water sample was then drawn through the flow-through pCO_2 analyzer over a 10-min interval, with values recorded every second. Data were averaged to provide an appropriate comparison with the sampling time of the test instruments. Two water samples were collected from the outlet of flow-through pCO_2 analyzer for direct measurements of pH, TA, and CO_2 titration. These laboratory reference samples were immediately poisoned with mercuric chloride and put in a darkened, thermally insulated container at environmental temperatures and taken directly to the laboratory. One sample was analyzed within a few hours of collection for pH and TA. An RBR TR-1060 thermometer was placed in the cooler to monitor all temperatures.

At the Hawaii test site, two modifications were made to the sample collection and handling procedures because of the size of the boat and location of the buoy near the barrier reef. After the cooler was soaked in surface water to bring it to thermal equilibrium, seawater was pumped from near the inlets of the instruments into a

150-L cooler, giving an 11-min integrated water sample. The reference water sample was immediately transported back to the laboratory at the Hawaii Institute of Marine Biology on Coconut Island, Kaneohe Bay, where it was then pumped through the pCO_2 flow-through analyzer. Instead of collecting water at the outlet of flow-through analyzer for direct titration, reference water was collected directly from the cooler. These water samples were taken directly to the laboratory and measured for pH and TA. Before the field test, comparison tests were conducted to confirm that this procedure gave accurate values.

All reference samples were cataloged individually with ancillary field collection data. Chain-of-custody protocols were practiced for transported samples, specifying time, date, sample location, unique sample number, requested analyses, sampler name, required turnaround time, time and date of transaction between field and laboratory staff, and name of receiving party at the laboratory. Independent field and laboratory audits were conducted to ensure that the demonstration project was performed in accordance with test protocols and the quality assurance plan. These audits included review of the reference methods, all sample collection and analytical procedures, and data acquisition and analysis procedures.

Results

The environmental conditions at the field sites were representative of the challenges of making pCO_2 measurements in coastal water, specifically, rapid short-term changes in temperature and pCO_2 coupled to long-term changes. Temperature of surface water varies from daily heating and cooling, vertical and small-scale mixing within the mixed layer, and from relatively slow changes associated with month-long changes in weather. Although this may seem obvious to researchers in coastal dynamics, some instrument packages do not account for the nature of inherent problems associated with making measurements in dynamic and productive coastal waters. At the Twanoh Buoy in Hood Canal, water temperature varied from 11.1 to 19.6°C over the month of deployment. Water temperature also varied extremely rapidly, about 1°C per 1 h and 6°C in 8 h (Figure 2). Salinity varied from 24 to 29 practical salinity units (PSU) (Figure 3). The discrete reference water samples showed a variation in pCO_2 of only 334 to 488 µatm, but continuous *in situ* sampling showed extremely rapid changes in pCO_2 of 350 to 750 µatm within several hours (Figure 4). This is yet another example of how discretely collected water samples can completely miss real events, and long-term averages can be in large error. All sensors in the ACT Demonstration captured the excursions in pCO_2 (Figure 4), validating these events.

At the NOAA Crimp 2 buoy in Kaneohe Bay, water temperatures varied from 23.2 to 28.3°C, with daily changes in temperature of about 1 degree in 10 h (Figure 5). Salinity was higher than at Hood Canal and only varied about 1 PSU (Figure 6). The pCO_2 measured in the discrete reference water samples varied from 280 to 600 µatm, but the sensors indicated a much wider range (Figure 7).

Aliasing of water sampling missed some of the extreme and rapid changes in pCO_2 often observed in these environments (Figures 4 and 7). This significant and rapid variability is one of the inherent problems in making these measurements in coastal water. It is not clear whether data outliers are extreme events, such as internal waves and tides bringing high pCO_2 water upwards, as in Hood Canal, or low tide and high daily rates of photosynthesis and respiration, as in Hawaii. Thus, these natural environments make very good places to test the calibrations over a large range in pCO_2 as well as response times and averaging in the software of the instrument.

All pCO_2 instruments tested had different methods of gas equilibration and different sampling integration times and response times, making a direct comparable reference measurement difficult. This is one of the important issues to consider when using field reference samples to calibrate instruments in the field for long term, even if the reference sample is taken within a few minutes of the instrument's actual time of measurement.

If we define error as the difference between an instrument value and the reference water sample, then there are a number of different sources of error. One source of error is a mismatch in integrating the sampling of the water, either through equilibration techniques and timing or by subsampling the water column. These errors can be exacerbated by differing methods of sharpening the signal and averaging techniques. We believe that several of the test instruments can be improved by altering the algebraic methods to deal with the response of the instrument. Also, there is clearly small-scale heterogeneity in the water column, both correlated to temperature and not correlated to temperature. This appears to be less of a problem, but the rapid changes in pCO_2 can interact with the response characteristics and

FIGURE 2

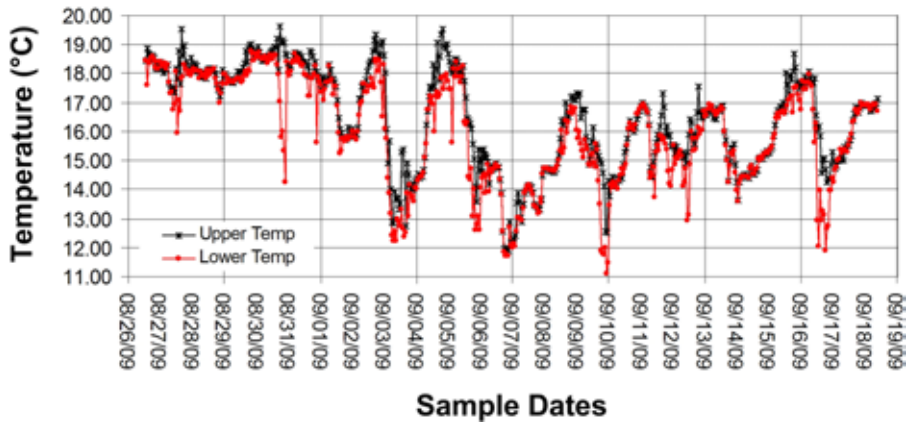Washington—Hood Canal. Data are from two temperature recorders mounted at 0.8 m depth (upper) and 1.5 m depth (lower). (Color versions of figures available at: http://www.ingentaconnect.com/content/mts/mtsj/2011/00000045/00000001.)

FIGURE 3

Washington—Hood Canal. Practical salinity units from a CTD mounted at 1 m below the surface.
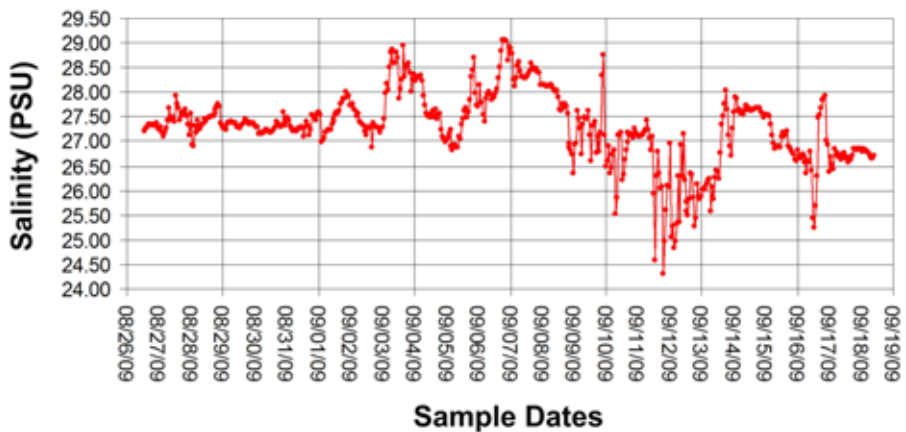
FIGURE 4

Washington—Hood Canal: PMEL-Mapps data with blue points for reference water samples and a calculation from CO2sys.
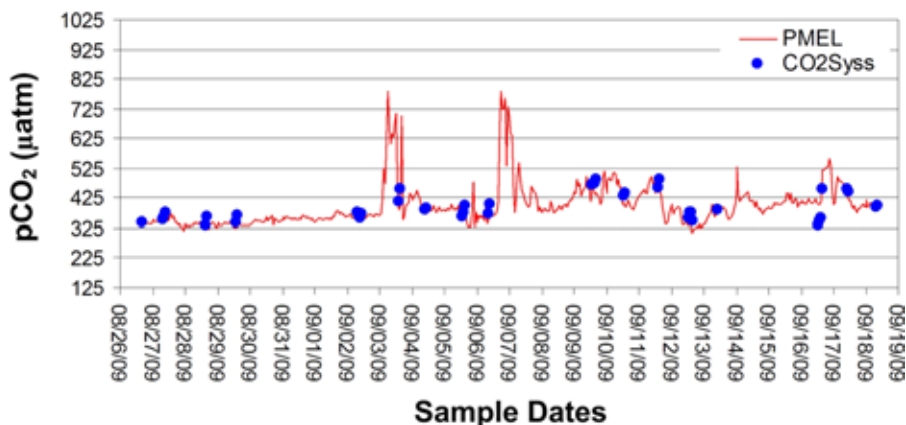
increase error. Additional sources of error may be in the collection and analysis of the reference samples and the maintenance and calibration of the flow-through pCO_2 analyzer. Finally, instrument performance itself, such as response time, sharpening filters, control of heat, and biofouling are all issues. On the basis of our current analysis of the test data, analytical techniques of reference samples are confined to about 5 µatm, whereas standard deviations of errors with the instruments are about 20–30 µatm. Mean differences between instruments and references are ranging from less than 5 µatm to as much as 95 µatm. We believe that most of these errors can be remedied very quickly with some changes in calibration. It is also important to note that all test instruments performed over the month period with no decay in the signal and no power problems. Thus, biofouling did not appear to have a significant effect on any of the instrument's performance.

Detailed test protocols and complete data sets and analyses for each of the pCO_2 sensors evaluated by ACT can be found in the individual Demonstration Statements. Downloads are available at www.act-us.info.

Discussion

ACT is providing both the organization and logistical framework to demonstrate the feasibility of using pCO_2 sensors in coastal environments, providing feedback to companies to help improve *in situ* measurements and highlighting the capabilities and potential of this important emerging class of instruments. This process exposes the companies to real issues in the coastal environment and the actual use of their instrument

FIGURE 5

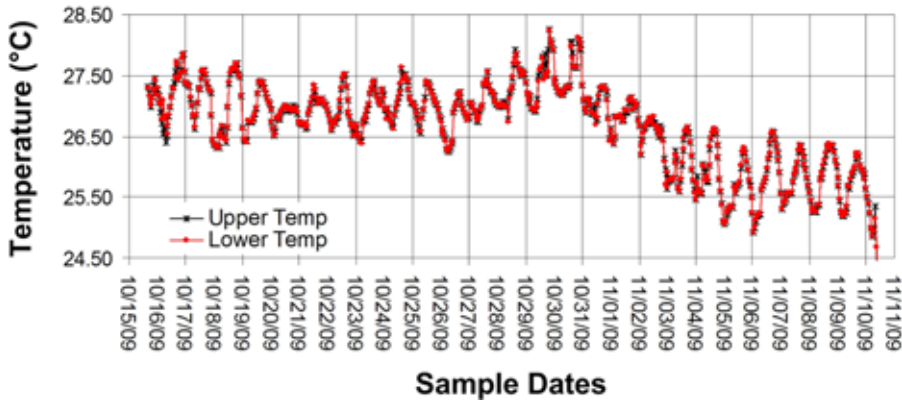Hawaii—Kaneohe Bay: Data are from two temperature recorders mounted 50 cm depth (upper) and 80 cm depth (lower).

FIGURE 6

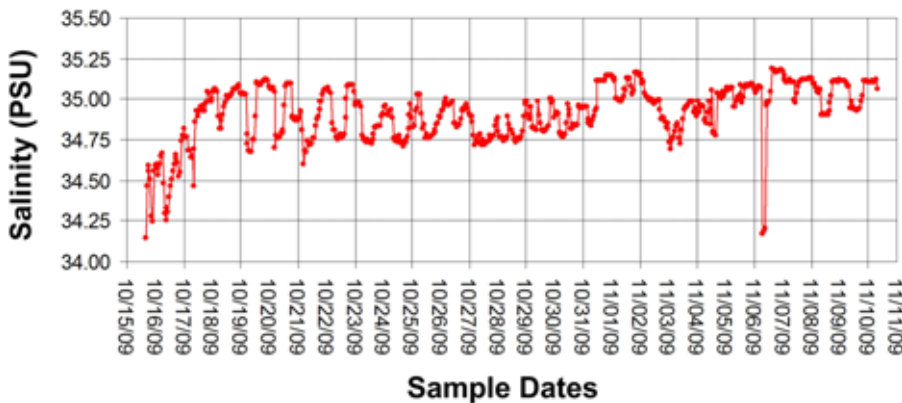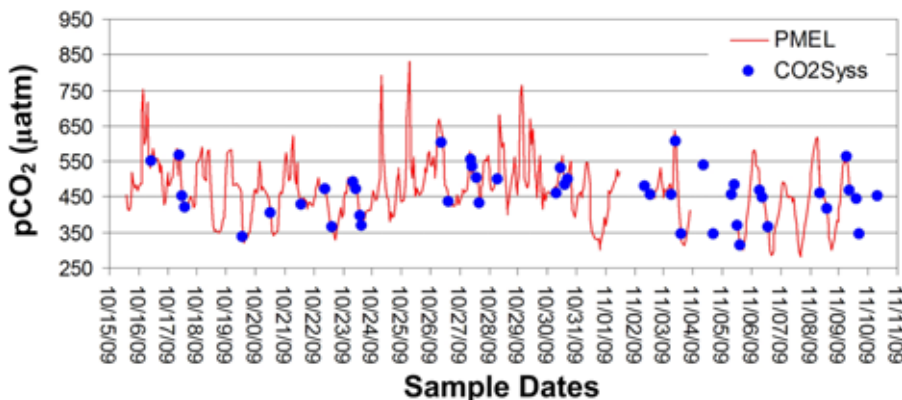Hawaii—Kaneohe Bay: These data are practical salinity units from a CTD mounted 1 m depth.

FIGURE 7

Hawaii—Kaneohe Bay: PMEL-Mapps data with points for reference water samples using CO2Syss.

on a mooring. All pCO_2 instruments evaluated show promise in being applied to these environments, and in some cases with a few improvements, they will provide excellent data for the coastal use. On the basis of this ACT Demonstration, packaging, handling, power consumption, and biofouling are not major issues. However, it appears that initial conditions on calibrations and improvements in data reduction within the instruments will greatly improve the statistics of the errors and the quality of *in situ* moored pCO_2 measurements. We hope this exercise ultimately facilitates the development and adoption of novel instrumentation, while minimizing the risk of artifacts and problems associated with young technology (e.g., Schiermeier, 2007).

Efforts on pCO_2 sensors to address issues of ocean acidification is just the latest example of how ACT has emerged as a national program for facilitating the transition and adoption of critical technologies to routine use in coastal and ocean environments. The overall objectives of ACT are: (a) to rapidly and effectively transition emerging technologies to operational use; (b) to maintain a dialogue among technology users, developers, and providers; (c) to identify technology needs and novel tools and approaches to meet those needs; (d) to document the technology performance and potential; and (e) to provide IOOS with information required for the deployment of reliable and cost-effective networks. In addition to serving as a third-party test bed for quantitatively evaluating the performance of new and existing instrumentation, ACT also is a forum for capacity-building through technology-specific workshops and an information clearinghouse, through published

reports and a searchable online database of environmental technologies. To date, ACT released reports on over 226 evaluations of the performances of 40 individual instruments from 24 different international companies, conducted 38 technology workshops, involving over 1,500 participants, and provides listings of over 4,000 instruments, from over 300 companies through the searchable database.

Some generalizations in sensor performance can be made on the basis of ACT's Technology Evaluations to date. First, there is a clear difference in instrument performance between laboratory and field, and instrument performance in the field usually depends on the type of application (e.g., moored, vertical profiling, surface mapping), the environment (rivers, lakes, estuaries, coral reefs, fjords, and open ocean), and the nature and severity of biofouling. Although anti-fouling approaches are available (such as coatings, copper screens, and mechanical wipers), deployments of more than 2 to 3 weeks are typically not possible during spring and summer months in highly productive coastal waters. Second, many widely used instruments, which measure basic physical or chemical parameters, may not always perform to manufacturers' specifications in the field, and users should be cautioned on their limitations. Finally, power management and sampling/response time is often an issue for instruments deployed in coastal water with rapidly changing parameters. Thus, instrument validation under diverse conditions is critical considering the range of environments targeted by IOOS, Ocean Observatories Initiative, academic researchers, and resource managers.

In summary, the public and the private sectors have a growing demand for accurate and reliable environmental observations, which allow for a basic science understanding, forecasting, and informed management decisions. To meet this demand, the federal government (1) has established operational systems and services, which provide the basis for production and dissemination of official assessments, predictions, and warnings, and (2) supports research and technology and systems development to improve operational observation capabilities, such as higher quality data through the introduction of new or enhanced environmental sensors. By fostering the development and adoption of effective and reliable instrumentation for monitoring and long-term resources stewardship, ACT is a critical link between these two national priorities. Ultimately, through the validations of new and existing technologies, ACT also provides assurance that our basic science understanding, forecasting, and management decisions are based on accurate, precise, and comparable observing data.

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