



PERFORMANCE DEMONSTRATION STATEMENT

PMEL MAPCO₂/Battelle Seaology pCO₂ Monitoring System

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|------------------------------|--|
| TECHNOLOGY TYPE: | Direct measurement of pCO ₂ in natural water using gas equilibration and infrared detection of a gas stream |
| APPLICATION: | <i>In-situ</i> 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. |

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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 pCO₂ 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 two MAPCO₂ systems operated and maintained by the NOAA Pacific Marine Environmental Laboratory, Seattle, WA.

Briefly, test instruments were mounted on surface moorings in a temperate stratified estuary (Twano 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 pCO₂. Water samples were collected to determine pH and Total Alkalinity (TA) for calculation of pCO₂ (CO₂Sys; Pierrot et.al. 2006) and direct measurements of pCO₂ using a flow-through pCO₂ analyzer (Oregon State University; gas equilibration and infrared gas detection). In situ pCO₂ 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 Twano buoy, Hood Canal, temperature varied from 11.09 to 19.62 °C and salinity varied from 24.3 to 29.1 over the deployment. Measured pCO₂ values of reference samples varied from 334 to 488 μatm while the hourly measured of the MAPCO₂ system varied from 325 to 725 μatm providing a more complete assessment of the variability in the ecosystem. The mean and standard deviation of the difference for individual MAPCO₂ determinations and the Flow Analyzer reference measurements were $-9 \pm 8 \mu\text{atm}$ (n=31; MAPCO₂ - Flow Analyzer). The mean and standard deviation of the difference for individual MAPCO₂ determinations and the pCO₂Sys reference measurements were $-12 \pm 30 \mu\text{atm}$ (n=42; MAPCO₂ - pCO₂Sys).

At NOAA Crimp 2 buoy, Kaneohe Bay, temperature varied from 23.24 to 28.27 °C and salinity varied from 34.1 to 35.2 over the deployment. Measured pCO₂ values of reference samples varied from 314 to 608 μatm, while the hourly MAPCO₂ measurements varied from 300 to 800 μatm, again capturing more of the full variability in the ecosystem. The mean and standard deviation of the difference for individual MAPCO₂ determinations and the Flow Analyzer measurements were $-3 \pm 9 \mu\text{atm}$ (n=13; MAPCO₂ - Flow Analyzer). The mean and standard deviation of the difference for individual MAPCO₂ determinations and the pCO₂Sys reference measurements were $3 \pm 9 \mu\text{atm}$ (n=45; MAPCO₂ - pCO₂Sys).

Both of the instrument systems on the moorings functioned throughout the month long test period. At Washington, 100 percent of expected data were retrieved, while at Hawaii two individual sample points were not retrieved out of the more than 620 values reported for the time-series. The extensive time-series provided by the MAPCO₂ at both test sites revealed diel patterns in pCO₂ 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, pCO₂, TA and TCO₂*, Honolulu, Hawaii, February 2005, was that ACT should conduct a “demonstration project” to evaluate pCO₂ sensors. Workshop participants concluded that pCO₂ 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 pCO₂ 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 MAPCO₂ instruments in place and experience significant changes in temperature, salinity, photosynthesis, respiration, calcification, etc. that would result in significant variation in pCO₂ 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 pCO₂ from high rates of photosynthesis, respiration and calcification.

There are three important reasons for measuring pCO₂ continuously from coastal moorings: first, to evaluate whether coastal areas are functioning as a source or sink of atmospheric CO₂. 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 CO₂ to the atmosphere. Furthermore, coastal areas are expected to be vulnerable to climate change, and this potential impact has direct consequence on managing CO₂ as a pollutant in the 21st century. Near-continuous measurements of pCO₂ 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 pCO₂ measurements in conjunction with direct measurements of one other parameter of the marine CO₂ 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 pCO₂ 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 pCO₂.

The basic objectives of this performance demonstration were: (1) to highlight the potential capabilities of *in situ* pCO₂ 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

Working with the Monterey Bay Aquarium Research Institute (MBARI), NOAA's Pacific Marine Environmental Laboratory (PMEL) researchers have developed an autonomous pCO₂ system that uses a Licor-820 non-dispersive infrared detector together with a calibration gas to make pCO₂ measurements in surface seawater and atmosphere that are traceable back to World Meteorological Organization (WMO) standards. The *in situ* calibration system guarantees data integrity and comparability between instruments. In operation since 2003, PMEL currently maintains pCO₂ systems at 22 mooring locations around the globe. A modular design allows the pCO₂ system to operate in a variety of surface buoy designs. In 2008-09 the CO₂ sensor technology was transferred to Battelle Memorial Institute to be manufactured and sold commercially. The two units tested for the ACT demonstration, one in Washington and a different one in Hawaii, were both manufactured at PMEL but are identical in form and function to the systems produced by Battelle.

The standard configuration of the CO₂ sensor system includes three separate watertight cases containing the electronics, a reference gas and a D-Cell battery pack. The system also includes a bubble-type equilibrator and an atmospheric inlet device (air block). The electronics case (tube diameter 7.4", height with connectors 42", weight 39 pounds) contains the detector, gas handling systems and computer control. The data collected by the system are recorded internally on a compact flash card, but an optional component included in both of the systems tested was an Iridium satellite data transmission component that allows remote operation of the system and automatically sends data and diagnostic information back to the laboratory once per day. The reference gas case (tube diameter 8.6", height with connectors 42", weight 52 pounds) contains a Luxfer aluminum N60 type gas cylinder filled with calibrated CO₂ in air at a nominal pressure of 2000-psi. Our gas mixtures are filled and calibrated at the WMO central calibration laboratory at NOAA Earth Systems Research Laboratory in Boulder Colorado. With each sampling sequence the NDIR undergoes a two point calibration with a zero CO₂ gas (air with the CO₂ stripped by soda lime) and a high CO₂ standard span gas (typically around 500 ppm). The battery case (tube diameter 7.4", height with connectors 36", weight 72 pounds including batteries for satellite transmissions) produces a nominal voltage of 10-V (7-V to 14.5-V) with 2.43-kWh (approx 243-A-hr) for system operation. The transmitter power source is nominally 9-V (8.5-V to 9.0-V) with 252-Wh. The system is nominally designed to take readings every 3 hours with daily data transmissions for 400 days, but we have had systems operate continuously in the field for well over 1.5 years.

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

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 pCO₂ 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 °C) 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 pCO₂ 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 pCO₂ 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 (CO₂) abundance in air and water is reported in a variety of units. In air, CO₂ ratios (xCO₂; e.g., ppm, μmol/mol, μatm/atm, ml/m³) are often reported rather than actual CO₂ partial pressures (pCO₂; μatm). These units account for fluctuations in CO₂ that are controlled by changes in ambient atmospheric pressure and humidity, however, physical, chemical and biological processes are controlled by pCO₂, not xCO₂. The reported xCO₂ data must be converted to pCO₂ by accounting for local pressure and humidity to compare with the pCO₂ of water. Water-sample pCO₂ is a thermodynamically-defined property, inherent to the water sample, independent of any headspace or atmospheric conditions and is given by:

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

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 CO₂ 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, pCO₂ of a water sample is defined only by the properties of the water sample.

Confusion regarding pCO₂ arises from the fact that pCO₂ and xCO₂ are often similar in value, and most analysts calibrate their primary detectors with mixtures of known xCO₂ as opposed to pCO₂. 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 pCO₂ 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 pCO₂ with dimensions of pressure and units of μatm, corrected to the *in situ* water temperature at the time of water sample collection.

Reference sample pCO₂ concentrations were determined in two ways: (1) direct measurements of pCO₂ on discrete water samples using a flow-through pCO₂ 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 pCO₂ Measurements using Flow-through pCO₂ 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 ($\sim 0.1\%$) 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 $x\text{CO}_2$ ($\mu\text{mol/mol}$) 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 $x\text{CO}_2$ measurements were converted to $p\text{CO}_2$ 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 $p\text{CO}_2$ at equilibrator temperature. The accuracy of $p\text{CO}_2$ measured in this way is estimated to be $\sim 2 \mu\text{atm}$, 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 $7 \mu\text{atm}$. 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 pCO₂ 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 °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 CO₂Sys (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). CO₂Sys (Pierrot et.al. 2006) was used to calculate in-situ pCO₂. 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 °C). This approach to data processing gave 3-4 values of pCO₂ for each water sample. The pooled standard deviation of pCO₂ 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 pCO₂ was not correlated to the absolute value of pCO₂. 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 pCO₂ of about 8 µatm. We also note that one standard deviation in the K₁ 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 pCO₂. 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 pCO₂ 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 pCO₂ 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 °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 deployment 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-MAPCO₂ instrument is in the buoy and other 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 °C, with strong gradients and temperature changes that could exceed 5 °C 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 pCO₂ in discrete reference samples (n=42) varied from 334 to 488 μatm while continuous, hourly measurements (n=550) from the MAPCO₂ system varied from 325 to 725 μatm (Fig. 3a). The mean and standard deviation of the difference for individual MAPCO₂ determinations and the Flow Analyzer reference measurements were $-9 \pm 8 \mu\text{atm}$ (n=31; MAPCO₂ - Flow Analyzer) (Fig. 3b). The mean and

standard deviation of the difference for individual MAPCO₂ determinations and the pCO₂Sys reference measurements were $-12 \pm 30 \mu\text{atm}$ (n=42; MAPCO₂ - pCO₂Sys).

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 °C and the standard deviation of that mean difference was 0.69 °C. These temperature differences correspond to pCO₂ differences of about 10-14 μatm. However the maximum temperature difference was 4.4 °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.

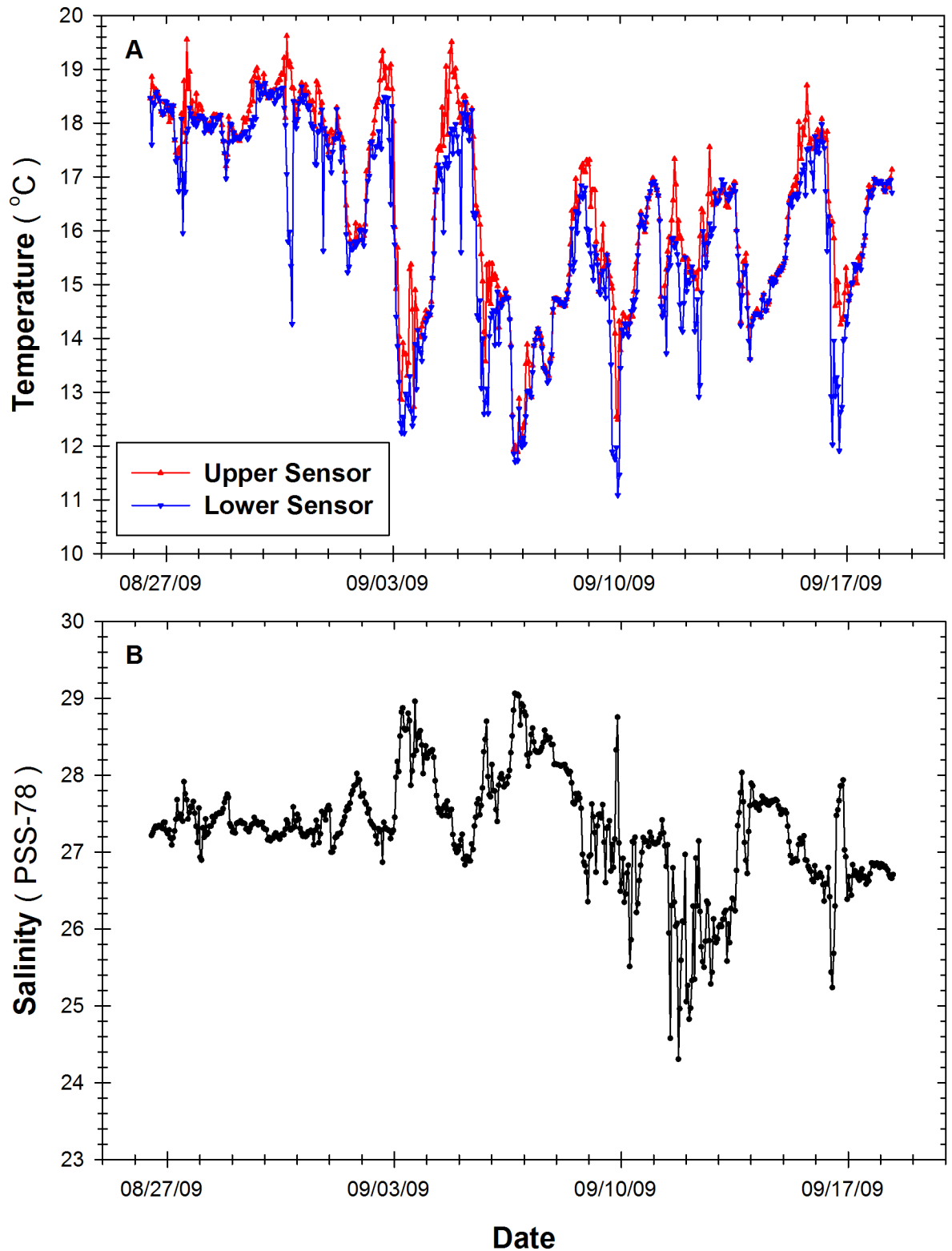


Figure 2. Environmental conditions at the mooring used for pCO₂ instrument deployments in Hood Canal, WA. Panel A: Water temperature from two RBR TR-1060 temperature loggers positioned above and below test instruments. Panel B: Salinity of water recorded by a SeaBird Electronics SBE 26 with 4M conductivity cell. All data sub-sampled at 1 h intervals corresponding to instrument sampling events.

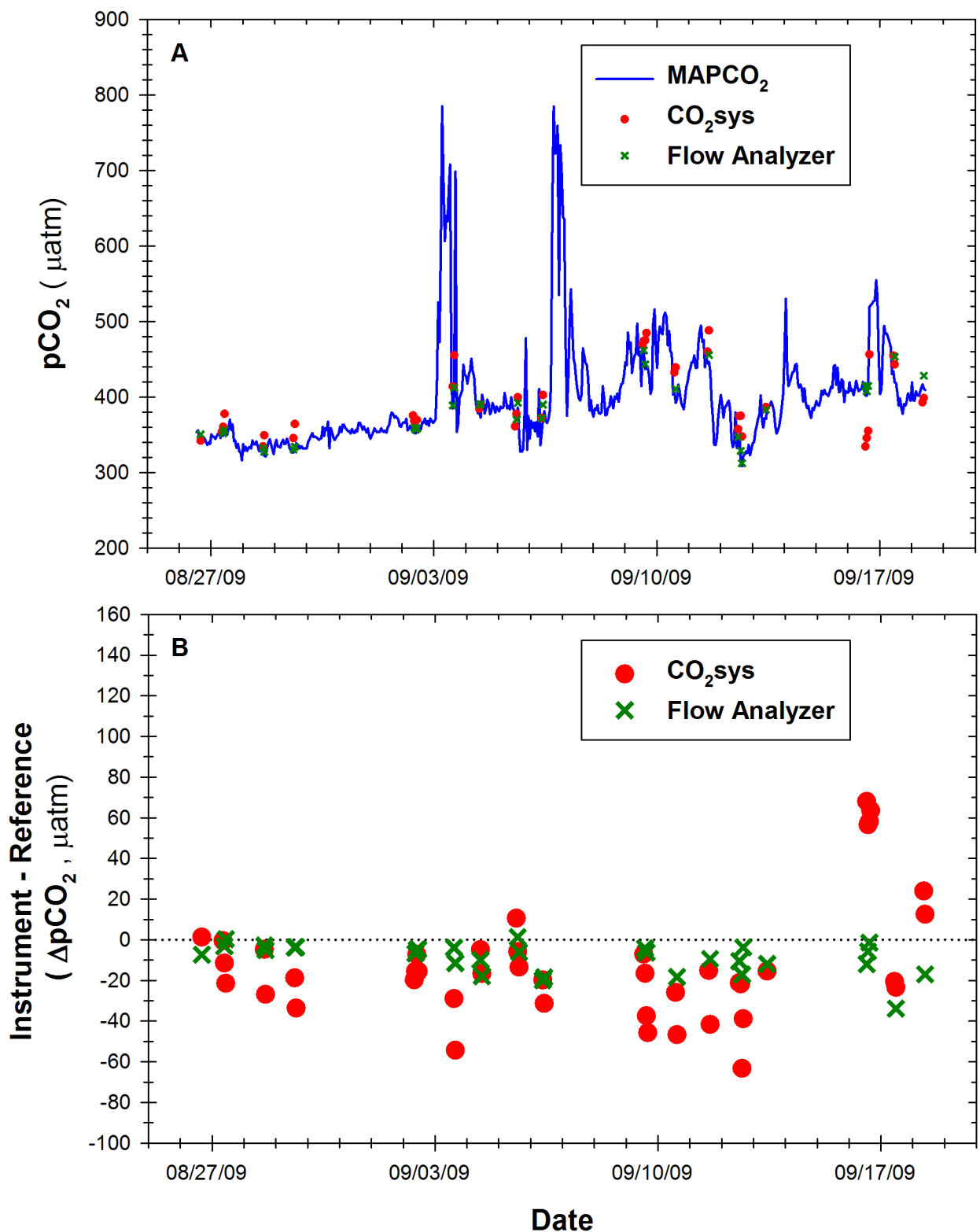


Figure 3. Field data from the PMEL MAPCO₂ pCO₂ instrument during deployment in Hood Canal, WA. Panel A: Time series of instrument values (blue lines) with overlaid values from two reference samples, one from a Flow Analyzer (green X) and the other based on calculations from pH and total alkalinity measurement using CO₂Sys (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

The MAPCO₂ was previously installed on the buoys at both field test sites, making before and after photos unobtainable. Photographs below show the system displayed on a bench top and as deployed on a buoy with the equilibrator tube submersed in the inside well of the buoy with a float to keep it fixed at the surface (Fig. 4).



MAPCO₂ on Bench



MAPCO₂ Deployed

Figure 4. Photograph of the MAPCO₂ Instrument System and submersed equilibrator as deployed at the buoy.

Moored Deployment off Coconut Island in Kaneohe Bay, Hawaii

The mooring in Kaneohe Bay was located at 21.46 °N, 157.80 °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 – Kaneohe Bay: Site map and photo of the field test site located in Kaneohe Bay, northeast side of Oahu, Hawaii. The PMEL-MAPCO₂ instrument is on the buoy and therefore there are no photos of fouling before and after, see below. 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 °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 time scales (Fig. 6b), and ranged from 34.1 to 35.2 during the deployment. Measured pCO₂ from reference samples (n=45) varied from 314 to 608 μatm, while the continuous, hourly measurements (n=620) from the MAPCO₂ varied from 300 to 800 μatm, demonstrating a more complete assessment of the variability in the ecosystem (Fig. 7a). The mean and standard deviation of the difference for individual MAPCO₂ determinations and the Flow Analyzer measurements were $-3 \pm 9 \mu\text{atm}$ (n=13; MAPCO₂ - Flow Analyzer; Fig. 7b). The mean and standard deviation of the difference for individual

MAPCO₂ determinations and the pCO₂Sys reference measurements were $3 \pm 9 \mu\text{atm}$ (n=45; MAPCO₂ - pCO₂Sys; Fig. 7b).

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 °C and the standard deviation of that mean difference was 0.047 °C. These temperature differences correspond to pCO₂ differences of about 1 μatm. The maximum temperature difference was 0.6 °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 of the instrument systems on the moorings functioned throughout the month long test period. At Washington, 100 percent of expected data were retrieved, while at Hawaii two individual sample points were not retrieved out of the more than 620 values reported for the time-series. The extensive time-series provided by the MAPCO₂ system at both test sites revealed diel patterns in pCO₂ 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.

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

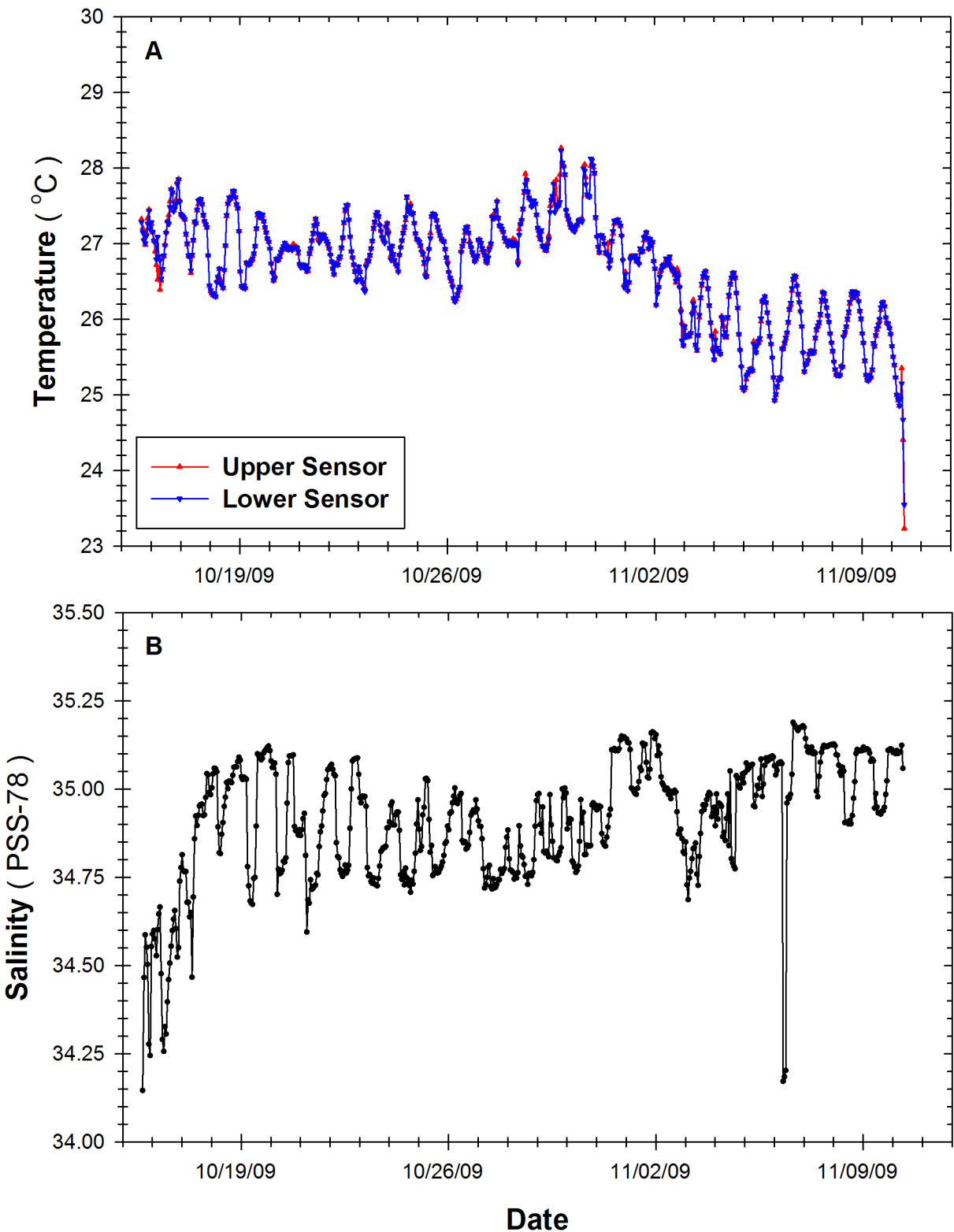


Figure 6. Environmental conditions at the mooring used for pCO₂ instrument deployments in Kaneohe Bay, HI. Panel A: Water temperature from two RBR TR-1060 temperature loggers positioned above and below test instruments. Panel B: Salinity of water recorded by a SeaBird Electronics SBE 26 with 4M conductivity cell. All data sub-sampled at 1 h intervals corresponding to instrument sampling events.

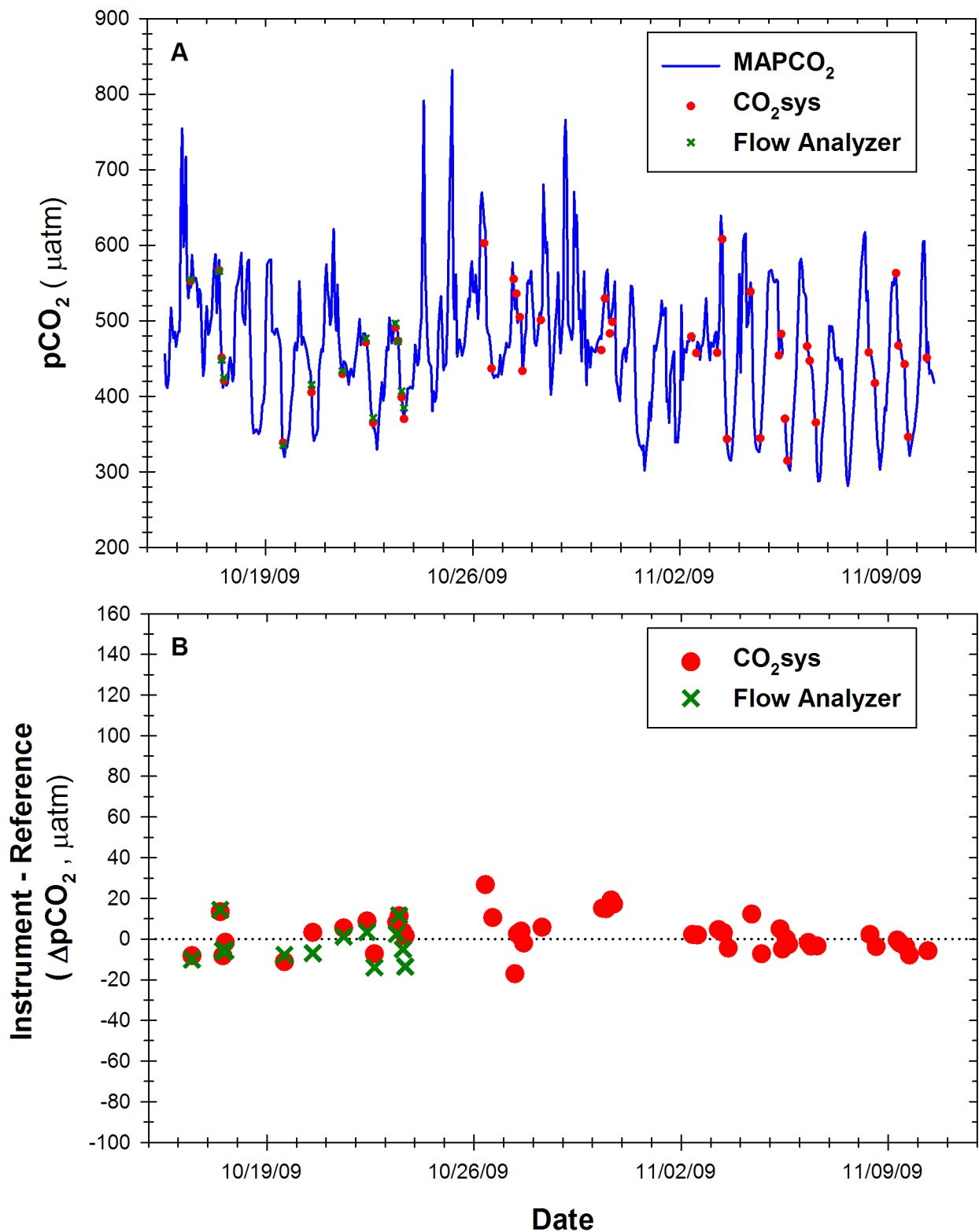


Figure 7. Field data from the PMEL MAPCO₂ pCO₂ instrument during deployment in Kaneohe Bay, HI. Panel A: Time series of instrument values (blue lines) with overlaid values from two reference samples, one from a Flow Analyzer (green X) and the other based on calculations from pH and total alkalinity measurement using CO₂Sys (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.

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

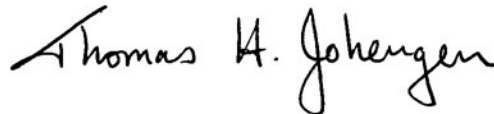
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Approved By: Dr. Mario Tamburri
ACT Executive Director

September 15, 2010

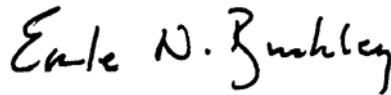
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Approved By: Dr. Tom Johengen
ACT Chief Scientist

September 15, 2010

Date



Approved By: Dr. Earle Buckley
Quality Assurance Supervisor

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APPENDIX 1: COMPANY RESPONSE LETTER TO SUBMITTED PCO2 DEMONSTRATION REPORT



U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
OAR Laboratories

Pacific Marine Environmental Laboratory
NOAA Building Number 3
7600 Sand Point Way NE
Seattle, WA 98115

RE: PMEL Response to the ACT pCO₂ Demonstration Report

The PMEL carbon group was excited to have the opportunity to participate in the Alliance for Coastal Technology (ACT) Demonstration Project for moored pCO₂ sensors. In 2009 the PMEL MAPCO₂ sensor technology was transferred to Battelle Memorial Institute to be manufactured and sold commercially. The Demonstration Project provides a great service to the community by offering an independent evaluation of the instrument performance at a time when these systems are just becoming available to the general public. We commend the ACT personnel for their efforts to make this a useful demonstration. Both the ACT staff and the technical advisors put in a great deal of work into making this a fair and informative study despite many technical challenges.

Four commercially available sensors were tested for approximately one month each in two very different environments for this study. The first site was near the southern end of Hood Canal, an extremely dynamic estuary near Seattle, Washington. PMEL placed a MAPCO₂ system on the Twanoh ORCA surface buoy on August 22, 2009, shortly before the official start of the demonstration project (Aug 26-Sept. 18, 2009), to provide some preliminary information on the expected variability at the site before the study was started. As a result, we were not able to participate in the pre-deployment tank test performed with the other instruments. The setup of the MAPCO₂ instrument on the Twanoh buoy was not ideal. Typically we like to have the instrument package imbedded in the surface buoy (either in a buoy well or mounted in the buoy structure) to thermally insulate the system from diurnal air temperature changes, but the configuration of this buoy with a profiling CTD system required that we strap the instrument above the deck of the buoy. Another atypical configuration for this site was that the buoy layout required us to use what we call a "fixed equilibrator" instead of our "standard floating equilibrator" (see right versus left photo in figure 4 of the report). Our standard equilibrator (figure 4, left) includes flexible tubing and a float that allows the equilibrator to self-adjust to the appropriate depth as environmental and buoy conditions change over a deployment. With the complications of the profiling CTD and protected location of the ORCA buoy, we decided that mounting a first generation rigid equilibrator at a fixed depth (figure 4, right) would be acceptable for this site.

Despite the strong diurnal changes in detector temperature and the older style fixed equilibrator, the system appeared to operate properly for the demonstration. The MAPCO₂ values were not statistically different from the validation measurements. One complication with the Hood Canal study site was the strong temporal and spatial variability. One can get a sense of the variability by looking at figure 2 in the report, where salinity changed by as much as 3 units over a few hours and the differences between the temperature sensors located 20-30 cm above and below the instruments showed differences of as much as 4.4°C at times. This variability can be difficult to characterize in an estuary like Hood Canal because the changes tend to be rapid and appear to be stochastic. The gradients can be so large that offsets in the location of the instruments or the intake for the validation measurements as well as differences in the integration times for the various measurements can result in seemingly dissimilar values. This may explain

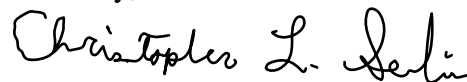
some of the differences between individual comparisons between the MAPCO₂ system and the validation measurements or even differences between the two validation approaches. The hope is that enough validation measurements were made that the average differences are representative. The ACT personnel worked very hard to collect validation measurements over a range of time scales, but they were not able to sample at the same frequency as the *in situ* instruments and thus could not capture the full range of variability. The MAPCO₂ system recorded two very large high CO₂ events lasting several hours around September 3rd and September 7th that were not captured with the validation measurements (see figure 3). We are confident that these events were real as they were captured by the other *in situ* instruments as well.

The second demonstration was conducted on a mooring PMEL has been maintaining in Kaneohe Bay, HI with University of Hawaii researchers for a number of years. The mooring has been at its current location, immediately adjacent to an actively calcifying coral reef, since June 2008. This system was set up using a standard configuration with a floating equilibrator as shown in the left photo of the report's figure 4 and is typically serviced approximately once per year. The MAPCO₂ instrument used for the Hawaii demonstration (Oct. 16-Nov.10, 2009) had been deployed in the CRIMP2 buoy since June 2009 and was not serviced or altered before the demonstration. The system, therefore, was not available for the pre-deployment tank test.

Variability in temperature and salinity were significantly smaller at the CRIMP2 site compared with Hood Canal so the observed changes in pCO₂ were more likely the result of local processes rather than advection of different waters past the mooring. The range of pCO₂ values was similar between the two sites, but the CRIMP2 site showed a much more regular diurnal cycle with variations primarily in the daily magnitude of the minimum and maximum values. As with the Hood Canal demonstration, the average difference between the MAPCO₂ measurements and the validation values were not statistically significant. In our view the signals at this site were easier to interpret, making the consistency between the MAPCO₂ values and the validation measurements more meaningful. The flow-through validation measurements were only available for the beginning of the study, but they also seemed to be more consistent with the discrete measurements than in Hood Canal. However, as with the Hood Canal study, the periodic nature of the validation measurements were not able to capture the full range of pCO₂ values observed by the *in situ* instruments.

In summary, given the observed variability and the technical complications with conducting a study like this in coastal environments, we were very pleased with the overall results. The primary advantage of the PMEL MAPCO₂/Battelle Seaology system for coastal waters is the fact that the only component exposed to seawater, the equilibrator, is primarily made of a copper-nickel alloy so it does not seem to experience significant biofouling, even over extended deployments. We believe that calibrating the system with a traceable CO₂ standard gas with every measurement is also a key to the long-term stability and accuracy of the instrument. We greatly appreciate the efforts of the ACT team and look forward to working with ACT on future demonstration projects.

Sincerely,



Christopher L. Sabine

Developer and lead P.I. for the PMEL MAPCO₂ system