



## PERFORMANCE DEMONSTRATION STATEMENT

### Contros HydroC™/CO<sub>2</sub>

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<b>TECHNOLOGY TYPE:</b>	Direct measurement of pCO <sub>2</sub> in natural water using gas equilibration and infrared detection of the gas stream
<b>APPLICATION:</b>	<i>In-situ</i> measurements of pCO <sub>2</sub> for coastal mooring.
<b>PARAMETERS EVALUATED:</b>	Accuracy, precision and reliability
<b>TYPE OF EVALUATION:</b>	Field Performance Demonstration
<b>DATE OF EVALUATION:</b>	Testing conducted from August 2009 through November 2009
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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 pCO<sub>2</sub> 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 Contros HydroC™/CO<sub>2</sub>.

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 pCO<sub>2</sub>. Water samples were collected to determine pH and Total Alkalinity (TA) for calculation of pCO<sub>2</sub> (CO<sub>2</sub>Sys; Pierrot et.al. 2006) and direct measurements of pCO<sub>2</sub> using a flow-through pCO<sub>2</sub> analyzer (Oregon State University; gas equilibration and infrared gas detection). In situ pCO<sub>2</sub> 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 35.2 over the deployment. Measure pCO<sub>2</sub> values of reference samples varied from 334 to 488 μatm while the hourly measured values from the HydroC™/CO<sub>2</sub> varied from about 200 to 820 μatm providing a more complete assessment of the variability in the ecosystem. The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> values and the Flow Analyzer reference measurements were  $-7 \pm 20$  μatm (n=29; HydroC™/CO<sub>2</sub> - Flow Analyzer). The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> determinations and the pCO<sub>2</sub>Sys reference measurements were  $-16 \pm 26$  μatm (n=37; HydroC™/CO<sub>2</sub> - pCO<sub>2</sub>Sys).

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 pCO<sub>2</sub> values of reference samples varied from 314 to 608 μatm, while the hourly instrument measurements varied from 360 to 900 μatm, again demonstrating the full variability in the ecosystem. The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> determinations and the Flow Analyzer measurements were  $+55 \pm 17$  μatm (n=5; HydroC™/CO<sub>2</sub> - Flow Analyzer). The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> determinations and the pCO<sub>2</sub>Sys reference measurements were  $+96 \pm 25$  μatm (n=37; HydroC™/CO<sub>2</sub> - pCO<sub>2</sub>Sys).

Both of the instrument systems tested functioned throughout the month long test period, and 100 percent of expected data were retrieved. Issues with shipping and customs did result in a delayed start of the deployment at Hawaii by 6 days. The time-series data provided by the instruments (n=504 and 436 for HI and WA, respectively) revealed diel patterns in pCO<sub>2</sub> 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<sub>2</sub>, TA and TCO<sub>2</sub>*, Honolulu, Hawaii, February 2005, was that ACT should conduct a “demonstration project” to evaluate pCO<sub>2</sub> sensors. Workshop participants concluded that pCO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> instruments in place and experience significant changes in temperature, salinity, photosynthesis, respiration, calcification, etc. that would result in significant variation in pCO<sub>2</sub> 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<sub>2</sub> from high rates of photosynthesis, respiration and calcification.

There are three important reasons for measuring pCO<sub>2</sub> continuously from coastal moorings: first, to evaluate whether coastal areas are functioning as a source or sink of atmospheric CO<sub>2</sub>. 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<sub>2</sub> to the atmosphere. Furthermore, coastal areas are expected to be vulnerable to climate change, and this potential impact has direct consequence on managing CO<sub>2</sub> as a pollutant in the 21<sup>st</sup> century. Near-continuous measurements of pCO<sub>2</sub> 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<sub>2</sub> measurements in conjunction with direct measurements of one other parameter of the marine CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

The basic objectives of this performance demonstration were: (1) to highlight the potential capabilities of *in situ* pCO<sub>2</sub> 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 HydroC™/CO<sub>2</sub> is an optical, headspace-based underwater sensor for the measurement of the partial pressure of carbon dioxide (pCO<sub>2</sub>). It is available for different operating depths with a maximum of 6000 m and 2000 m depth capability by default. The standard measuring range is 200 to 1000 ppm (μmol/mol) for CO<sub>2</sub> in the gas phase, but other ranges are available as well depending on user requirements (200-3000 ppm, 200-5000 ppm). Its titanium housing has a cylindrical shape with a diameter of 90 mm and a length of 500 mm. Due to its small size and weight (5.9 kg in air and 2.6 kg in water) an integration of the instrument into various static (i.e. buoys, moorings) as well as moving platforms (i.e. research vessels, ships of opportunity, ROVs, AUVs) can be easily achieved.

Within the HydroC™ a headspace is realized in the form of an equilibrated gas stream in which the CO<sub>2</sub> concentration is measured optically by means of non-dispersive infrared (NDIR) absorption spectrometry. The air within the gas stream is continuously pumped and circulates between the membrane equilibrator in the sensor head and the NDIR-detector. A flat silicone membrane with an effective layer thickness of around 10 μm is used within the equilibrator as a semi-permeable phase boundary between the water and internal gas circuit. The entire two-beam NDIR-unit is temperature stabilized as well as temperature calibrated. Furthermore, the gas within the circuit passes a heater to stabilize the measuring conditions. Additional sensors for temperature, relative humidity and pressure at different positions within the gas stream are included. Their data is used for both a proper correction of the NDIR-unit output and as an indicator for conditions differing largely from calibration conditions. The whole system is managed by a micro-controller. A data logger can be included into the sensor or the data is transmitted via cable connection (RS-232, RS-485, analog) either in auto-transmission mode or by command-driven data request.

A temperature probe at the back of the sensor for the measurement of the water temperature is optional. Its data can be used to derive the actual amount of dissolved CO<sub>2</sub> (CO<sub>2,aq</sub>) if necessary rather than just the partial pressure by assuming a constant salinity.

Every HydroC™ is calibrated individually and *in-situ* within a special insulated water tank in which the pH value is altered to set up different amounts of dissolved CO<sub>2</sub> (CO<sub>2,aq</sub>). The pCO<sub>2</sub> of the tank water is permanently monitored during calibration by means of a proven underway instrument. By calibrating the sensors *in situ* under conditions close to the deployment conditions the entire instrument is calibrated and possible sources of error are minimized, e.g.

varying equilibration properties of the membrane or effects caused by changing temperature and humidity conditions. As drift correction tools the HydroC™ features a repeated zero point calibration beside the two-beam design of the NDIR-unit. The zero point calibration is carried out regularly at discrete intervals during long-term deployments. During the time of such a zeroing the CO<sub>2</sub> within the gas stream passing the NDIR-unit is chemically removed from the sample gas.

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

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

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

## **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<sub>2</sub> Analyzers* (ACT PD09-01) and can be downloaded from the ACT website ([www.act-us.info/evaluation\\_reports.php](http://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](http://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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>) abundance in air and water is reported in a variety of units. In air, CO<sub>2</sub> ratios (xCO<sub>2</sub>; e.g., ppm, μmol/mol, μatm/atm, ml/m<sup>3</sup>) are often reported rather than actual CO<sub>2</sub> partial pressures (pCO<sub>2</sub>; μatm). These units account for fluctuations in CO<sub>2</sub> that are controlled by changes in ambient atmospheric pressure and humidity, however, physical, chemical and biological processes are controlled by pCO<sub>2</sub>, not xCO<sub>2</sub>. The reported xCO<sub>2</sub> data must be converted to pCO<sub>2</sub> by accounting for local pressure and humidity to compare with the pCO<sub>2</sub> of water. Water-sample pCO<sub>2</sub> 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.  $\mu\text{atm}\cdot\text{kg}\cdot\mu\text{mol}^{-1}$ ) is defined by the temperature and salinity of the water sample, and  $[\text{CO}_{2,\text{aq}}]$  is the concentration of dissolved  $\text{CO}_2$  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,  $p\text{CO}_2$  of a water sample is defined only by the properties of the water sample.

Confusion regarding  $p\text{CO}_2$  arises from the fact that  $p\text{CO}_2$  and  $x\text{CO}_2$  are often similar in value, and most analysts calibrate their primary detectors with mixtures of known  $x\text{CO}_2$  as opposed to  $p\text{CO}_2$ . 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  $p\text{CO}_2$  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  $p\text{CO}_2$  with dimensions of pressure and units of  $\mu\text{atm}$ , corrected to the *in situ* water temperature at the time of water sample collection.

Reference sample  $p\text{CO}_2$  concentrations were determined in two ways: (1) direct measurements of  $p\text{CO}_2$  on discrete water samples using a flow-through  $p\text{CO}_2$  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 $p\text{CO}_2$ Measurements using Flow-through $p\text{CO}_2$ 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  $\sim 8 \text{ L min}^{-1}$  from the sample reservoir (described below) through a  $50 \mu\text{m}$  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  $150 \text{ ml min}^{-1}$ .

Detector  $x\text{CO}_2$  ( $\mu\text{mol/mol}$ ) was calibrated against standard gases supplied by three cylinders of known  $\text{CO}_2$  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  $\text{CO}_2$  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  $\sim 5$  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  $\sim 700$  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  $\text{CO}_2$  mixing ratios, the accuracy is likely to be worse by an amount equivalent to the uncertainty in the gas-standard mixing ratio ( $\sim 5 \text{ ppm}$ ), 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 $p\text{CO}_2$ 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  $0.02 \text{ }^\circ\text{C}$ . (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  $\text{CO}_2\text{sys}$  (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  $1.9 \mu\text{equiv/kg}$  ( $n=87$ ).  $\text{CO}_2\text{Sys}$  (Pierrot et.al. 2006) was used to calculate in-situ  $p\text{CO}_2$ . 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 °C). This approach to data processing gave 3-4 values of pCO<sub>2</sub> for each water sample. The pooled standard deviation of pCO<sub>2</sub> 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<sub>2</sub> was not correlated to the absolute value of pCO<sub>2</sub>. 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<sub>2</sub> of about 8 μatm. We also note that one standard deviation in the K<sub>1</sub> 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<sub>2</sub>. Based on the above discussion, we conclude that the uncertainty in the reference measurements is estimated to be 8 μatm.

*Details for Hood Canal, Washington 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<sub>2</sub> 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 Kaneohe Bay, 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<sub>2</sub> 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  $\sim 0.1^{\circ}\text{C}$ , this term could contribute an additional  $\sim 0.5\%$  uncertainty, or as much as  $3 \mu\text{atm}$  for the Hawaii tests.

**Quality Assurance and Control**

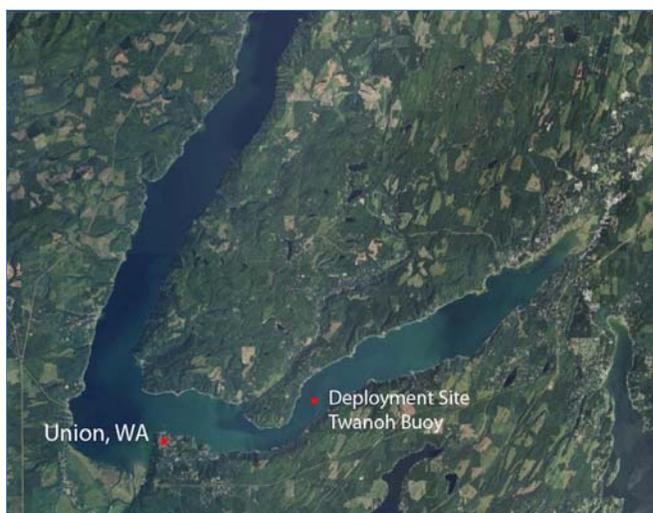
All reference samples were cataloged individually with ancillary field collection data. For samples transported, chain-of-custody (COC) protocols were practiced, specifying time, date, sample location, unique sample number, requested analyses, sampler name, required turnaround time, time and date of 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  $47^{\circ} 22.5' N$ ,  $123^{\circ} .5' W$  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

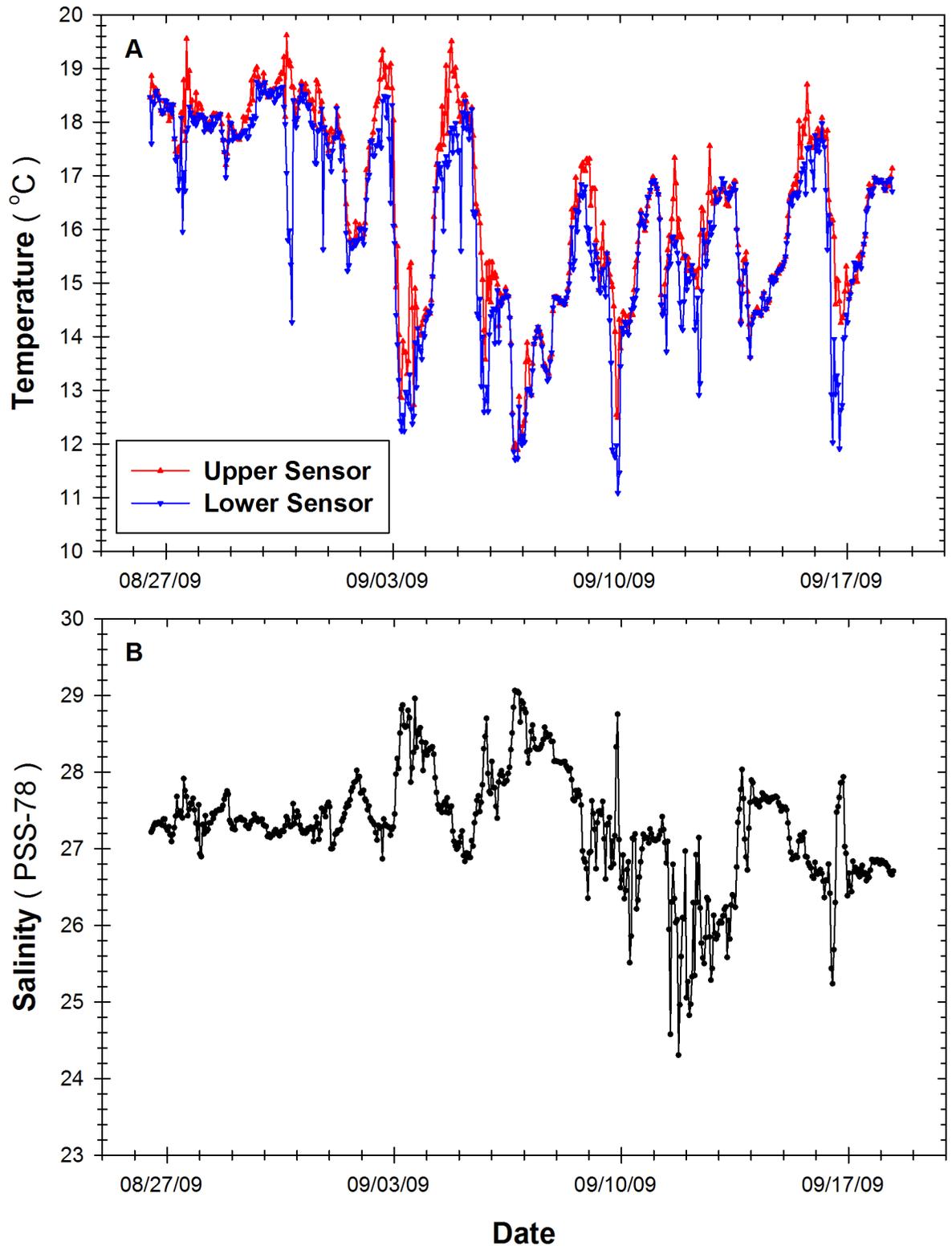


Twanoh Buoy Field Site

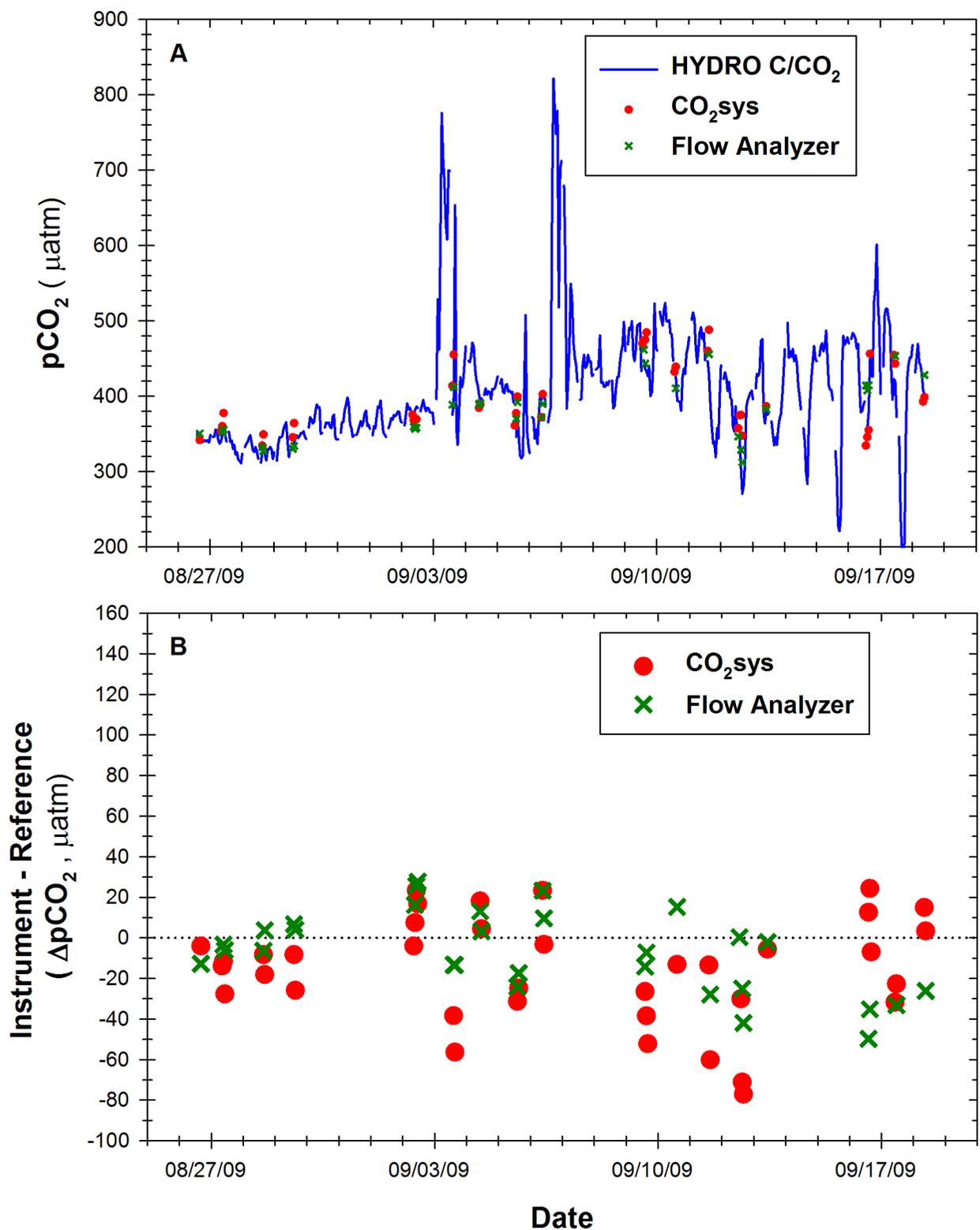
**Figure 1.** Washington –Hood Canal: Site map and photo of the field test site located in Hood Canal north of Union, Washington. The PMEL-MAPCO<sub>2</sub> instrument is in the buoy and the vendor instruments were mounted about 1 meter under the surface. (<http://orca.ocean.washington.edu/mooringDesign.html>).

### *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 to 29.1 during the deployment (Fig. 2b). Measured pCO<sub>2</sub> in discrete reference samples (n=42) varied from 334 to 488 μatm, while the hourly measurements of the HydroC™/CO<sub>2</sub> (n=504) varied from about 200 to 820 μatm (Fig. 3a). The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> values and the Flow Analyzer reference measurements were  $-7 \pm 20 \mu\text{atm}$  (n=29; HydroC™/CO<sub>2</sub> - Flow Analyzer; Fig. 3b). The mean and standard deviation of the difference for individual HydroC™/CO<sub>2</sub> determinations and the pCO<sub>2</sub>Sys reference measurements were  $-16 \pm 26 \mu\text{atm}$  (n=37; HydroC™/CO<sub>2</sub> - pCO<sub>2</sub>Sys; Fig. 3b).



**Figure 2.** Environmental conditions at the mooring used for pCO<sub>2</sub> 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.



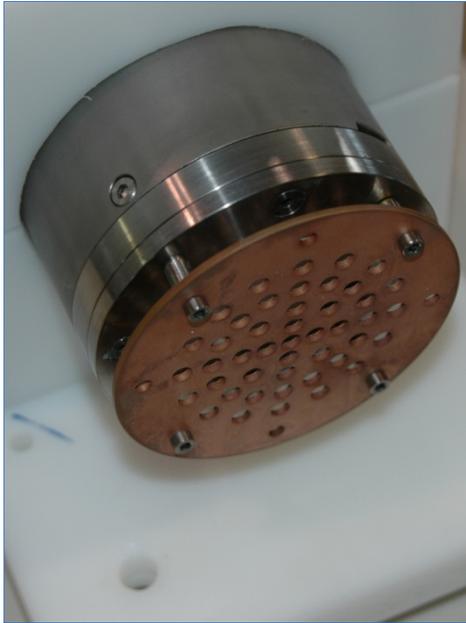
**Figure 3.** Field data from the Contros HYDRO C/CO<sub>2</sub> pCO<sub>2</sub> instrument during deployment in Hood Canal, WA. Panel A: Time series of instrument values (blue lines) with overlaid values from two reference samples, one from a Flow Analyzer (green X) and the other based on calculations from pH and total alkalinity measurement using CO<sub>2</sub>Sys (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.

*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 pCO<sub>2</sub> 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.

### 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.** Contros instrument 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 °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<sup>-1</sup>.



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-MAPCO<sub>2</sub> 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 °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 34.15 to 35.20 during the deployment. Measured pCO<sub>2</sub> from reference samples (n=45) varied from 314 to 608 μatm, while the hourly measurements of the HydroC<sup>TM</sup> /CO<sub>2</sub> (n=436) varied from about 360 to 900 μatm, providing a more complete characterization of the variability in the ecosystem (Fig. 7a). The mean and standard deviation of the difference for individual HydroC<sup>TM</sup> /CO<sub>2</sub> determinations and the Flow Analyzer measurements were +55 ± 17 μatm (n=5; HydroC<sup>TM</sup> /CO<sub>2</sub> - Flow Analyzer; Fig. 7b). The mean and standard deviation of the difference for individual HydroC<sup>TM</sup> /CO<sub>2</sub> determinations and the pCO<sub>2</sub>Sys reference measurements were +96 ± 25 μatm (n=37; HydroC<sup>TM</sup> /CO<sub>2</sub> - pCO<sub>2</sub>Sys; 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 pCO<sub>2</sub> 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.

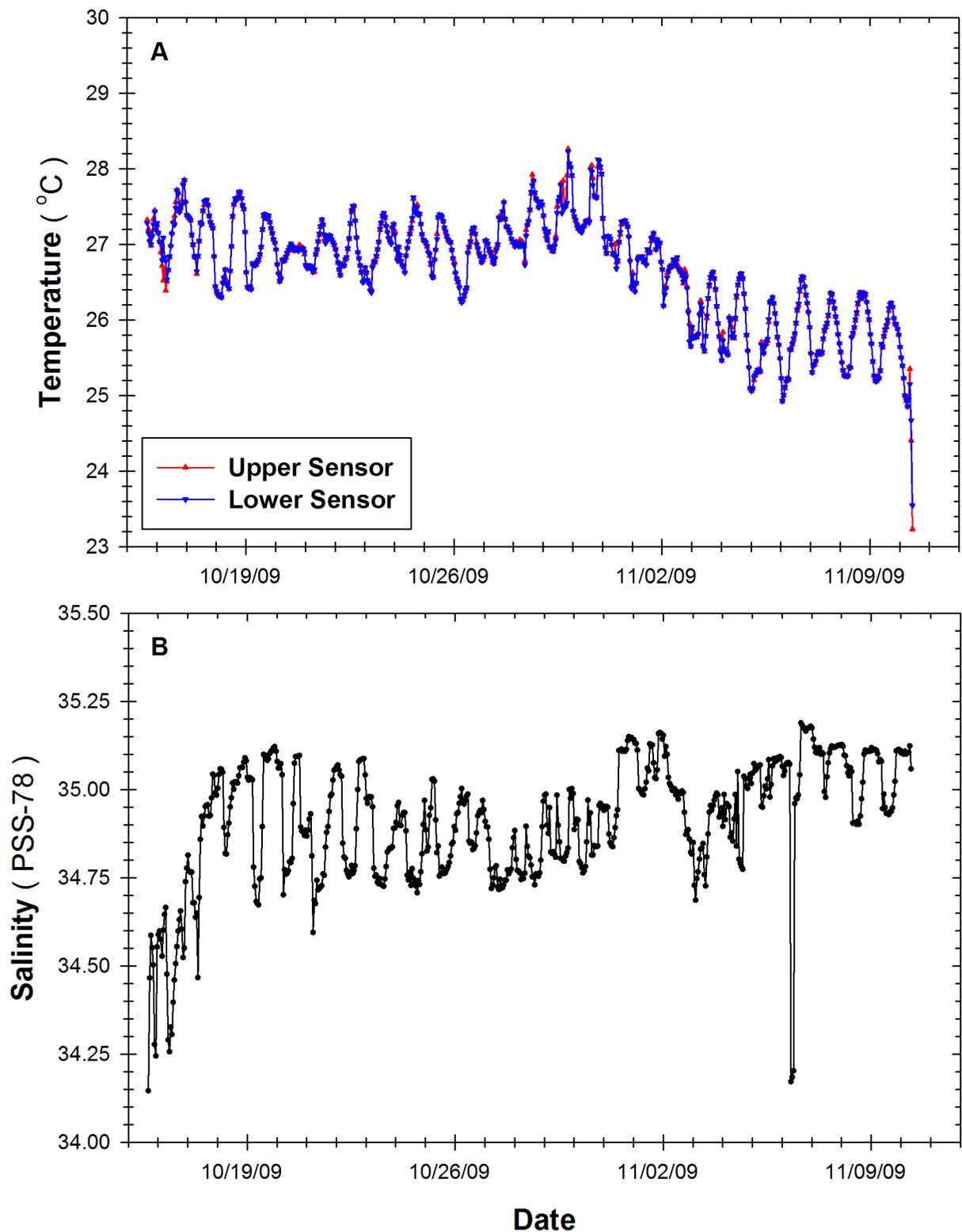
### **Reliability**

Both test instruments deployed on the moorings functioned throughout the month long test periods, and 100 percent of expected data were retrieved. Problems with shipping and customs did result in a delayed start for the Hawaii deployment by 6 days. The time-series provided by the HydroC™ /CO<sub>2</sub> revealed diel patterns in pCO<sub>2</sub> 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.

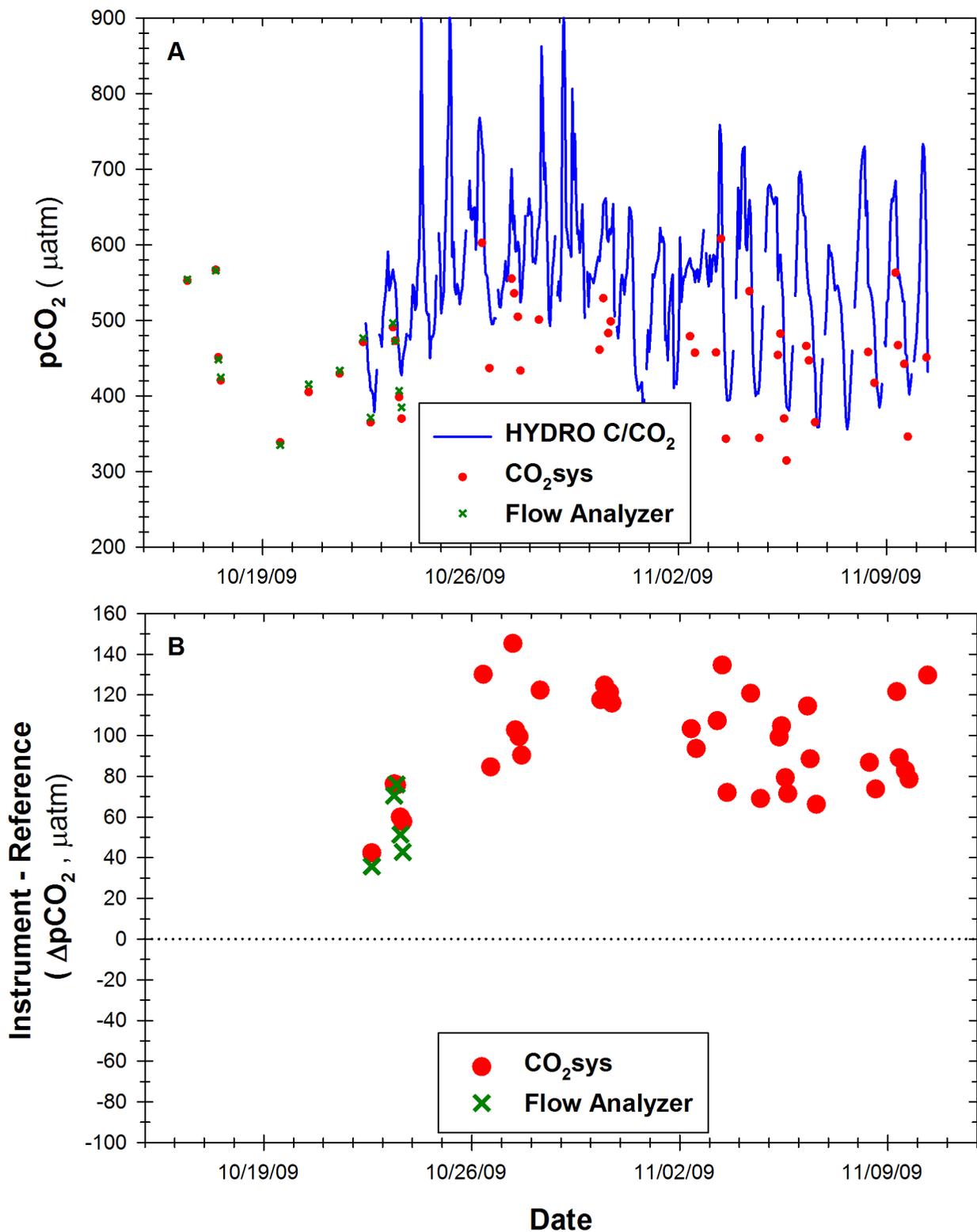
### **TECHNICAL SYSTEM AUDITS**

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 pCO<sub>2</sub> 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 Contros HYDRO C/CO<sub>2</sub> pCO<sub>2</sub> 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<sub>2</sub>Sys (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.** Contros instrument 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**

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**Date**



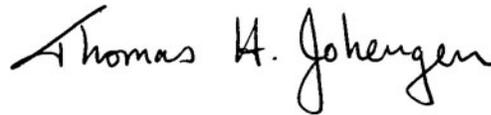

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**Approved By: Dr. Mario Tamburri**  
**ACT Executive Director**

**September 15, 2010**

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**Date**



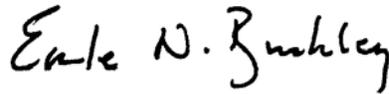

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**Approved By: Dr. Tom Johengen**  
**ACT Chief Scientist**

**September 15, 2010**

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**Date**




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**Approved By: Dr. Earle Buckley**  
**Quality Assurance Supervisor**

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**APPENDIX 1: COMPANY RESPONSE LETTER TO SUBMITTED pCO<sub>2</sub> DEMONSTRATION REPORT**

## Comment on the Performance Demonstration Statement–CONTROS HydroC™/CO<sub>2</sub>

To whom it may concern,

With pleasure we have participated in this technology demonstration, which was conducted with a lot of effort and assiduously finalized. CONTROS acknowledges the work of and thanks all the involved ACT staff, organizers and participating university personnel as well as the members of the Technical Advisory Committee for their contribution and constructive feedback. We appreciate to be part of the comprehensive demonstration and esteem its outcome as it suits our philosophy of continuous improvement.

### ***Comment on the Hood Canal, Washington field test***

The mean difference of the  $\Delta p\text{CO}_2$  (HydroC™ - Reference) is within the given uncertainty interval defined by the uncertainties of the reference methods and the given overall uncertainty of the HydroC™ (1 percent of the upper measuring value being 10  $\mu\text{atm}$ ). With 20  $\mu\text{atm}$  and 26  $\mu\text{atm}$  respectively the standard deviation of the difference between the HydroC™ measurements and the reference values is close to the suggested environmental variability of the  $p\text{CO}_2$  due to the (thermal) patchiness of the water of 10-15  $\mu\text{atm}$ . Variability in timing and response time effects might even increase this effect. The mean and standard deviation of the difference between the flow-through analyzer reference  $p\text{CO}_2$  and the  $p\text{CO}_2\text{Sys}$  reference measurement is  $-5 \pm 29 \mu\text{atm}$  ( $n=31$ , Flow Analyzer  $p\text{CO}_2 - p\text{CO}_2\text{Sys}$ ). The mean value of the differences between the two reference datasets is quite small and hence well within the given uncertainty range for the methods. The standard deviation instead is of the same magnitude as the standard deviation of the differences between the HydroC™ data and the two reference data sets. This surprises since the Flow Analyzer  $p\text{CO}_2$  values were averaged over a 20 min interval and the discrete pH/TA samples were taken at the end of that interval. Due to the averaging a smoothing effect should have been expected leading to a reduced standard deviation.

The peaks seen at Sept. 3<sup>rd</sup> and at Sept. 6<sup>th</sup> to Sept. 7<sup>th</sup> represent real events rather than outliers as they were e.g. recorded by the PMEL MAPCO<sub>2</sub> instrument as well. Unfortunately flow-through and pH/TA reference data is missing for these intervals. During the days of late August and early September the semi-diurnal influence of the tides on the  $p\text{CO}_2$  can be nicely identified. Later during the deployment at around Sept. 11<sup>th</sup> a diel fluctuation in the  $p\text{CO}_2$  is more distinct.

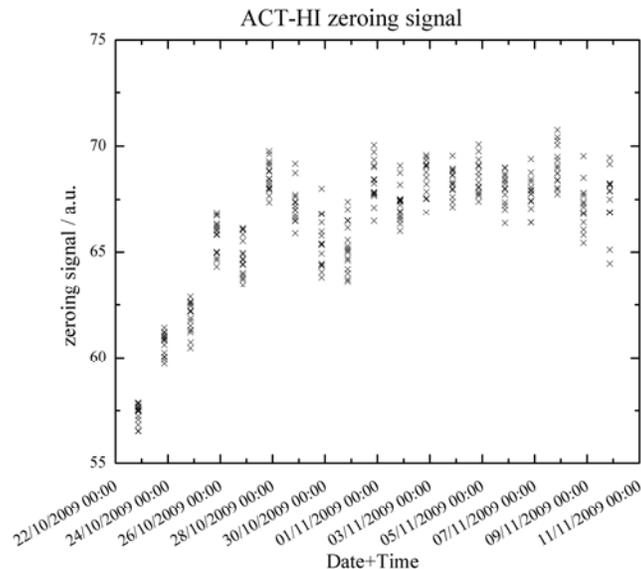
The quality of the HydroC™ data of the Washington deployment is highly satisfying, considering the uncertainties and variations discussed above.

### ***Comment on the Kaneohe Bay, Hawaii field test***

The standard deviations of the  $\Delta p\text{CO}_2$  (HydroC™ - Reference) of 17  $\mu\text{atm}$  and 25  $\mu\text{atm}$  for the flow-through and pH/TA sample reference respectively are slightly smaller compared to the Washington data. This goes well with the observed patchiness of the waters in Hood Canal, which can be also seen in the increased mean temperature difference of the RBR thermistors during the Washington test over the Hawaii measurement.

The at first increasing and after October 25<sup>th</sup> constant offset of the  $\Delta p\text{CO}_2$  of the HydroC™ is neither related to the water temperature decrease from October 31<sup>st</sup> to November 11<sup>th</sup> nor is it likely caused by fouling. Odds-on, the NDIR unit itself has caused the unwanted signal increase during the first days of the test. This offset could not be identified anymore during the post-deployment calibration of the instrument.

A fogged cuvette surface can be excluded as a possible reason as the internal humidity and gas stream temperature data did not show any indications for a possible condensation. Dust, dirt or any other reversible contamination on the cuvette surface is unlikely as well, but as a preventive measure filters will be included into the internal gas stream in the future. After the applied drift correction to the data the character of the  $\Delta p\text{CO}_2$  trend is still visible in the recorded NDIR zeroing signals.



We took these measurement results seriously and increased the quality standards for the built-in NDIR sensors. Every infrared unit in the HydroC™ is now extensively checked and tested for stability/drift as well as for cross sensitivity. By that unwanted effects caused by e.g. intensity changes of the light source and the detector characteristics for the two channels can be precociously identified and fixed. Furthermore the algorithms for the NDIR data processing are about to be updated.

#### *General comments*

The standard measuring range of the HydroC™, which is 0-1000  $\mu\text{mol/mol}$  (referred to the measurement in the gas phase) perfectly fits the observed  $\text{CO}_2$  variations at the two test sites.

Fouling has not significantly affected the quality of the collected datasets. Any drift could effectively be removed.

Adapted to the expected  $p\text{CO}_2$  trend at the sites and for a better comparison the HydroC™ data points were provided every 15 min with every point representing a mean value over 5 min of 1 Hz data. Both instruments proved their reliability as they returned 100 percent of the continuous monitoring data stored on the internal data logger.

Sincerely

Peer Fietzek

Kiel, Sept. 14th 2010