PERFORMANCE DEMONSTRATION STATEMENT
Sunburst Sensors SAMI-CO_2

TECHNOLOGY TYPE:	Direct measurement of pCO_2 in natural water using gas equilibration and spectrophotometric pH-dye indicator
APPLICATION:	*In-situ* measurements of pCO_2 for coastal mooring.
PARAMETERS EVALUATED:	Accuracy, precision and reliability
TYPE OF EVALUATION:	Field Performance Demonstration
DATE OF EVALUATION:	Testing conducted from August 2009 through November 2009
EVALUATION PERSONNEL:	D. Schar, M. Atkinson, T. Johengen, A. Pinchuk, H. Purcell, C. Robertson, G.J. Smith, M. Tamburri.

NOTICE:

ACT Demonstration Projects are evaluations of technology performance under specific protocols, criteria, and quality assurance procedures that are established by mutual agreement of the ACT technical committee, technical staff and participating vendors. ACT and its Partner Institutions do not certify that a technology will always operate as demonstrated, nor does ACT guarantee future performance of technologies. ACT does not seek to establish nor determine any regulatory compliance; does not rank nor compare technologies; does not label nor list technologies as acceptable or unacceptable; and does not seek to determine "best available technology" for any purpose. The user is solely responsible for complying with any and all applicable federal, state, and local requirements.

This document has been peer-reviewed by ACT Partner Institutions and a technology-specific advisory committee, and was recommended for public release. Mention of trade names or commercial products does not constitute endorsement or recommendation by ACT for use.

Questions and comments should be directed to: Dr. Thomas Johengen
c/o Alliance for Coastal Technologies
Chesapeake Biological Laboratory
PO Box 38 / One Williams Street
Solomons, Maryland 20688, USA
Email: Johengen@umich.edu
Email: Johengen@umich.edu

UMCES Technical Report Series: Ref. No. [UMCES]CBL 10-094

Table of Contents

Executive Summary **3**

Background and Objectives **4**

Technology Tested **5**

Summary of Demonstration Protocols **5**

Moored Field Deployment Tests *6*

Reference Standards and Analytical Procedures *6*

Quality Assurance and Control *10*

Results of Moored Field Tests **11**

Moored Deployment in Hood Canal, Washington *11*

Moored Deployment off Coconut Island in Kaneohe Bay, Hawaii *16*

Reliability *17*

Technical System Audits **17**

Acknowledgements **21**

References **22**

Appendix 1: Company Response Letter to Submitted pCO2 Demonstration Report **23**

EXECUTIVE SUMMARY

Alliance for Coastal Technology (ACT) demonstration projects are designed to characterize performance of relatively new and promising instruments for applications in coastal science, coastal resource management and ocean observing. ACT has evaluated four commercial pCO_2 instruments that are capable of being moored for weeks to months. This document is termed a "Demonstration Statement" and provides a summary of the results for the Sunburst SAMI-CO_2.

Briefly, test instruments were mounted on surface moorings in a temperate stratified estuary (Twanoh Buoy, Hood Canal Washington; August-September 2009; http://orca.ocean.washington.edu/mooringDesign.html;) and a coral reef (Kaneohe Bay Hawaii; October-November 2009; http://www.pmel.noaa.gov/co2/coastal/HI/). The sites were chosen based on existing moorings and the expected rapid changes in seawater temperature and pCO_2. Water samples were collected to determine pH and Total Alkalinity (TA) for calculation of pCO_2 (CO_2Sys; Pierrot et.al. 2006) and direct measurements of pCO_2 using a flow-through pCO_2 analyzer (Oregon State University; gas equilibration and infrared gas detection). In situ pCO_2 measurements are compared to both of these references and estimates of analytical and environmental variability are reported. Quality Assurance (QA) and oversight of the demonstration process was accomplished by the ACT QA specialists, who conducted technical, protocol and data quality audits.

At Twanoh buoy, Hood Canal, temperature varied from 11.09 to 19.62 ^oC and salinity varied from 24.3 to 29.1. Measured pCO_2 values of reference samples varied from 334 to 488 µatm, while the 30 minute measurements by the SAMI-CO_2 varied from about 340 to 900 µatm, demonstrating a more complete assessment of the variability in the ecosystem. The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the Flow Analyzer reference measurements were +23 ± 13 µatm (n=31; SAMI-CO_2 - Flow Analyzer). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the pCO_2Sys reference measurements were +18 ± 40 µatm (n=42; SAMI-CO_2 - pCO_2Sys).

At NOAA Crimp 2 buoy, Kaneohe Bay, temperature varied from 23.24 to 28.27 ^oC and salinity varied from 34.1 – 35.2 over the deployment. Measured pCO_2 values of reference samples varied from 314 to 608 µatm, while the 30 minute measurements by the SAMI-CO_2 varied from about 320 to 900 µatm, again capturing more of the full variability in the ecosystem. The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the Flow Analyzer measurements were +28 ± 9 µatm (n=13; SAMI-CO_2 - Flow Analyzer). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the pCO_2Sys reference measurements were +40 ± 13 µatm (n=45; SAMI-CO_2 - pCO_2Sys).

The instrument on both test moorings functioned throughout the month-long deployment, and 100 percent of expected data were retrieved. The continuous, 30 minute time-series data (plotted hourly; n=535 and n=618 for WA and HI, respectively) provided by the instruments revealed diel patterns in pCO_2 and captured a significantly greater dynamic range and temporal resolution than could be obtained from discrete reference samples. There were no changes in the differences between instrument and reference measurements during either test, indicating that biofouling and instrument drift did not affect measurement performance over the duration of the test.

BACKGROUND AND OBJECTIVES

One of the recommendations from the Alliance for Coastal Technology (ACT) workshop, *In-situ measurement of dissolved inorganic carbon speciation in natural waters: pH, pCO_2, TA and TCO_2,* Honolulu, Hawaii, February 2005, was that ACT should conduct a "demonstration project" to evaluate pCO_2 sensors. Workshop participants concluded that pCO_2 technologies were sufficiently accurate and low-powered to be used on coastal moorings and monitoring systems. Instrument performance verification is necessary to ensure that current technologies are effective and that promising new technologies are made available to support coastal science, resource management and ocean observing efforts. To this end, NOAA supports ACT to serve as an unbiased, third-party to evaluate sensors and sensor platforms for use in coastal environments.

ACT has two activities to evaluate moored, in-situ instruments: one is a "technology verification," in which the evaluation is to verify the quoted standards, operational capabilities and handling characteristics of commercially-available instruments. The other evaluation is a "technology demonstration," in which the evaluation is to "demonstrate' the feasibility of using instruments on coastal moorings, helping the vendor identify and address limitations of the instruments, explore instrument performance under diverse applications and environmental conditions, and to build community awareness of emerging technologies. The demonstration evaluation is focused on developing technologies, in which there are only a few established commercially-available instruments; thus this evaluation for pCO_2 instruments is a demonstration project. Due to a limited budget, tests were conducted at two sites. We chose sites that were representative of coastal ocean environments, had existing $MAPCO_2$ instruments in place and experience significant changes in temperature, salinity, photosynthesis, respiration, calcification, etc. that would result in significant variation in pCO_2 over daily and weekly cycles. Specifically, one site was a relatively cold stratified estuary, with large tidal changes, providing rapid changes in temperature and salinity from diel heating and cooling, tidal currents, and vertical mixing. The other site was a sub-tropical coral reef with large changes in pCO_2 from high rates of photosynthesis, respiration and calcification.

There are three important reasons for measuring pCO_2 continuously from coastal moorings: first, to evaluate whether coastal areas are functioning as a source or sink of atmospheric CO_2. Coastal and shallow near-shore ecosystems are variable in temperature, salinity and dissolved carbon dioxide species making it difficult to determine whether they act as sources or sinks of CO_2 to the atmosphere. Furthermore, 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. Near-continuous measurements of pCO_2 will provide some understanding of the fluxes, their variability and forcing parameters. The second reason for continuous monitoring is to understand the changes in saturation state of the water with respect to carbonate minerals and its impact on the health of calcifying ecosystems. Surface pCO_2 measurements in conjunction with direct measurements of one other parameter of the marine CO_2 system (pH, TA or total DIC) can be used to calculate saturation state (for calcite and aragonite). The third important use of near-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 and daily, to seasonal and inter-annual.

Thus, it is vital to further promote, develop and improve measurement capabilities for seawater pCO_2.

The basic objectives of this performance demonstration 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 a forum for thoroughly testing their products in a scientifically defensible program, at relatively minor costs in terms of time and resources to vendors.

TECHNOLOGY TESTED

The Submersible Autonomous Moored Instrument (SAMI) for CO_2 is a compact, fully autonomous instrument for the measurement of pCO_2 in marine and freshwater environments with a precision $< \pm 1$ µatm. The SAMI housing permits deployments to depths of 500 m and contains sufficient power and reagent to sample hourly for up to one year (8 alkaline D-cells, 1 liter reagent). The SAMI 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 SAMI-CO_2 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.

For a given 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 is corrected for the difference between the calibration and measurement temperature with an accurately known temperature coefficient.

Fouling protection is provided by a copper mesh cage covering the membrane. For higher fouling environments, the membrane is enclosed in a chamber and a Seabird pump is used to circulate sample.

SUMMARY OF DEMONSTRATION PROTOCOLS

The protocols used for this performance verification were developed in conference with ACT personnel, the participating instrument manufacturers and a technical advisory committee. A description of the testing protocols is available in the report, *Protocols for Demonstration the*

Performance of In Situ pCO_2 Analyzers (ACT PD09-01) and can be downloaded from the ACT website (www.act-us.info/evaluation_reports.php). Additional details or modifications that occurred at the field test sites are described below. As defined by the protocols, manufacturer representatives directly assisted in the initial set-up and calibration of the instruments, instrument retrieval, and data management.

Moored Field Deployment Tests

Moored field deployment tests were conducted at two coastal sites, one in Hood Canal off Puget Sound, Washington, (http://orca.ocean.washington.edu/mooringDesign.html) and the second in Kaneohe Bay, Hawaii (http://www.pmel.noaa.gov/co2/coastal/HI/). The test instrument was deployed for approximately four weeks at each site. ACT personnel worked with the instrument manufacturer to design an appropriate deployment arrangement on a buoy at each of the field test sites. The test instrument was moored such that the field reference water sample was collected no more than 0.5- m apart from the sampling inlet. The instrument was deployed at a fixed depth, approximately 1m below the water surface. A calibrated CTD package (SBE-26) 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 (accuracy = 0.002 ^oC) 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.

Prior to deployment, the instrument was set-up and calibrated by a manufacturer representative with assistance from ACT staff. Internal clocks were set to local time and synchronized against the time standard provided by www.time.gov. The instrument was programmed to record data as close to that of the reference sampling time as possible. Due to varying equilibration times and methods of averaging data, mismatches of up to 5-10 minutes between vendor instruments and collection of reference data certainly occurred. To check instrument functioning a pre-deployment tank-test was conducted before the instruments were moored in the field. To provide a qualitative estimate of bio-fouling during the field tests, photographs of the instrument and mooring rack were taken just prior to deployment and just after recovery.

The sampling frequency of reference samples was structured to distinguish changes in pCO_2 concentrations over hourly to weekly time scales. Twice each week, we conducted an intensive sampling event that consisted of 4 consecutive samples spaced at several hour 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 a 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.

Reference Standards and Analytical Procedures

Measured and reported quantities:

Carbon dioxide (CO_2) abundance in air and water is reported in a variety of units. In air, CO_2 ratios (xCO_2; e.g., ppm, µmol/mol, µatm/atm, ml/m^3) are often reported rather than actual CO_2 partial pressures (pCO_2; µatm). These units account for fluctuations in CO_2 that are

controlled by changes in ambient atmospheric pressure and humidity, however, physical, chemical and biological processes are controlled by pCO_2, not xCO_2. The reported xCO_2 data must be converted to pCO_2 by accounting for local pressure and humidity to compare with the pCO_2 of water. Water-sample pCO_2 is a thermodynamically-defined property, inherent to the water sample, independent of any headspace or atmospheric conditions and is given by:

$$pCO_2 = K_H \left[CO_{2,aq} \right]$$

where, the thermodynamic solubility constant K_H (units e.g. μatm•kg•μmol^{-1}) is defined by the temperature and salinity of the water sample, and $[CO_{2,aq}]$ is the concentration of dissolved CO_2 gas in the water sample. If a sample is properly equilibrated—e.g. gas-water exchange has gone to completion and the water sample is infinitesimally altered by that exchange, pCO_2 of a water sample is defined only by the properties of the water sample.

Confusion regarding pCO_2 arises from the fact that pCO_2 and xCO_2 are often similar in value, and most analysts calibrate their primary detectors with mixtures of known xCO_2 as opposed to pCO_2. Larger uncertainties can arise, however, from equilibrated headspace pressures that deviate significantly from atmospheric or differ from the actual water temperature, and from varying analytical approaches to removing water vapor from gas streams. Reported water-sample pCO_2 data must be accompanied by discussion of how headspace pressure and sample stream water vapor are handled quantitatively. In this report, reference values are reported as pCO_2 with dimensions of pressure and units of μatm, corrected to the *in situ* water temperature at the time of water sample collection.

Reference sample pCO_2 concentrations were determined in two ways: (1) direct measurements of pCO_2 on discrete water samples using a flow-through pCO_2 analyzer provided by Burke Hales (Oregon State University), hereafter termed Flow Analyzer; and (2) from pH, TA titrations performed on discrete water samples collected near the instruments.

Reference pCO_2 Measurements using Flow-through pCO_2 Analyzer:

The Flow Analyzer consisted of a NDIR detector (LICOR LI840), interfaced with a membrane-contactor equilibrator, following Hales et al. (2004). Water was pumped continuously at a rate of ~8 L min^{-1} from the sample reservoir (described below) through a 50 μm pre-filter, to the membrane contactor, and then to a thermo-salinograph (SeaBird SBE45), which provided the temperature of the water flowing through the contactor. Contactor headspace pressure was measured by adding a differential pressure to the atmospheric pressure recorded by the LI840. The differential pressure can be measured and/or calculated from flow-rates and plumbing configurations, and is always a small (~0.1%) contribution to the pressure correction. LI840 pressure readings were verified by comparison to local meteorological measurements of barometric pressure. Carrier gas was ambient air, delivered to a mass-flow controller upstream of the contactor, and the flow to the equilibrator was set at a constant 150 ml min^{-1}.

Detector xCO_2 (μmol/mol) was calibrated against standard gases supplied by three cylinders of known CO_2 mixing ratio, and applying a linear-regression based on these calibrations to the sensor data. Sensor data was corrected for drift between standardization sequences by linear interpolation versus time. These cylinders were gravimetrically prepared by Scott-Marrin Specialty Gases, California, with nominal mixing ratios of 100, 700, and 1300 ppm CO_2 in ultrapure air. Actual preparation mixtures were 100.2, 693, and 1303 ppm for the

Washington field tests and 100.0, 701, and 1301 ppm for the Hawaii tests. Previous calibration of gas mixtures prepared in this way in the Hales' and Takahashi's labs has shown that the preparation mixtures are usually accurate to within ~5 ppm. Calibrations were highly linear (r^2>0.9999) and average deviations between regression-predicted and actual concentrations were generally less than 2 ppm. Specifically, the ~700 ppm standard, which was closest in composition to the carrier gas equilibrated with the sample waters, was generally predicted by the regression to within 2 ppm of the actual value.

Analytical gas streams delivered from the equilibrator to the detector were not dried, and thus conserved the water vapor content of the equilibrator headspace. Calibrated xCO_2 measurements were converted to pCO_2 by multiplying by the absolute total pressure (including the contribution from water vapor) in the membrane-contactor. Raw data collection rates were 1 Hz, but these were reduced by means of a running centered polynomial to give smoothed data at 15-second intervals. Primary data were provided to ACT as pCO_2 at equilibrator temperature. The accuracy of pCO_2 measured in this way is estimated to be ~2 µatm, and this has been verified through a variety of inter-comparisons (Hales et al. 2004; Hales and Takahashi, in prep; Hales and Wanninkhof, unpubl. res.). In this case, where we relied on gravimetric preparation estimations of the standard gas CO_2 mixing ratios, the accuracy is likely to be worse by an amount equivalent to the uncertainty in the gas-standard mixing ratio (~5 ppm), for a total uncertainty near 7 µatm. ACT personnel corrected measurements to the *in situ* temperature using the temperature dependence of Takahashi et.al. (1993).

The system performed well throughout the Washington tests, and through the first 2 weeks of the Hawaii tests. At that point the system was flooded twice, once to a small extent by condensation on the positive pressure side of the air recirculation pump, and once more extensively with seawater due to operator error on 10/25/2010. Following the second flooding event, the IR detector needed to be recalibrated because the response was off-scale. Following calibration, the system never returned to the levels of performance it had shown prior to flooding. There appeared to be issues with slower response as well as with poorer statistics associated with the calibration procedures. Reference sample data measured by the Flow Analyzer after 10/25/2010 were removed from the analysis.

Reference pCO_2 Measurement using pH and TA measurements:

Water samples were collected from the sampling coolers and times noted. In Washington this occurred during filling of the cooler; while in Hawaii water samples were collected after transport back to the laboratory, always within 15 minutes of collection. Water samples were collected in glass BOD bottles, stopped and immediately transported back to the laboratory for analysis. In Washington, we discovered that fresh – live – water samples showed more noise in the spectrometer, so the water samples were poisoned with mercuric chloride and measured within 12 hours. In Hawaii, water samples were measured for pH within an hour of collection. The measurement procedure was as follows: pH and temperature of the sample were measured 4 times using the indicator dye meta-cresol purple and a Eutechnics (Model 4400) digital thermometer, accurate to 0.02 ^{o}C. (Dickson et.al. 2007, The SOP Guide). Every several days pH and temperature were also measured on two Dickson Certified Reference Material (Batch #82 and #96) as well as a Dickson seawater buffer (provided by A. Dickson personal communication). A linear regression was created to correct the dye-pH measurements to the pH's of the above standards. Thus a single point pH-dye and temperature corresponds with a

single pH, calculated from either temperature correction of the buffer or pH calculated from known TA and DIC, using CO_2Sys (dissociation constants from Millero 2006). Total alkalinity was measured using the bromo-cresol green dye method (Yao and Byrne 1998; Dickson et al. 2007, The SOP guide). TA was measured 4 times; if one sample was an outlier, the remaining 3 were averaged. Normality of acid was back-calculated to fit with one of the CRM, checked daily. "Pooled" standard deviation for TA is 1.9 µequiv/kg (n=87). CO_2Sys (Perriot et.al 2006) was used to calculate in-situ pCO_2. Inputs were mean TA (as above), 3-4 pH with 3-4 corresponding temperatures, know salinity from the Flow Analyzer and converting to field temperatures (to within 0.005 ^oC). This approach to data processing gave 3-4 values of pCO_2 for each water sample. The pooled standard deviation of pCO_2 is 1.9 µatm (87 sets of 3-4 values). Thus the precision of the water sampling was less than 2 µatm. The standard deviation of pCO_2 was not correlated to the absolute value of pCO_2. The predicted uncertainty of the pH correction, however, gave an error estimate of 0.005 pH units (consistent with Dickson 2010), or an uncertainty in the accuracy of pCO_2 of about 8 µatm. We also note that one standard deviation in the K_1 dissociation constant corresponds to 5 µatm at 350 µatm and 20 µatm at 1400 µatm (Millero et al 2006), thus the standard deviation of values can be considered to be about 5-10 µatm for the measured range in pCO_2. Based on the above discussion, we conclude that the uncertainty in the reference measurements is estimated to be 8 µatm.

Details for Washington Hood Canal Field Test:

The IR detector of the Flow Analyzer was calibrated in the laboratory immediately prior to installing it on a small research vessel. Onboard the research vessel, the equilibration and thermo-salinograph units were mounted in a cooler to minimize thermal effects on the system. Another 20-liter cooler was brought to thermal equilibrium with seawater by repeated flushing for 10 minutes prior to water sampling. Water was then pumped (10 liter per minute) from near the inlets of the pCO_2 instruments mounted on the buoy (0.6-1.0 m deep) through a ¾ inch garden hose to the cooler.

The cooler acted as a reservoir with a running 2-minute integrated water sample. The integrated water sample was then drawn through the Flow Analyzer over a 20-minute period, 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 cooler after at least 20 minutes of continuous measurements, times noted. Water samples were processed for pH and TA (see below). An RBR-TR-1060 sensor was placed in the cooler to monitor all temperatures. The IR detector of the Flow Analyzer was re-calibrated again in the laboratory after returning from field measurements.

Details for Hawaii Field Test:

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 a 150 liter cooler was soaked in surface water to bring it to thermal equilibrium, seawater was pumped from near the inlets of the instruments (0.5 m deep) into the cooler giving an 11-minute integrated water sample. The lid of the cooler was tightly sealed to reduce gas transfer and heat exchange. The cooler, containing 150 liters of sample water, was immediately transported back to Coconut Island, where the water was immediately pumped through the flow-

through pCO_2 analyzer. Water was pumped in the analyzer within 15 minutes of collection. Water was also directly sampled from the cooler for water chemistry. These water samples were taken directly to the laboratory and measured for pH and TA. Prior to the field test, we conducted comparison tests to ensure this procedure gave accurate values. Water samples at Washington thus included some real temporal variability in the conditions near the mooring, while those at Hawaii included some averaging over the time-scale of filling the cooler. Water temperatures at the time of collection were carefully recorded using RBR temperature recorders (TR-1060: accuracy =0.002 ^{o}C).

Final data corrections and reduction:

ACT personnel performed further reductions and corrections to these data. The 15-second resolution data were averaged over 5-minute intervals, bracketing the target sample times. ACT personnel corrected measurements to the in situ temperature using the temperature dependence of Takahashi et.al. (1993). Assuming uncertainty in the temperature correction of ~ 0.1°C, this term could contribute an additional ~ 0.5% uncertainty, or as much as 3 μatm for the Hawaii tests.

Quality Assurance and Control

All reference samples were cataloged individually with ancillary field collection data. For samples transported, chain-of-custody (COC) protocols were practiced, 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.

Field and lab audits were performed by a Quality Assurance Manager, who did not have responsibility for conduct of the demonstration. The audits were conducted to ensure the demonstration project was performed in accordance with test protocols and the quality assurance plan. As part of these audits, the Quality Assurance Manager reviewed the reference methods used, compared actual test procedures to those specified or referenced in the test/QA plan, and reviewed data acquisition and handling procedures.

RESULTS OF MOORED FIELD TESTS

Moored Deployment in Hood Canal, Washington

The mooring test in Washington took place in Hood Canal on the Twanoh Buoy located at 47° 22.5' N, 123° .5' W in a depth of 35 meters (Fig.1). The deployed occurred from August 26 to September 18, 2009. The instruments were attached to the outer rim of the buoy's surface ballast ring so they would not interfere with the buoy's vertical profiling system; the intakes of the instruments were 0.75 meters below the water surface. Tides in Hood Canal are semi-diurnal with a summer mean tidal range of approximately 2.4 meters.



Hood Canal Deployment Site Location


Twanoh Buoy Field Site

Figure 1. Washington –Hood Canal: Site map and photo of the field test site located in Hood Canal north of Union, Washington. The PMEL-MAPCO_2 instrument is in the buoy and vendor instruments were mounted about 1 meter under the surface. (http://orca.ocean.washington.edu/mooringDesign.html)

Test Results

At Twanoh buoy, Hood Canal, temperature varied from 11.09 to 19.62 ^oC, with strong gradients and temperature changes that could exceed 5 ^oC in several hours (Fig. 2a). Salinity typically varied inversely with temperature during these rapid excursions and ranged from 24.3 – 29.1 during the deployment (Fig. 2b). Measured pCO_2 in discrete reference samples (n=42) varied from 334 to 488 while the continuous, 30 minute measurements from the SAMI-CO_2 (plotted hourly; n=535) varied from about 340 to 900 µatm (Fig. 3a). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the Flow Analyzer reference measurements were +23 ± 13 µatm (n=31; SAMI-CO_2 - Flow Analyzer) (Fig. 3b). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the pCO_2Sys reference measurements were +18 ± 40 µatm (n=42; SAMI-CO_2 - pCO_2Sys).

Environmental Variability

Variability or uncertainty can occur from taking a seawater sample from a different patch of water from that the instrument measured. To minimize this effect, instruments were placed as close as possible on the mounting ring, within 1 m, and seawater was sampled adjacent to the intakes of the instruments. Environmental uncertainty due to patchiness can be estimated by the temperature difference between upper and lower RBR thermistors. The mean temperature difference was 0.45 ^{o}C and the standard deviation of that mean difference was 0.69 ^{o}C. These temperature differences correspond to pCO_2 differences of about 10-14 µatm. However the maximum temperature difference was 4.4 ^{o}C and corresponds to 90 µatm. Oddly, however, the larger deviations were not associated with the large temperature differences. Thus we suggest that most of the environmental variability is constrained to the 10-15 µatm.

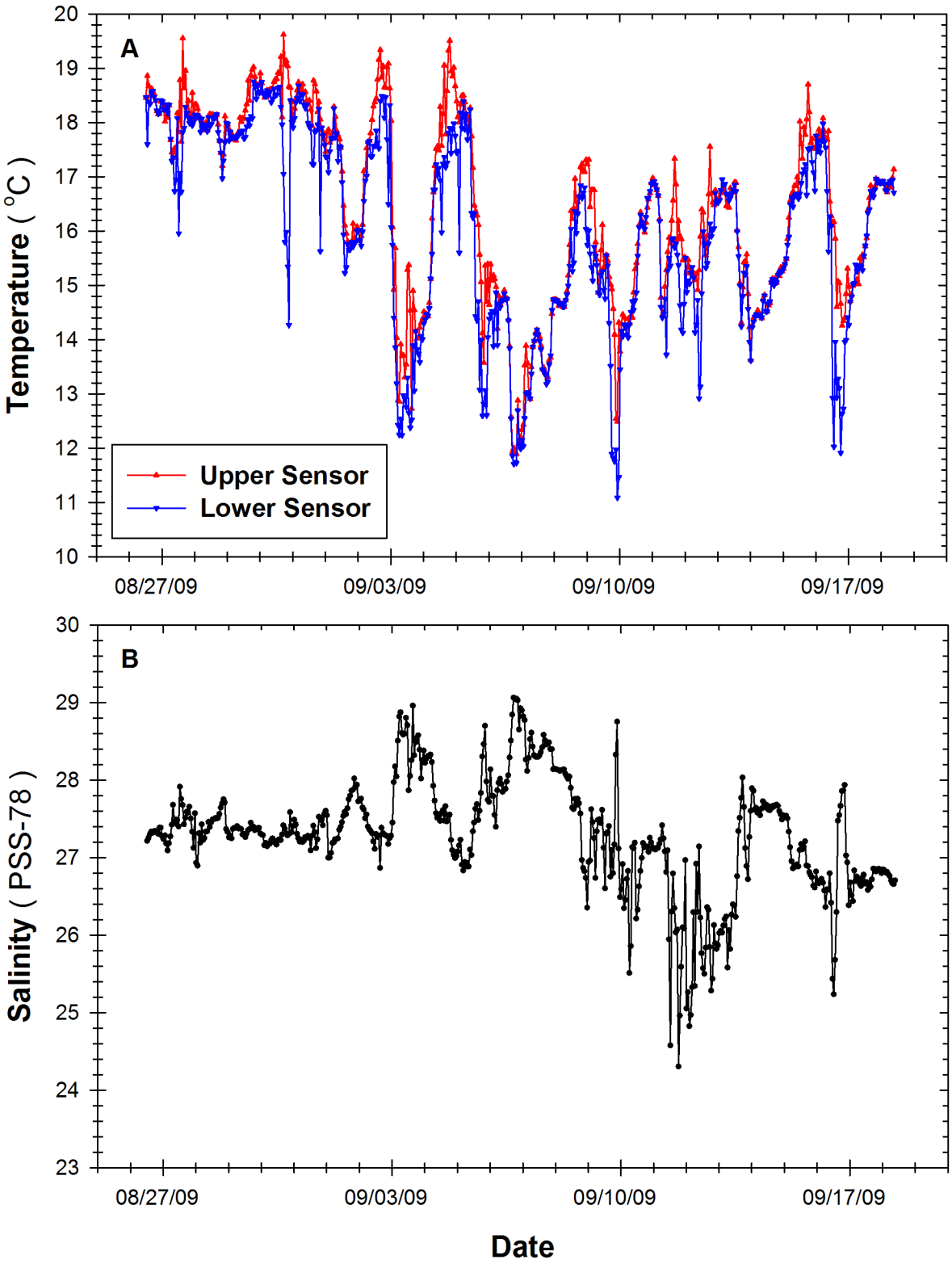


Figure 2. Environmental conditions at the mooring used for pCO_2 instrument deployments in Hood Canal, WA. Panel A: Water temperature from two RBR TR-1060 temperature loggers positioned above and below test instruments. Panel B: Salinity of water recorded by a SeaBird Electronics SBE 26 with 4M conductivity cell. All data sub-sampled at 1 h intervals corresponding to instrument sampling events.

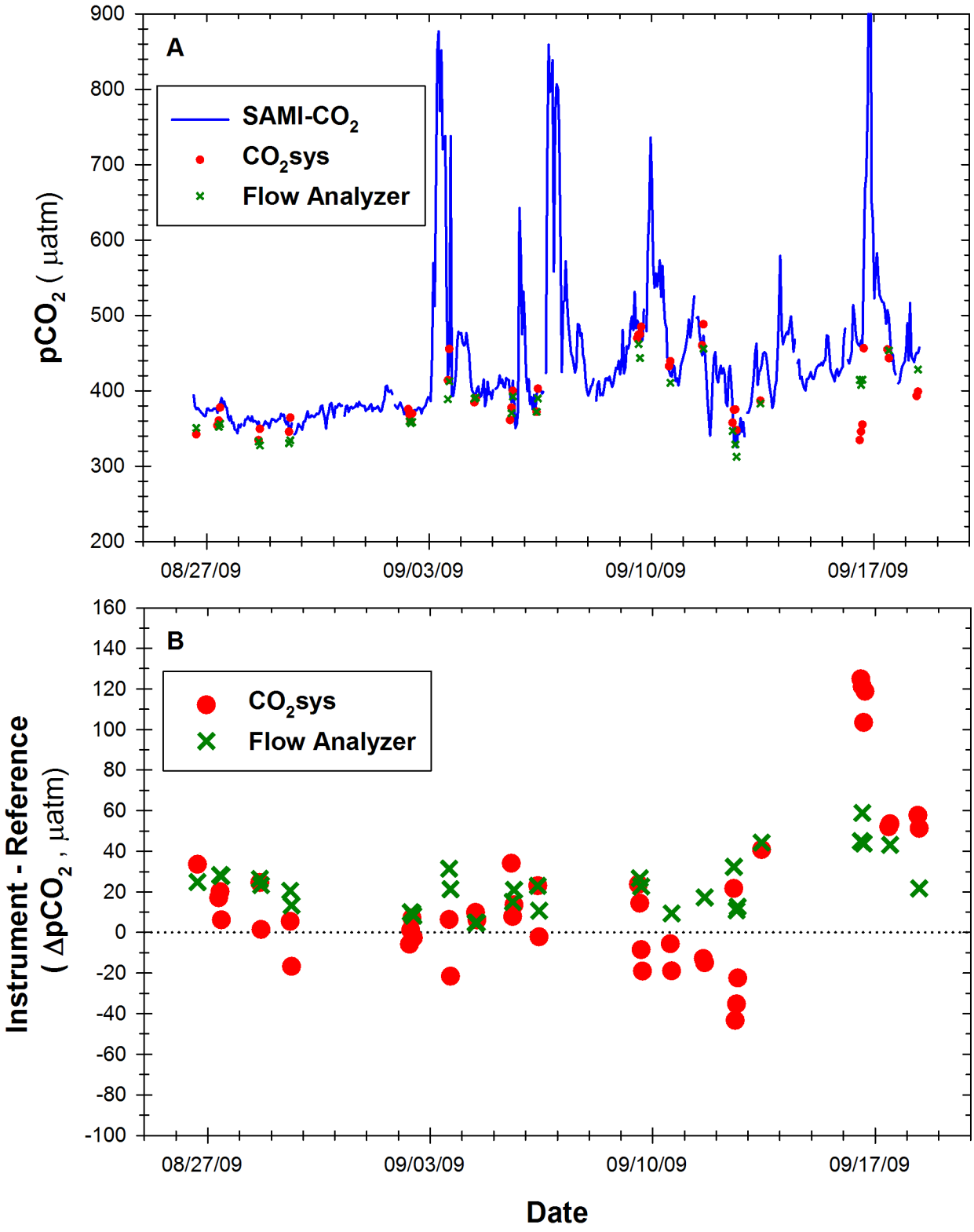


Figure 3. Field data from the Sunburst SAMI-CO_2 pCO_2 instrument during deployment in Hood Canal, WA. Panel A: Time series of instrument values (blue lines) with overlaid values from two reference samples, one from a Flow Analyzer (green X) and the other based on calculations from pH and total alkalinity measurement using CO_2Sys (red dot). Panel B: The difference between instrument values and reference values. Dotted line represents perfect agreement or zero difference. Reference data symbol size is scaled to 8 µatm, corresponding to the uncertainty in the reference, see text for explanation.

Instrument Photographs

Before and after photos were taken of the instrument to examine the extent and possible impacts of bio-fouling (Fig. 4).



Prior to Deployment (Close-up)



Prior to Deployment (Full View)



After Deployment (Close-up)

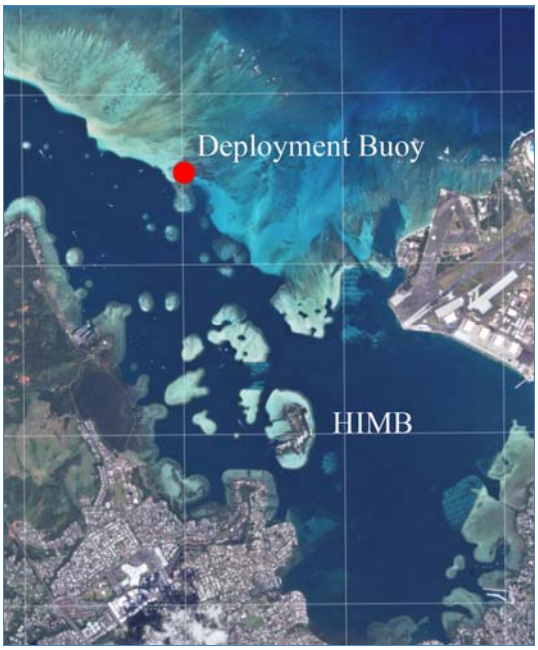


After Deployment (Full View)

Figure 4. Sunburst SAMI-CO_2 photos from Hood Canal, WA test site before and after deployment.

Moored Deployment off Coconut Island in Kaneohe Bay, Hawaii

The mooring in Kaneohe Bay was located at 21.46 ^{o}N, 157.80 ^{o}W in the back-reef region of the Kaneohe Bay barrier reef offshore of Coconut Island in a depth of 3 meters (Fig. 5). The deployment occurred from October 16 to November 10, 2009. Kaneohe Bay, located on the eastern side of Oahu, Hawaii, is a complex estuarine system with a large barrier coral reef, numerous patch reefs, fringing reefs, and several riverine inputs. Tides in Kaneohe Bay are semi-diurnal with mean tidal amplitude of approximately 68 cm day^{-1}.



Deployment Site in Kaneohe Bay, Hawaii



Crimp II Deployment Buoy

Figure 5. Hawaii – Kanoehe Bay: Site map and photo of the field test site located in Kaneohe Bay, northeast side of Oahu, Hawaii. The PMEL-MAPCO_2 instrument is on the buoy and vendor instruments were mounted about 1 meter under the surface. (http://www.pmel.noaa.gov/co2/coastal/HI/)

Test Results

At NOAA Crimp 2 buoy, Kaneohe Bay, temperature ranged from 23.24 to 28.27 ^{o}C during the deployment, with a consistent diurnal pattern and an overall decline starting mid-way through the deployment due to seasonal shifts in the trade winds (Fig. 6a). Salinity also varied diurnally but with occasional sharp excursions at hourly scales (Fig. 6b), and ranged from 34.1 to 35.2 during the deployment. Measured pCO_2 from reference samples (n=45) varied from 314 to 608 µatm, while the continuous, 30 minute measurements from the SAMI-CO_2 (plotted hourly; n=618) varied from about 320 to 900 µatm, demonstrating a more complete representation of the variability in the ecosystem (Fig. 7a). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the Flow Analyzer measurements were +28 ± 9 µatm (n=13; SAMI-CO_2 - Flow Analyzer) (Fig. 7b). The mean and standard deviation of the difference for individual SAMI-CO_2 determinations and the pCO_2Sys reference measurements were +40 ± 13 µatm (n=45; SAMI-CO_2 - pCO_2Sys).

Environmental Variability

Variability or uncertainty can occur from taking a seawater sample from a different patch of water from that the instrument measured. To minimize this effect, instruments were placed as close as possible on the mounting ring, within 1 m, and seawater was sampled adjacent to the intakes of the instruments. Environmental uncertainty due to patchiness can be estimated by the temperature difference between upper and lower RBR thermistors. The mean temperature difference was 0.000 ^{o}C and the standard deviation of that mean difference was 0.047 ^{o}C. These temperature differences correspond to pCO_2 differences of about 1 µatm. The maximum temperature difference was 0.6 ^{o}C and corresponds to 12 µatm. Oddly, however, the larger deviations were not associated with the large temperature differences. Thus we suggest that most of the environmental uncertainty is constrained to 2 µatm.

Reliability

Both test instruments deployed on the moorings functioned throughout the month long test periods, and 100 percent of expected data were retrieved. The time-series provided by the instruments revealed diel patterns in pCO_2 and captured a significantly greater dynamic range and temporal resolution then could be obtained from discrete reference samples. There were no changes in the differences between instrument and reference measurements during either test, indicating that biofouling and instrument drift did not affect measurement performance over the duration of the test.

TECHNICAL SYSTEM AUDITS

An independent Quality Assurance Manager conducted technical systems audits (TSA) at the Hood Canal site during August 27-28 and at the Coconut Island / Kaneohe Bay site during October 15-17. A TSA is an on-site review and examination of the field and laboratory procedures to ensure that the demonstration was being conducted in accordance with the test protocols and ACT quality assurance / quality control procedures. As part of the TSA, field deployment of the test instruments and sample collection and handling were compared to those specified in the protocols, and data acquisition and handling procedures, as well as the reference methods, were reviewed.

There were no adverse findings at either of the test sites. There were several modifications in the field deployment and sampling methods due to site conditions, which did not affect the overall test. These were documented by ACT test personnel and included as an amendment to the test protocols in accordance with ACT QA/QC procedures

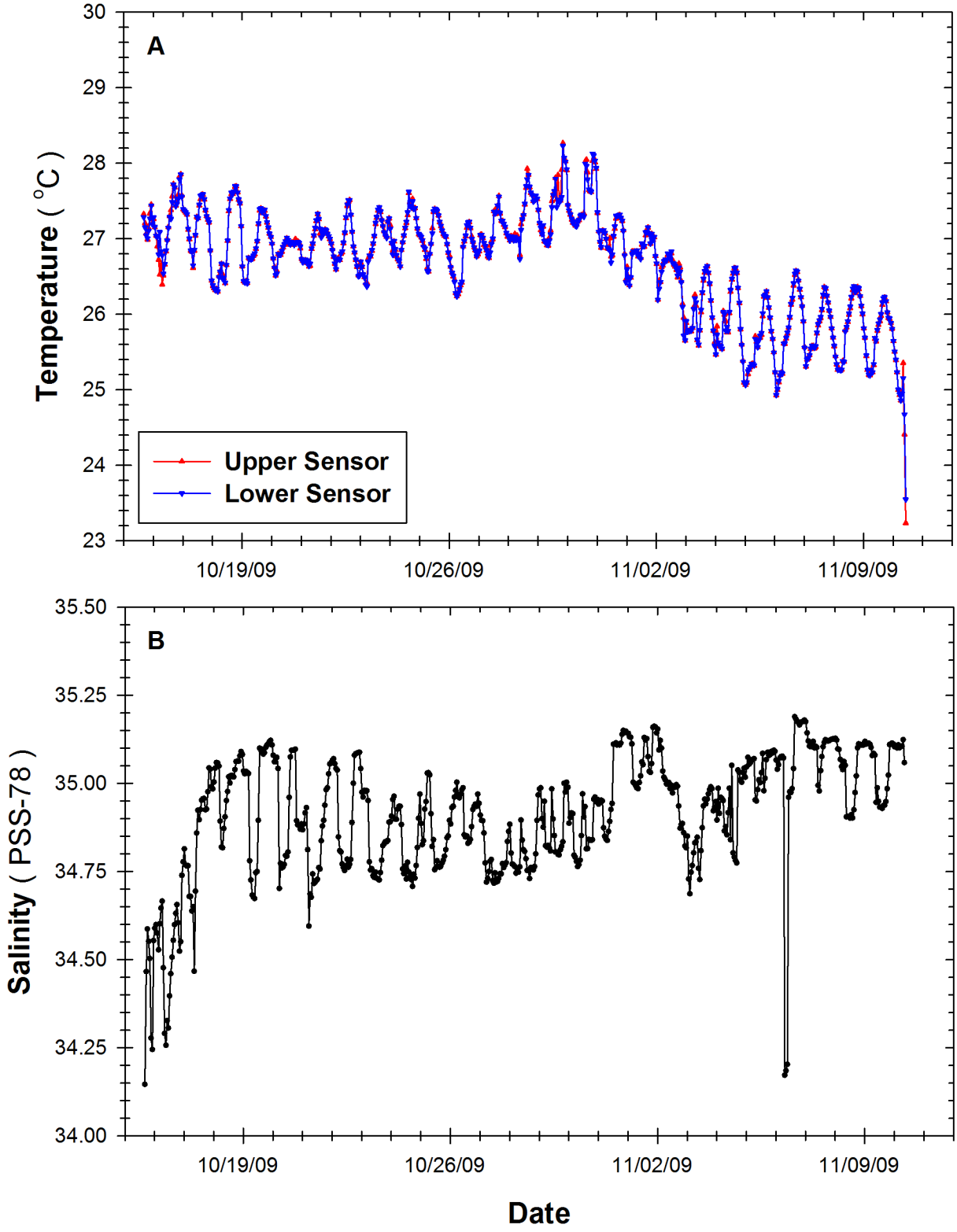


Figure 6. Environmental conditions at the mooring used for pCO_2 instrument deployments in Kaneohe Bay, HI. Panel A: Water temperature from two RBR TR-1060 temperature loggers positioned above and below test instruments. Panel B: Salinity of water recorded by a SeaBird Electronics SBE 26 with 4M conductivity cell. All data sub-sampled at 1 h intervals corresponding to instrument sampling events.

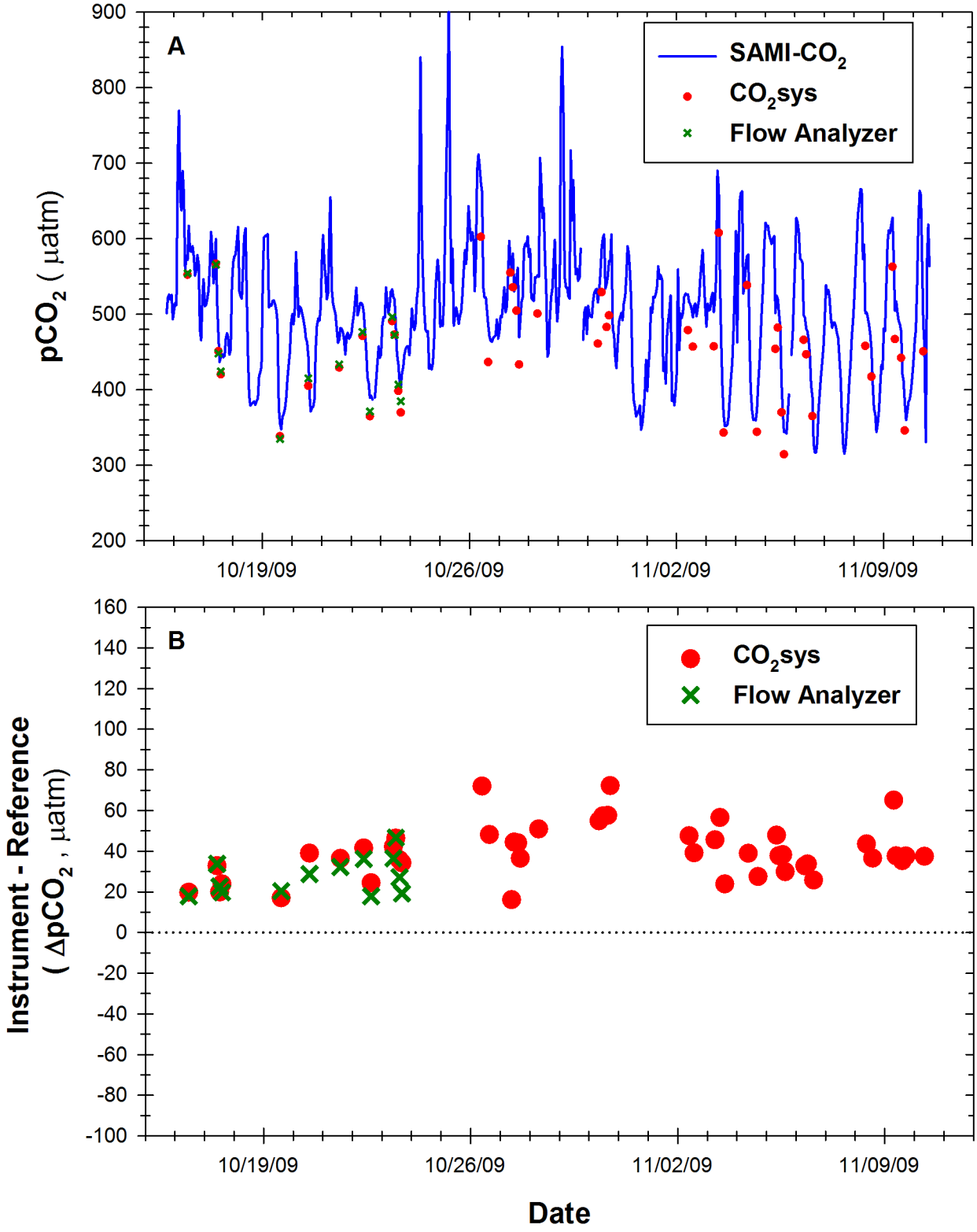


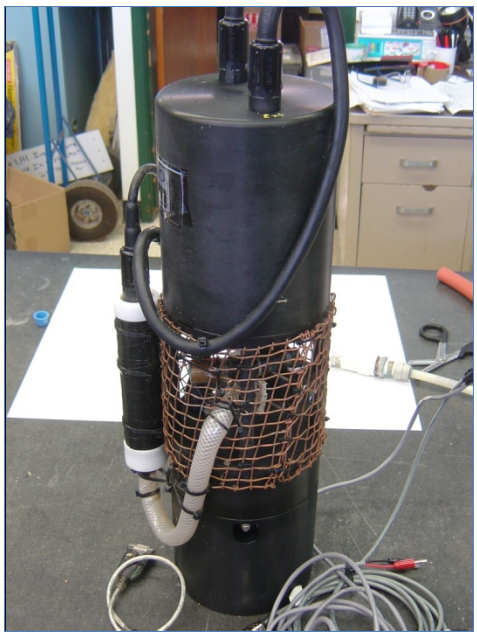
Figure 7. Field data from of the Sunburst SAMI-CO_2 pCO_2 instrument during deployment in Kaneohe Bay, HI. Panel A: Time series of instrument values (blue lines) with overlaid values from two reference samples, one from a Flow Analyzer (green X) and the other based on calculations from pH and total alkalinity measurement using CO_2Sys (red dot). Panel B: The difference between instrument values and reference values. Dotted line represents perfect agreement or zero difference. Reference data symbol size is scaled to 8 µatm, corresponding to the uncertainty in the reference, see text for explanation.

Instrument Photographs

Before and after photos were taken of the instrument to examine the extent and possible impacts of bio-fouling (Fig. 8).



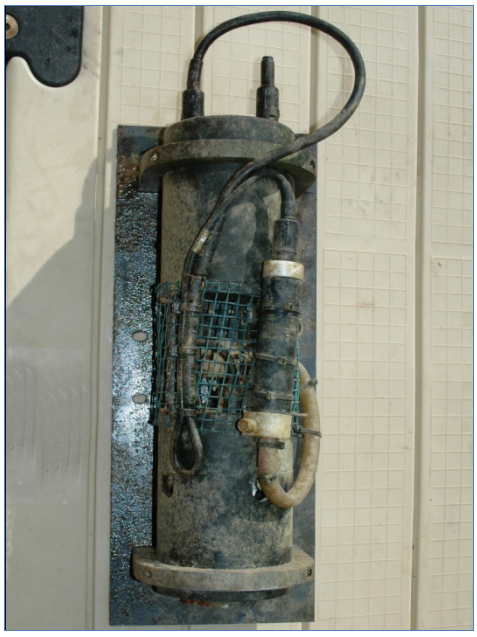
Prior to Deployment (Close-up)



Prior to Deployment (Full View)



After Deployment (Close-up)



After Deployment (Full View)

Figure 8. Sunburst SAMI-CO_2 photos from Kaneohe Bay, Hawaii test site before and after deployment.

ACKNOWLEDGEMENTS

ACT acknowledges the contribution of the external Technical Advisory Committee who helped develop the Demonstration protocols and reviewed this report. Committee members included: Rik Wanninkhof (NOAA-AOML), Eric DeCarlo, (University of Hawaii), Arne Kortzinger (Leibniz Institute of Marine Sciences), Alan Devol (University of Washington), Jan Newton (University of Washington) and Burke Hales (Oregon State University). ACT also thanks Dan Hannafious from the Hood Canal Salmon Enhancement Group for their generous support with facilities, boats and personnel during the Washington field test.

September 15, 2010

Date

Approved By: Dr. Mario Tamburri
ACT Executive Director

September 15, 2010

Date

Approved By: Dr. Tom Johengen
ACT Chief Scientist

September 15, 2010

Date

Approved By: Dr. Earle Buckley
Quality Assurance Supervisor

REFERENCES

Dickson A.G., C.L. Sabine, J.R. Christian (2007). Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.

Dickson A.G., J.D. Afghan and G.C. Anderson (2003). Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity. *Marine Chemistry* 80:185-197

Dickson, A.G. (2010). The carbon dioxide system in seawater: equilibrium chemistry and measurements. In *Guide to best practices for ocean acidification research and data reporting.* Riebesell, U., Fabry, V. J., Hansson, L., & Gattuso, J.-P. (Eds), Chapter 1, pp. 17–40, EUR 24328 EN, European Commission, Brussels, Belgium.

Hales, B. and T. Takahashi (2004). High-resolution biogeochemical investigation of the Ross Sea, Antarctica, during the aesops (U.S. JGOFS) program. *Global Biogeochemical Cycles* **18**, GB3006, doi:10.1029/2003GB002165

Hales B., D. Chipman and T. Takahashi (2004). High-frequency measurements of partial pressure and total concentration of carbon dioxide in seawater using microporous hydrophobic membrane contactors. Limnol. Oceanogr. Methods 2, 356-364.

Millero F.T., T.B. Graham, F. Huang, H. Bustos-Serrano and D. Pierrot (2006). Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* 100:80-94.

Pierrot, D. E. Lewis, and D.W.R. Wallace (2006). MS Excel program developed for CO_2 system calculations. ORLN/CDIAC-105, Carbon dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy. Oak Ridge, TN.

Takahashi et.al. (2009). Climatological mean and decadal change in surface pCO_2 , and net sea-air CO_2 flux over the global oceans. *Deep-Sea Research II* doi:101016/j.dsr2.2008.12.009

Takahashi, T., J. Olafsson, J. Goddard, D. Chipman, and S. Sutherland (1993). Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. Global Biogeochemical Cycles, 7, 843-878.

Yao W. and R.H. Byrne (1998). Simplified seawater alkalinity analysis: use of linear array spectrometers. *Deep-sea Research I* 45:1383-1392.

APPENDIX 1: COMPANY RESPONSE LETTER TO SUBMITTED pCO2 DEMONSTRATION REPORT

Sunburst Sensors Response
September 14, 2010

General comments: We thank the ACT personnel for their hard work in performing this challenging pCO_2 sensor demonstration project. The study of marine pCO_2 and ocean carbonate chemistry is critical to more accurately predict global warming and ocean acidification. This ACT demonstration project benefits researchers by providing them with an understanding of the available tools necessary to achieve these goals. The study was also timely from our point of view, with our new SAMI-CO_2 design having just been completed, and with other pCO_2 sensors becoming commercially-available.

The tests were conducted in highly productive coastal and estuarine environments with large short-term changes in pCO_2, temperature and salinity. Collecting water for the reference samples is difficult under these conditions because of spatial (both vertical and horizontal) and temporal mismatches between the sample and in situ instruments. The sample quality can also be altered by exchange with air and, because pCO_2 is temperature dependent, the sample measurement temperature requires correction to the in situ temperature. Considering all of these uncertainties, we commend the ACT personnel for collecting an excellent reference data set. We do have some specific concerns, however, that are addressed below.

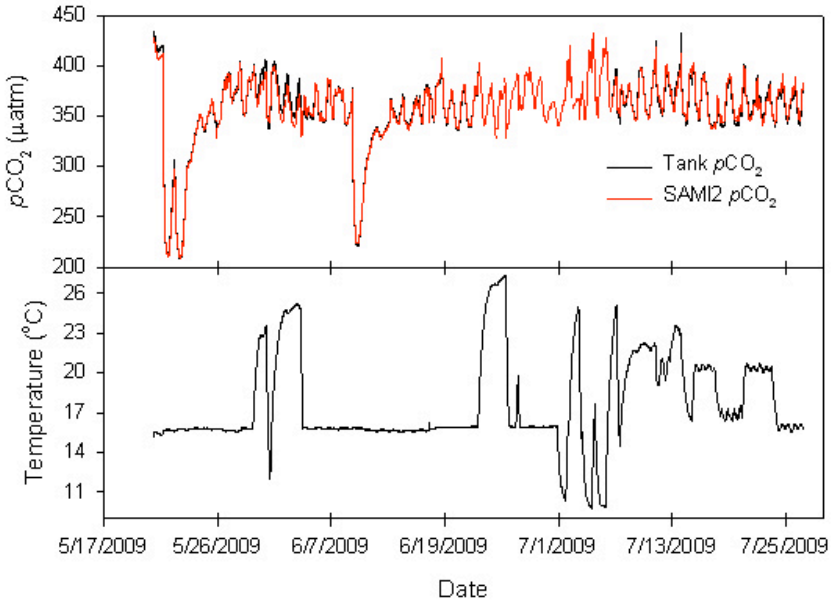


Figure 1: SAMI-CO_2 tank data tracked against calibrated Licor 840 over almost 3 month period.

In both the Hood Canal and Kaneohe Bay testing, we used the first non-prototype unit of the new SAMI-CO_2 design. Overall, we are very pleased with the performance of the new SAMI-CO_2 sensor. The SAMI recorded pCO_2 every 30 minutes during the tests with no data lost and with no detectable drift due to biofouling or other sources (the data gaps in Figures 3 and 7 are periods when optical blanks were measured). It is important to note that the SAMIs are calibrated at our facility in Missoula, Montana (USA) and then sent to the field sites.

In this case, the SAMI was calibrated on 5/24/09, after which it was run in a test tank for several months (Figure 1). The unit was not re-calibrated prior to being transported to the Hood Canal field site on 8/23/09. The unit was returned 9/28/09 and then sent to the Hawaii field site on 10/9/09. Because of the potential for extreme biofouling, the instrument sensor membrane was enclosed in a flow chamber. For each measurement, the cell was flushed for 10 seconds using an in

situ pump with copper inlet and outlet tubing (see Figures 4 and 8). The SAMI measurement therefore represents the pCO_2 integrated over a 10 second interval.

Hood Canal tests: Considering the mean differences and the large standard deviation between the two reference methods shown in Figure 3, there is no significant difference between the SAMI and the reference methods for this field test. While the mean is positive (SAMI-reference) for both methods, the large outliers on 9/16/2009 (Figure 3) biased the mean error, particularly for the error between the SAMI and CO_2sys reference method (red dots). Removal of these points from the calculation reduces the mean SAMI and CO2sys difference from +18 µatm to +8 µatm. The large errors were caused by the shallow stratification during this period (Figure 2). The standard deviation is much larger than the SAMI precision but is not surprising considering the measurement and sampling uncertainties as discussed previously in this report.

Kaneohe Bay tests: Results from this field test show no detectable drift but have a significant positive bias (SAMI-reference). Although we cannot establish with certainty the source of the offset, there are two primary possibilities. First, the different sampling periods for the SAMI (10 seconds) and reference (> 10 minutes), could lead to either positive or negative biases. The pCO_2 in Kaneohe Bay was changing by >1 µatm/minute for ~20% of the time (Figure 7) suggesting that temporal sampling errors could be significant. The bias could also be caused by an error in calibration for the high pCO_2 levels found in Kaneohe Bay. The SAMI was calibrated for Hood Canal at 15 °C over the range 240-400 µatm and, because of time constraints, we did not recalibrate prior to shipment to Hawaii. Because of the non-linearity in the SAMI response, systematic errors can occur if the response is extrapolated far beyond the calibration range, as was the case for the Kaneohe Bay tests.

Summary: These field tests help establish the reliability of the new SAMI-CO_2 sensor design. The measures taken to minimize biofouling were very effective. Accuracy during the second deployment was not within our specifications. In hindsight, given the large temperature and pCO_2 differences between sites, we should have requested more time to allow recalibration of the instrument prior to this deployment. We recommend SAMI data be compared to field measurements when possible. The data sets collected in this study do point out the value of long term semi-continuous measurements. A great deal of the short-term changes were missed by the reference methods in Hood Canal and Kaneohe Bay. The data sets from other participants confirm this larger range of variability compared to the reference data. We look forward to working with ACT on future demonstration projects.

Sincerely,

James Beck
President

Mike DeGrandpre
Director, Research and Development