Protocols for Demonstrating the Performance of In Situ pCO_2 Analyzers

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Protocols for the ACT Demonstration of In Situ pCO_2 Analyzers

1. Background on ACT Technology Evaluations

One of the recommendations from the ACT workshop, *In-situ measurement of dissolved inorganic carbon speciation in natural waters: pH, pCO_2, TA and TCO_2*, Honolulu Hawaii, February 2005, was that ACT conduct a "demonstration project" or evaluation of pCO_2 sensors. The workshop participants concluded that pCO_2 technologies were sufficiently accurate and low-powered to be used on coastal moorings. ACT is now conducting that demonstration project at two sites both with existing observing-buoys, a coral reef in Hawaii, and Puget Sound Washington.

These protocols delineate how ACT will evaluate the performance characteristics of *in situ* pCO_2 analyzers, either commercial-ready or prototype, through the collection and analysis of quality-assured environmental data. The goal of ACT's demonstration program is to provide industry with an opportunity to have a third-party (ACT) test their instruments in the field, and to provide users of this technology with an independent and credible assessment of instrument performance. ACT will also use this opportunity to promote this emerging technology to the scientific and management communities. Instrument performance characteristics examined in the demonstration will reflect the needs of the broader research and management communities.

ACT does not certify technologies, nor guarantee that technologies will operate at the verified standards, especially under conditions other than those used in testing; ACT does not seek to determine regulatory compliance; does not rank technologies, nor compare performance between specific instruments; ACT does not label, nor list technologies as "acceptable" or "unacceptable;" and does not seek to determine "best available technology" in any way. ACT will avoid all potential language to pick "winners or losers". Thus, although the following protocols will apply to all instruments tested in this program, there will be no direct comparisons of instruments. As a final report, Instrument Performance Demonstration Statements for each instrument will be released to the public.

2. Introduction to Technology

There are three important reasons for measuring pCO_2 continuously from coastal moorings. The first is to evaluate whether coastal oceans are functioning as a source or a sink of atmospheric CO_2. The open ocean and more distal parts of the shelves are reasonably well characterized as either typical CO_2 sinks or sources (Takahashi et al., 2009), while the inner shelves are most variable and (with a general predominance of a source function) least well constrained; coastal areas are expected to be rather vulnerable to climate change in the 21st century. This of course has direct consequence of managing CO_2 as a pollutant. Near continuous measurements of pCO_2 will provide some understanding of the fluxes, their variability and their forcing parameters. The second reason involves the changes in saturation state of the water with respect to carbonate minerals and the impact on calcifying ecosystems. Surface pCO_2 measurements in conjunction with direct measurements of one other parameter of the marine CO_2 system (pH, TA or total DIC) can be used to calculate saturation state (for calcite and aragonite). The third important use is the direct measurement of net community production in shallow waters, and thus further understanding how the carbon cycle is affected by climate changes parameters such as temperature, and pH. Changes in pCO_2 can occur on wide range time scales; from hourly and diel to seasonal and inter-annual. All these parameters are potentially being altered by progressive ocean acidification. Thus it is vital to further promote, develop and improve measurement capabilities for seawater pCO_2.

The ACT workshop on pCO_2 posed the following question: What are the major impediments to transform existing shipboard pCO_2 systems for use on cost-efficient autonomous platforms such moorings? Answers were:

The measurement of pCO_2 is believed by industry to be reliable and ready for use on moorings. The issues of interest follow in order of greatest concern:

1. Reliability (precision and accuracy, long-term stability) and biofouling resistance - the system is designed as a number of components all of which have error and intrinsic limitations.
2. Software should be designed for easy use (e.g. educational use and use by managers), not just experts in the analysis and geochemistry of dissolved inorganic carbon.
3. Supportive financing in terms of supplementing costs, identifying focused markets, and facilitating the movement of technology applications from addressing the questions of individual researchers to broader, regional management issues. These needs could be addressed with the creation of focused RFPs issued by governing agencies.
4. Technologies need to be made relatively compact, portable and of rugged design.
5. Provide venues for training people to not only use the technologies, but on how to understand and interpret the data.

Action items regarding pCO_2 from the workshop were:

1. More measurements of pCO_2 in coastal waters are needed to better quantify CO_2 fluxes in coastal environments, not just open-ocean environments. These data need to be coordinated with other spatially dependent physical and biogeochemical information.
2. Verify that *in situ* pCO_2 sensing works within a broad range of environments as prescribed with comparison and availability. Companies working with Euro-ACT should be involved.

3. Objectives and Focus of pCO_2 Analyzer Performance Demonstration

The basic objectives of this Performance Demonstration are to: (1) highlight the potential capabilities of in situ pCO_2 analyzers by demonstrating their utility in two different coastal environments, a shallow coral reef and a vertically stratified sound; (2) promote the awareness of this emerging technology to the scientific and management community responsible for monitoring coastal environments, and (3) work with 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 time and resources to the companies.

At present there are three basic ways to measure CO_2 gas with moored instruments, equilibration of a gas phase with seawater and subsequent CO_2 measurement by an infrared analyzer, equilibration of a pH sensitive dye with seawater, and fluorescence. We envision that *in situ* pCO_2 sensors will be widely deployed to measure patterns in CO_2 gas flux in many coastal regions, on relatively small platforms. This includes larger offshore moorings and small shallow water moorings, in time scales of days to months.

4. Performance Parameters to be Investigated

Field tests will provide data to help evaluate accuracy, precision and stability.

Accuracy – Accuracy is typically difficult to determine with *in-situ* instruments, because "calibration standards" are often not available or difficult to apply to field conditions. pCO_2 measurements in this regard are not different than other sensors tested by ACT. This present activity is an ACT demonstration project, which is directed toward highlighting potential capabilities of new instrument technologies rather than an independent verification of stated performance characteristics. Thus we will not consider the reference measurements as "standards" but merely provide the reference measurements for comparison. For comparison, the field test instruments will be compared to 1) a flow-through underway pCO_2 instrument (provide by Burke Hales, Oregon State), and 2) calculation of pCO_2 from a independently measured pH and TA. At this time, a flow-through underway system has been chosen over a bench-top analysis because of changes in temperature equilibration between in-situ and the equilibrator and these instruments are showing good accuracy. (see below for methods and specifics). Data will be expressed as the difference in the measurements as a function of time. There will be two measures of accuracy, the first during the laboratory calibration, both before deployment and after deployment, and the second as the data from the month field test.

Precision – Precision will be determined by repeated measures during the pre and post laboratory calibration.

- **Reliability** –Reliability of instruments will be determined by: 1) examining the percent of data recovered versus percent of data expected, and 2) by performance evaluation of pre- and post-measures of blanks and reference standards to quantify drift during deployment periods. Comments on the physical condition of the instruments (e.g., physical damage, flooding, corrosion, battery failure, etc.) will also be recorded.

5. Field Tests on Moorings

Instruments will be moored on buoys at two coastal sites, one in Kaneohe Bay, Hawaii (see Crimp #2 at http://www.pmel.noaa.gov/co2/coastal/HI/), and the second in Puget Sound, Washington, (http://orca.ocean.washington.edu/mooringDesign.html). One analyzer from each manufacturer will be deployed for approximately four weeks at each site. Instruments will only be removed from the water after the test period is complete, or in the event of an obvious problem or environmental condition that could jeopardize the safety of the instruments. Field tests will be run sequentially so that each manufacturer will only have to provide one instrument. Following the first deployment, instruments will be returned to their manufacturers for a maximum of 3 weeks for reconditioning before shipping to the second test site.

Instrument Setup - Prior to deployment, all instruments will be set-up and calibrated by a manufacturer representative with assistance provided by ACT staff. Instruments will then be programmed to record data based on a time interval that will allow for a 30 day deployment. Specific sampling intervals may vary among test instruments. We envision that the sampling interval will range between several minutes to two hours. We will work out a schedule so that all instruments being tested at the same time will overlap in their sampling timepoints at a minimum time period of 2 hours. Internal clocks will be set to local time and synchronized against the time standard provided by www.time.gov. To provide a qualitative estimate of biofouling during the field tests, photographs of the instrument rack and each instrument will be taken just prior to deployment and just after recovery.

Pre- and Post-Deployment Tank Exposure – One day before instruments are moored in the field we will conduct a laboratory based tank exposure test. Instruments will be placed in a well-mixed tank filled with ambient seawater and equilibrated for a period of at least 30 minutes. Independent reference sample measurements will then be taken at 15 minute intervals over the next 60 minutes. Reference water samples will be collected at the corresponding time points of instrument readings. Reference samples will be processed and analyzed the same as field reference samples to determine in situ pCO_2 concentrations during the exposure (defined below). At the end of the field deployment the tank exposure test will be repeated under as similar conditions as possible. The pre and post tank exposure test will help provide a laboratory measure of the instrument drift characteristics.

Instrument Deployment - All instruments will be deployed for a minimum of 3 weeks, according to the schedule outlined below. Instruments will be set-up as self-recording, but manufacturers may choose to add real-time telemetry component to the instrument. The manufacturer will be responsible for adding this additional component, including all required hardware and software. ACT can provide server space or web portal access. Manufacturers will determine the protocols for retrieval and data down-loading, and provide these to the ACT Chief Scientist. Companies may perform the retrieval and down-loading procedures or train ACT staff to conduct these functions. All instruments will be returned to the companies containing all of the original data.

Deployment Buoy – ACT personnel will work with the instrument manufacturer to design an appropriate deployment arrangement on a common NOAA-operated buoy at each of the field test sites. We will arrange all test instruments so that a single representative field sample can be collected no more than 1- m apart from any of the individual sampling inlets. The deployment frames will be arranged so that all of the instruments remain at a fixed depth of 1-2 m below the water surface at all times. A calibrated CTD package will also be 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. Two calibrated RBR 1060 logging thermometers will also be deployed surrounding the instruments to characterize any fine scale temperature variation near the sampling depth. The mooring design will be standardized as much as possible between the two test sites.

Reference Water Sampling Schedule – The sampling frequency will be structured to examine changes in pCO_2 concentrations over hourly to weekly time scales. Specific frequency and timing will be dictated by weather and ship availability but with the overall plan for sampling four times per week. Twice each week we will conduct an intensive sampling event that consists of 4 to 6 consecutive samples spaced at one to two hour intervals. For the remaining two sampling days of the week we will sample twice per day. This sampling schedule should be sufficient to capture both diurnal and event based scales of variation and provide a 'continuous' check on instrument performance throughout the deployment. The specific timing of pCO_2 water sampling will be determined on-site, but with the goal to measure the maximum variation in concentration. In the event of bad weather, or un-avoidable schedule conflicts, it will be permissible to miss a single-timepoint sampling day and simply collect a second sample on the following day to keep a similar number of reference points for each test site. All sampling times will be recorded on logsheets and entered into a database for final data comparisons.

Reference Water Sample Collection – For the Hood Canal test site, reference sample pCO_2 analysis will be conducted at the buoy using a ship-board flow-through analyzer by drawing water from an inlet located centrally to all deployed instruments into a 20L cooler. The cooler will be filled and emptied for a 5-10 minute flush to help reach temperature equilibration and obtain a clean sample before filling with a final integrated time sample to be analyzed. The cooler will contain a 10 minute integrated sample that is collected from 5 minutes before to 5 minutes after the scheduled sample time. The integrated water sample will be drawn through the flow-through analyzer over a 10 minute interval, surrounding the timepoint at which all test instruments are sampling, with values recorded every second; data will be averaged as needed to provide an appropriate comparison with the test instruments. In addition, a single reference sample will be collected at each timepoint for laboratory analysis of pH and TA (as described below) to provide a second independent determination of pCO_2 concentration. The laboratory sample will be collected from the outflow of the pCO_2 analyzer by filling from the bottle and allowing the bottle to overflow for 2 exchange volumes before taking the final sample. The sample will be immediately poisoned with Mercuric Chloride and put in a darkened, thermally insulated container at environmental temperatures and taken directly to the laboratory, where they will be immediately processed for pH and TA. At the time of collection, temperature will be recorded by the flow through pCO_2 analyzer, by way of an RBR temperature sensor in the cooler, and by a hand held digital thermometer inserted into the subsample bottles.

At the HI test site, we will follow identical analytical procedures but incorporate two modifications to the sample collection and handling procedures. First, reference water samples will be collected into a 40 gallon cooler and that water will be brought back to the laboratory where it will be pumped through the pCO_2 flow-through analyzer. At least 10 minutes of sample analysis time will be recorded on the sample water. Secondly the laboratory reference sample will be collected directly from the same cooler of water at the time the water is being drawn through the pCO_2 analyzer. This lab sample will be poisoned as above and immediately taken to the lab for pH and TA analysis. These sample handling modifications are necessary due to the size and configuration limits on our vessel at this test site which preclude using the flow through analyzer at the buoy. We have conducted test comparisons of temperature and lab-determined pCO_2 concentration for a sample processed in the field versus returned to the shore laboratory and found no significant variation.

6. Reference Sample Analysis

Reference sample pCO_2 concentrations will be determined in two ways: (1) from pH, TA titrations performed on discrete water samples, and (2) using the flow-through pCO_2 analyzer provided by Burke Hales (Oregon State University) with samples collected at the buoy mooring in real time.

For the titration analysis, pH will be measured using the dye technique (Dickson et al 2007, The SOP Guide). Total alkalinity will be measured using standard Dryssen titrations (Dickson et al. 2003) as well as the bromocresol green dye method (Yao and Byrne 1998; Dickson et al. 2007, The SOP guide). These data will enable calculation of pCO_2 using a standard program such as CO_2sys. The calculation is most sensitive to pH, not total alkalinity (1 ppm pCO_2 = 4 μequiv kg^{-1}). All measurements will be done in at least triplicate.

For the flow-through pCO_2 instruments, the analyzer will sample over a 10-minute interval, surrounding the time point at which all test instruments are sampling, with values recorded every second. Data will be averaged as needed to provide an appropriate comparison with the test instruments. The reference sample analyzer will be calibrated each day with known gas concentrations immediately before going into the field to collect the reference sample.

7. QA/QC

a) Lab Samples: Water samples analyzed in the laboratory will have 4 replicates for both pH and for TA. All pH measurements will be calibrated directly to Dickson buffers on the total hydrogen seawater scale. Normality of the added acid for the total alkalinity measurements will be adjusted to calibrate all alkalinities to Dickson seawater standards. This will insure accuracies of pCO_2 calculations consistent with a large number of oceanographic measurements. All these calibrations parameters will be available for review.

b) Field Samples: Field water samples and underway pCO_2 field measurements will be taken at least twice a day throughout the week. Two times a week we will take two separate field samples and another two times a week we will have two burst sampling periods of 4-6 measurements over a four to eight hour period. Sampling will be collected with the underway system over a ten minute period and data will be smoothed.

c) Sample Custody and Handling: All reference samples will be accompanied by the sample collection sheet and Chain-of-Custody (COC) forms. The COC specifies 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. The COC is a mechanism by which a sample can be tracked through the various phases of the process: collection, shipping, receiving, logging, sample prep/extraction, analysis and final data QA/QC review.

All collected reference samples at each test site will be handled in the same manner. Each reference sample should be dated and coded according to site and sample sequence. The actual sample container should be labeled with a number for identification. The reference sample number should be used in all laboratory records and COCs to identify the sample. Transfer of reference samples from field personnel to laboratory personnel is also recorded on the COC and records are maintained in the laboratory with the names and signature of persons leaving and receiving the custody. All logs shall be duplicated weekly. The original shall be retained at the ACT Partner site and a copy shall be sent to the ACT Chief Scientist. Samples stored for any period of time shall be routinely inspected by the TC to assure proper preservation and label integrity.

d) Audits: Audits shall be performed by QA Manager, who shall be independent of direct responsibility for performance of the Verification. ACT's QA Manager will perform a Technical Systems Audit (TSA) at both test sites. The purpose of this audit is to ensure that the Demonstration is being performed in accordance with the test/QA plan, published reference methods, and any SOPs used by the Partner test facility. In this audit, the ACT QA Manager may review the reference methods used, compare actual test procedures to those specified or referenced in the test/QA plan, and review data acquisition and handling procedures. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings.

ACT's QA Manager will audit at least 10% of the data acquired in the Verification to determine if data have been collected in accordance to the test/QA plan with respect to compliance, correctness, consistency, and completeness. The ACT QA Manager will trace the data from initial acquisition to final reporting.

Each assessment and audit will be documented, and assessment reports will include the following:

a. Identification of any adverse findings or potential problems,
b. Response to adverse findings or potential problems,
c. Possible recommendations for resolving problems,
d. Citation of any noteworthy practices that may be of use to others, and
e. Confirmation that solutions have been implemented and are effective.

e) Corrective Action: The ACT Chief Scientist, during the course of any assessment, audits, or review of laboratory results will identify to the party performing the specific activities any immediate corrective action that should be taken. If serious quality problems exist, the ACT Chief Scientist is authorized to stop work. Once the assessment report has been prepared, the ACT Chief Scientist will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The ACT QA Manager will ensure that follow-up corrective action has been taken.

f) QA/QC Document Control: It is the responsibility of the ACT Chief Scientist to maintain QA/QC records, which shall include the following: (1) records of the disposition of samples and data, (2) records of calibration of instruments, and (3) records of QA/QC activities, including audits and corrective actions.

8. Demonstration Schedule

Note that the below schedule is provisional and actual dates for each milestone may vary.

- The Final Demonstration Protocols and ACT Demonstration Contract will be sent to Manufacturers by May 22, 2009
- Signed contracts are due back to ACT Headquarters by June 5, 2009
- ACT staff will perform an initial training period and test-run of all sampling and analytical procedures during June 22 – July 10. Companies are welcome to visit the test site and observe these procedures and to bring their instrument packages and conduct any pilot sampling to assist in preparation for the actual field tests.
- All relevant deployment equipment or complete instrument packages should be delivered to the Seattle, WA test site by August 19, 2009
- Manufacturers should arrive on site August 23rd (or earlier if they desire) and plan on setting up their instruments on August 24th
- The pre tank-exposure test will be conducted on August 25th and then the instrument will be attached to the mooring frame and programmed for the field deployment test.
- Instruments will be taken to the buoy and moored in situ on August 26th (or the day earlier if there is sufficient time). The WA field-test will run from Aug 26 – Sept 18. ACT will provide its Chief Scientist, the HI principal investigator and 2 Technical Coordinators to help set-up instruments and initiate the deployment.
- A post tank-exposure test will be conducted on Sept 19th.
- A copy of all data will be downloaded from the instruments before they are returned to the manufacturers. Instruments will be cleaned and shipped on Sept 21st.
- There will be a three week total turn around time for the instruments to be reconditioned and sent to HI for the second field test.
- All instruments should be received in HI by October 12th
- Manufacturers arrive on 13th and set up their instruments by Oct 14th
- The pre tank-exposure test will be conducted on Oct 15th and then the instruments programmed and readied for the field deployment to start on the same day.
- The instruments will be mounted on the test buoy on Oct 15th and the field test will run through Nov 9th.
- The post tank-exposure test will be conducted on Nov 10th
- A copy of all data will be downloaded from the instruments before they are prepared for shipping back to the manufacturers by Nov 13th.
- ACT Performance Demonstration Statements for each individual instrument will be drafted and sent out for review by, Technical Advisory Committee, Technical

Coordinators, Quality Manager, Partners, and Stakeholders in March 2010

- Final Performance Demonstration Statements will be released to the public in April 2010.

9. Roles and Responsibilities

The Demonstration is coordinated and supervised by the ACT Chief Scientist and ACT Partner institution personnel. Staffs from the Partner institutions participate in this test by installing, maintaining, and operating the respective technologies throughout the test; operating the reference equipment, collecting and analyzing the reference water samples, downloading the data from the instrument package, and informing the ACT Chief Scientist staff of any problems encountered. Manufacturer's representatives shall train ACT staff in the use of their respective technologies and, at their discretion, observe the calibration, installation, maintenance, and operation of their instruments throughout the test. QA oversight is provided by the ACT QA Manager. In addition to aiding the development of these protocols, the external Technical Advisory Committee will be consulted during the evaluation in the event problems occur, will assist in the analyses of results, and will review the final Performance Demonstration Statement prior to release.

10. Technical Advisory Committee

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
Burke Hales, Oregon State University

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