

Workshop Proceedings



***IN SITU MEASUREMENT OF
DISSOLVED INORGANIC CARBON
SPECIATION IN NATURAL WATERS:
pH, pCO₂, TA, & TCO₂***

Honolulu, Hawaii

February 16-18, 2005

*Funded by NOAA's Coastal Services Center through
the Alliance for Coastal Technologies (ACT)*

An ACT 2005 Workshop Report

**A Workshop of Developers, Deliverers, and Users of
Technologies for Monitoring Coastal Environments:**

***In Situ* Measurement of Dissolved Inorganic Carbon
Speciation in Natural Waters:
pH, pCO₂, TA, & TCO₂**

Honolulu, Hawaii

February 16-18, 2005



Sponsored by the Alliance for Coastal Technologies (ACT) and NOAA's Center for Coastal Ocean Research in the National Ocean Service.

Hosted by ACT Partner organization the Hawaii Institute of Marine Biology (HIMB), School of Ocean, Earth Science and Technology (SOEST), University of Hawaii.

ACT is committed to develop an active partnership of technology developers, deliverers, and users within regional, state, and federal environmental management communities to establish a testbed for demonstrating, evaluating, and verifying innovative technologies in monitoring sensors, platforms, and software for use in coastal habitats.

TABLE OF CONTENTS

Table of Contentsi

Executive Summary1

Alliance for Coastal Technologies2

Organization of the Workshop3

Statement of Problem4

Technologies for the *In Situ* Measurement of Dissolved Inorganic Carbon Speciation7

Breakout Session #1: Discussion of Dissolved Inorganic Carbon
Measurement Technologies12

Breakout Session #2: Directed Questions from Session #114

Action Items15

Workshop Conclusions16

Workshop ParticipantsA-i

**ACT WORKSHOP: *IN SITU* MEASUREMENT OF
DISSOLVED INORGANIC CARBON**

EXECUTIVE SUMMARY

The Alliance for Coastal Technology (ACT) convened a workshop on the *in situ* measurement of dissolved inorganic carbon species in natural waters in Honolulu, Hawaii, on February 16, 17, and 18, 2005. The workshop was designed to summarize existing technologies for measuring the abundance and speciation of dissolved inorganic carbon and to make strategic recommendations for future development and application of these technologies to coastal research and management. The workshop was not focused on any specific technology, however, most of the attention of the workshop was on *in situ* pCO₂ sensors given their recent development and use on moorings for the measurement of global carbon fluxes. In addition, the problems and limitations arising from the long-term deployment of systems designed for the measurement of pH, total dissolved inorganic carbon (DIC), and total alkalinity (TA) were discussed. Participants included researchers involved in carbon biogeochemistry, industry representatives, and coastal resource managers. The primary questions asked during the workshop were:

1. *What are the major impediments to transform presently used shipboard pCO₂ measurement systems for use on cost-efficient moorings?*
2. *What are the major technical hurdles for the in situ measurement of TA and DIC?*
3. *What specific information do we need to coordinate efforts for 'proof of concept' testing of existing and new technologies, inter-calibration of those technologies, better software development, and more precise knowledge quantifying the geochemistry of dissolved inorganic carbon species in order to develop an observing system for dissolved inorganic carbon?*

Based on the discussion resulting from these three questions, the following statements were made:

Statement No. 1

Cost-effective, self-contained technologies for making long-term, accurate measurements of the partial pressure of CO₂ gas in water already exist and at present are ready for deployment on moorings in coastal observing systems.

Statement No. 2

Cost-effective, self-contained systems for the measurement of pH, TA, and DIC are still needed to both fully define the carbonate chemistry of coastal waters and the fluxes of carbon between major biogeochemical compartments (e.g., air-sea, shelf-slope, water column-sediment, etc.).

The role of carbonate mineral saturation states and carbonate activity on the biogeochemistry of carbonate minerals and calcifying organisms (e.g., plankton, coral, and macro-algae) necessitates that one of these three dissolved inorganic carbon parameters be measured in addition to pCO₂. Some development of these technologies has already been done by individual research scientists; however, these technologies are not yet commercially available nor are ready for mass production.

Statement No. 3

Even once these technologies become technically viable, there should be further development to make them cost-effective enough, portable enough, and simple enough to use by regional resource managers as well as graduate students in environmental sciences. All personnel using these technologies should receive some training with regards to geochemistry of carbonates in aquatic environments as well as to the technical aspects of the measurement.

ALLIANCE FOR COASTAL TECHNOLOGIES

There is widespread agreement that an Integrated Ocean Observing System (IOOS) is required to meet a wide range of the Nation's marine product and information service needs. There also is consensus that the successful implementation of the IOOS will require parallel efforts in instrument development and validation and improvements to technology so that promising new technology will be available to make the transition from research/development to operational status when needed. Thus, the Alliance for Coastal Technologies (ACT) was established as a NOAA-funded partnership of research institutions, state and regional resource managers, and private sector companies interested in developing and applying sensor and sensor platform technologies for monitoring and studying coastal systems. ACT has been designed to serve as:

- An unbiased, third-party testbed for evaluating new and developing coastal sensor and sensor platform technologies,
- A comprehensive data and information clearinghouse on coastal technologies, and
- A forum for capacity building through a series of annual workshops and seminars on specific technologies or topics.

The ACT workshops are designed to aid resource managers, coastal scientists, and private sector companies by identifying and discussing the current status, standardization, potential advancements, and obstacles in the development and use of new sensors and sensor platforms for monitoring, studying, and predicting the state of coastal waters. The workshop goals are to both help build consensus on the steps needed to develop and adopt useful tools while also facilitating the critical communications between the various groups of technology developers, manufacturers, and users.

ACT Workshop Reports are summaries of the discussions that take place between participants during the workshops. The reports also emphasize advantages and limitations of current technologies while making recommendations for both ACT and the broader community on the steps needed for technology advancement in the particular topic area. Workshop organizers draft the individual reports with input from workshop participants.

ACT is committed to exploring the application of new technologies for monitoring coastal ecosystem and studying environmental stressors that are increasingly prevalent worldwide. For more information, please visit <http://www.act-us.info/>.

ACT Headquarters is located at the UMCES Chesapeake Biological Laboratory and is staffed by a Director, Chief Scientist, and several support personnel. There are currently seven ACT Partner Institutions around the country with sensor technology expertise, and that represent a broad range of environmental conditions for testing. The ACT Stakeholder Council is comprised of resource managers and industry representatives who ensure that ACT focuses on service-oriented activities. Finally, a larger body of Alliance Members has been created to provide advice to ACT and will be kept abreast of ACT activities.

ORGANIZATION OF THE WORKSHOP

The workshop was sponsored by ACT and hosted by the Hawaii Institute of Marine Biology, School of Ocean and Earth Science and Technology, University of Hawaii. The workshop was organized by Drs. Marlin Atkinson and Jim Falter of the Hawaii Institute of Marine Biology, and Dr. Fred MacKenzie of the Department of Oceanography. Participants arrived on Wednesday February 16, 2005 at the Marriott Waikiki Beach Resort and gathered for a reception and dinner, during which a presentation of the ACT program by Director Dr. Ken Tenore was given. Dr. MacKenzie gave a personal history and view of the carbon biogeochemical cycles, both global and regional, as well as his experience studying the geochemistry of marine carbonates. The workshop discussions commenced on the next day, beginning with an introduction of the workshop goals, followed by a presentation and discussion of each of the technologies used to measure dissolved inorganic carbon species in water. Most of these technologies focused on the measurement of dissolved carbon dioxide gas. The afternoon included two breakout discussion groups and a summary discussion on the needs of researchers and managers, and impediments to monitoring coastal water. The following morning, Friday, February 18th, the whole group engaged in a discussion of future technology and recommendations. An afternoon field trip to Coconut Island was optional, but attended by many. Below are the workshop announcement and the agenda, provided to participants.

Workshop Announcement

The abundance and speciation of dissolved inorganic carbon in natural waters is used to infer rates of biogeochemical processes in aquatic systems. Rates of organic carbon production and respiration can be derived from changes in total dissolved inorganic carbon while rates of calcification and carbonate mineral dissolution can be derived from total alkalinity. The speciation of dissolved inorganic carbon also plays an important role in regulating fluxes of carbon in aquatic systems. Rates of calcification, whether through biologically mitigated skeletal growth or the abiotic formation of carbonate minerals, are dependent upon the activity of (CO_3^{2-}). Over- or under-saturation of aqueous CO_2 affects rates at which CO_2 is taken up or released by natural waters.

The complexity of many aquatic systems requires that measurements of dissolved inorganic carbon abundance and speciation be made *in situ* and be made frequently in space and time. This workshop will be useful for managers who are interested in monitoring effects of organic carbon loading in sediments, production and consumption of carbon in the water column and effects of increasing carbon dioxide on marine ecosystems. Industry representatives developing pH, p CO_2 sensors and technologies for measuring *in situ* alkalinity and total dissolved inorganic carbon will enjoy the open dialogue and interactions with managers and scientists at this workshop.

The Alliance for Coastal Technologies (ACT) is a NOAA-funded partnership of research institutions, industry and managers that is dedicated to the promotion and development of new technology for *in situ* monitoring of the biology and chemistry of coastal marine and fresh waters. The Hawaii Partner of ACT, at the University of Hawaii, will be holding a short, two and a half day workshop exploring both available and developing technologies for *in situ* characterization of dissolved inorganic carbon in natural waters. It is our intent to explore technologies relevant to a broad group of interests, from resource managers to research scientists to private industries developing and selling such technologies.

STATEMENT OF PROBLEM

There are at least two major reasons for the development of a network of sensors to measure dissolved inorganic carbon concentrations and speciation in coastal waters. One involves the oceanic sink of anthropogenic fossil fuel and land use emissions of CO_2 . Observational and modeling results show that the oceanic sink of these emissions amounted to approximately 30% of the fossil fuel emissions to the atmosphere in the late 20th century. However various regions of the ocean are behaving differently with respect to the anthropogenic emissions. The open ocean and the distal parts of the coastal ocean (the shelves) are presently acting as sinks of anthropogenic CO_2 while the proximal (near shore: estuaries, bays, banks, etc.) coastal zone still appears to be a source of CO_2 to the atmosphere owing to biogenic calcification and subsequent accumulation of carbonate sediments and the overall net heterotrophic nature of much of this region, particularly its estuarine systems. Indeed the specific area emissions of CO_2 to the

atmosphere from estuaries are considerably higher than the specific area uptake of anthropogenic CO_2 by the distal coastal zone and the open ocean. This leads to the present situation of the *global* coastal zone acting as a source of CO_2 to the atmosphere in the early 21st century. This situation will change in the near future with rising anthropogenic CO_2 emissions and atmospheric CO_2 concentrations and the global coastal zone will become a net sink for these emissions (Figure 1).

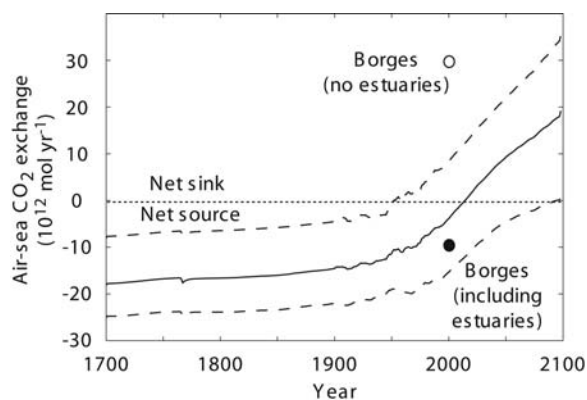


Figure 1. Air-sea exchange of CO_2 in the coastal zone. Figure courtesy of Andersson and Mackenzie (2004) *Shallow-water oceans: a source or a sink of atmospheric CO_2 ?* *Frontiers in Ecology and the Environment*, **2**(7): 348-353.

The second reason involves the effects of rising atmospheric CO_2 and temperature on coral reef ecosystems. Continuous burning of fossil fuels will lead to continuous future increases in CO_2 and dissolved inorganic carbon in the atmospheric and oceanic sinks of anthropogenic carbon, respectively. Future global mean temperature is also likely to increase. As the oceans have absorbed CO_2 , their saturation state with respect to carbonate minerals has fallen and will continue to fall in the future. This decrease in carbonate saturation state has led several investigators to conclude that carbonate secreting organisms may have difficulty in calcifying at present rates and that coral reef ecosystems may be subject to enhanced biological and mechanical erosion in the future. Most conclusions have been drawn based on experimental and field observations, although some modeling work is available.

As anticipated, due to the increase in atmospheric CO_2 , the dissolved inorganic carbon concentration of seawater has already been observed to increase in surface waters at the locations of the Hawaiian Ocean Time series (HOTS) and the Bermuda Atlantic Time-Series (BATS), HOTS located in the North Pacific subtropical gyre and BATS located in the North Atlantic subtropical gyre, respectively. In addition, the surface water carbonate saturation state has decreased at these locations (Figure 2). Furthermore, recent observations from open ocean environments have shown a shoaling of the carbonate saturation horizon in several regions of all major ocean basins.

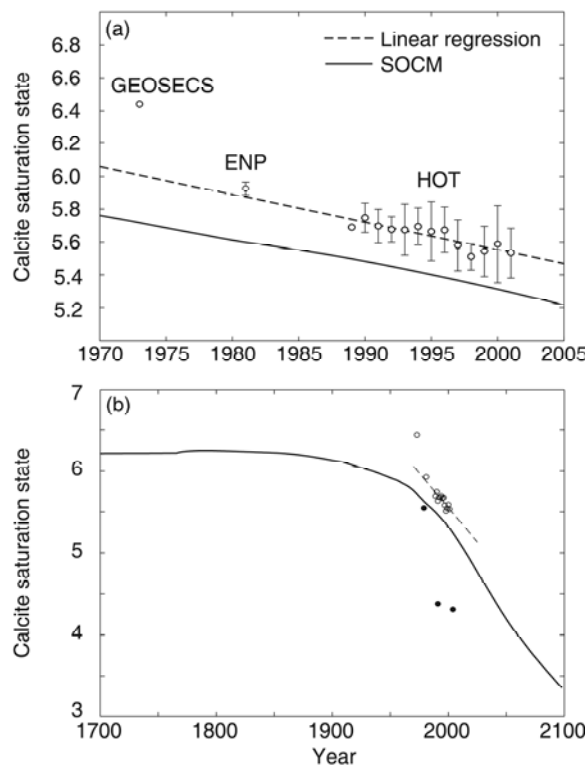


Figure 2. (A) Saturation state of calcite in surface ocean water 1970-2005 (B) same data plotted alongside with model predictions from 1700 to the year 2100. Figure courtesy of Andersson et al. (2005) Coastal ocean and carbonate ecosystems in the high CO₂ world of the anthropocene, *submitted*.

Model projections indicate that the carbonate saturation state of the surface water of the global coastal ocean may decrease by nearly 50 % by the year 2100 (Figure 2). Most surface waters will remain supersaturated with respect to both aragonite and calcite in the year 2100. However it is a distinct possibility that high latitude waters might even be undersaturated with respect to aragonite at this time. The trend predicted by model simulations agrees with surface water observations from the Hawaiian Ocean Time Series between 1989 and 2001 (Figure 2). If one incorporates data from nearby stations of the GEOSECS cruise in 1973 and the CO₂ dynamics cruise in 1981, a consistent decline in surface water carbonate saturation state can be seen in the North Pacific subtropical gyre in Figure 2. A decreasing carbonate saturation state trend is also seen in inshore data from Mangrove Bay, Bermuda, for the years 1979 to 2004.

Increasing atmospheric CO₂ and subsequent decreasing surface water carbonate saturation state may have a negative effect on marine calcifying organisms because their ability to calcify is dependent on the carbonate saturation state. Numerous experimental investigations have demonstrated the existence of a direct relationship between the rate of calcification and seawater carbonate saturation state or pCO₂ for a number of different calcifying organisms such as coccolithophorids, foraminifera, coralline algae and scleractinian corals. In addition, experiments on typical calcareous communities have been conducted in incubation chambers and mesocosms,

and on the artificial reef of Biosphere 2. Although substantial variations have been observed between species and communities, the major results and conclusions of most studies have been similar: the rate of calcification has been observed to decrease as a function of decreasing carbonate saturation state. Based on these experimental results and future projections of surface water carbonate saturation, marine biogenic calcification may decrease by 11 to 44% owing to a doubling of the atmospheric CO₂ concentration relative to pre-industrial conditions. As a consequence, calcareous organisms may not thrive as well in a world characterized by high CO₂, low carbonate saturation state and higher temperatures and may be less competitive in their environment than other more opportunistic non-calcifying organisms. For example, it would be anticipated that coral reef ecosystems might experience a successive transition from being dominated by corals and coralline algae to being dominated by seaweeds and fleshy macro algae.

The scientific issues discussed above require detailed knowledge of the marine carbon system, that is, the concentrations and distribution of the dissolved inorganic carbon species of seawater. To determine the marine carbon system in seawater, it is necessary to measure any two of four parameters of dissolved inorganic carbon (DIC), pCO₂, total alkalinity and pH from which the other parameters and the carbonate saturation state can be calculated. Because the carbon chemistry of shallow-water coral and estuarine ecosystems can vary significantly on a time scale as short as hours, the measurement of these parameters requires instrumentation that can measure concentrations continuously. Conventional grab sampling techniques will not suffice because of the need for sampling closely in time and the demand on manpower associated with this type of sampling strategy.

**TECHNOLOGIES FOR THE *IN SITU* MEASUREMENT OF
DISSOLVED INORGANIC CARBON SPECIATION**

To the best of our knowledge, the following is a comprehensive list of instruments currently available or in development:

Commercially Available Technologies

SAMI-CO₂

Sunburst Sensors, Inc.

www.sunburstsensors.com

The Submersible Autonomous Moored Instrument for CO₂ measurement (SAMI-CO₂) measures the partial pressure of aqueous CO₂ gas in seawater. The SAMI-CO₂ system makes these measurements by determining the CO₂ equilibrium between an indicator solution and seawater separated by a gas permeable membrane (DeGrandpre et al. 1995, 1997). The indicator solution consists of the sulfonephthalein bromothymol blue whose spectral absorption properties are affected by the solution pH, which is in turn, affected by the amount of aqueous CO₂ gas present. The SAMI-CO₂ has demonstrated long-term stability (up to 1 year) with a precision of 0.5-1 μatm and an accuracy of 1-2 μatm. It has also demonstrated consistent performance between sensors.

The SAMI-CO₂ can be deployed off research vessels, fixed moorings, and autonomous profilers. At the time of the workshop, the estimated cost of purchasing a SAMI-CO₂ system was ~\$18,000.

DeGrandpre, M.D., Hammar, T.R., Smith, S.P., and F.L. Sayles. (1995). *In situ* measurements of seawater pCO₂. *Limnol. Oceanogr.*, 40: 969-975.

DeGrandpre, M.D., Hammar, T.R., Wallace, D.W.R., and C.D. Wirick. (1997). Simultaneous mooring-based measurements of seawater CO₂ and O₂ off Cape Hatteras, North Carolina. *Limnol. Oceanogr.*, 42: 21-28.

PSI CO₂-Pro™

Pro-Oceanus

www.pro-oceanus.com

The PSI CO₂-Pro™ is a compact, light-weight, plug and play pCO₂ sensor that is designed for use on moorings (to 100 m), in under-way mode, and in the laboratory. The PSI CO₂-Pro™ is fitted with an IR detector and the new PSI pump-driven fast interface (patent pending). This revolutionary new interface provides a gas equilibrated sample to the detector. The PSI CO₂-Pro™ is factory calibrated from 0 - 600 ppm with calibration burned into EPROM. To maintain accuracy, the detector module has a power interruption or contact closure initiated automatic zero point calibration (AZPC). When the AZPC is initiated, the gas stream is routed through a CO₂ absorbent to provide a zero ppm CO₂ measurement. The CO₂ zero measurement compensates for changes in optical cell performance, and is used in determinations of ppm CO₂ until a new AZPC is performed (recommended once a day). Some of the features of the PSI CO₂-Pro™ include unique antifouling protection, an RS-232 data interface, both raw and converted data stream, and data necessary to compute fugacities. At the time of the workshop the estimated cost of a PSI CO₂-Pro™ system was ~\$11,000.

	<i>Accuracy</i>	<i>Precision</i>
CO ₂ concentration	±1 ppm	0.01 ppm
Gas stream humidity	±1 mbar	1 mbar
Gas tension	±2 mbar	1 mbar
Calibration range	0-600 ppm	
Temperature range	0-35°C	
Power consumption	0.8 A at 12 volts for warmup	
(excluding operation of pump)	0.4 A at normal operation	
Sample rate	0.6 Hz	
Equilibration time constant	~3 minutes	

Select specifications:

SBE 18

Sea-Bird Electronics

www.seabird.com

While there are many manufactures of pH sensors and meters, Sea-Bird Electronics commented on the potential application of electrode-based pH sensing systems on fixed moorings for extended periods of time (>6 months). The SBE 18 is the electrode-based pH sensor manufactured and sold by Sea-Bird, however, the Ag/AgCl electrodes used in the SBE 18 are actually fabricated by Innovative Sensors (Mississauga, Ontario, Canada). The SBE 18 has a working range of 0-14, an accuracy of ± 0.1 pH units, and a response time of 1 second. The accuracy of the SBE 18 relies on calibration against known pH standards (ocean, electrode electrolyte and NIST buffers). The SBE 18 has a maximum operating depth of 1200 meters and at the time of the workshop was estimated to cost \$1,440.

The major issue with using pH electrodes over long-periods of time is keeping them well-calibrated and using the proper calibration standard. The calibration standard should have the same ionic composition as the natural waters in which the pH is measured. This becomes a particularly difficult issue when the ionic strength of the measured water changes such as in estuarine systems.

LI-820; LI-840; LI-7000; LI-7500

LI-COR Biosciences, Inc.

www.licor.com

LI-COR Biosciences does not make complete systems designed for the measurement of aqueous CO₂. Rather, LI-COR Biosciences manufactures the gas analyzers used in many non-commercial aqueous CO₂ measurement systems. The LI-820, LI-840, LI-7000, and LI-7500 all measure the partial pressure of carbon dioxide (pCO₂) in air based on the absorption of infrared light by gaseous CO₂ over a known distance within an optical bench. The LI-820 can measure partial pressures of CO₂ up to 20,000 ppm with an accuracy of <2.5% -using the 14-cm bench, and 4% using the 5-cm bench; the general precision is about 1 ppm. The sensitivity of the pCO₂ measurement system to temperature is: a zero drift of <0.15 ppm/°C, a span drift of <0.03%/°C, and a total drift of <0.4 ppm/°C. The power required to run the LI-820 is 14 watts to warm-up the sensor and 3.6 watts following warm-up. Because the partial pressure of water vapor (pH₂O) affects the measurement of pCO₂, the LI-840, LI-7000, and LI-7500 all simultaneously measure pH₂O as well as pCO₂. The LI-840 measures pCO₂ with a similar degree of performance to the LI-820, however its operational range is 0-3000 ppm and measures with an accuracy of <1.5%. The LI-840 measures pH₂O between 0-80 ppm with an accuracy of <1.5% and its measurement is relatively insensitive to changes in temperature. The LI-7000 is another pCO₂/ pH₂O system which offers greater sensitivity and performance than the LI-840. See the LI-COR website for additional technical details. The LI-7500 is similar to the LI-7000, but makes direct, high-

frequency measurements of ambient $p\text{CO}_2$ to be coordinated with high-frequency turbulence measurements to generate direct measurements of $p\text{CO}_2$ fluxes via eddy-correlation.

CARIOCA (not represented)

SERPE-IESM, France

www.lodyc.jussieu.fr/equipements_lodyc/biogeochem_obs/carioca/carioca/

This technology was not represented at the present workshop, but was identified as an existing technology for the measurement of $p\text{CO}_2$ during one of the breakout sessions. This information was taken from the website given above.

The CARIOCA buoys are autonomous buoys that measure the fugacity (similar to partial pressure) of CO_2 , Sea Surface Temperature (SST), fluorescence, wind speed, air temperature, and air pressure. The buoys can be operated as drift buoys, equipped with a holey sock drogue, or can be tethered to a mooring. Data is retrieved via the ARGOS system. The ARGOS transmission equipment and power supply are sufficient for one year of operating autonomy making hourly measurements. A new version of the buoy, called the CARBON buoy, also measures pH and salinity. The precision and accuracy of the buoys have been determined at sea via intercomparison studies and the buoys show agreement with shipboard measurements to $\pm 5 \mu\text{atm}$, while laboratory tests show a reproducibility of $\pm 0.5 \mu\text{atm}$ over short time periods (< 1 day) at constant temperature. The measurement of CO_2 fugacity is made spectrophotometrically and is based on the optical absorbance of the pH indicator solution thymol blue diluted in seawater. Briefly, carbon dioxide in the surrounding seawater equilibrates with the indicator solution across a gas permeable (silicon) membrane in an exchanger cell, and the resulting change in optical absorbance induced by the pH change is measured by the spectrophotometer. (see Lefevre et al. 1993).

Lefèvre, N., J.P. Ciabrini, G.Michard, B. Brient, M. Duchaffaut, and L. Merlivat, A new optical sensor for $p\text{CO}_2$ measurement, *Mar. Chem.*, 42: 189-198, 1993.

Non-commercial Technologies

Mooring-based measurements of $p\text{CO}_2$

Gernot Friederich and Francisco Chavez

Monterrey Bay Aquarium Research Institute (MBARI)

The experimental system developed by Gernot Friederich and Francisco Chavez is similar to other self-contained $p\text{CO}_2$ sensor in that sample water is brought in contact with a gas-permeable membrane resulting in the transfer of dissolved gasses within the water sample to a LI-COR LI-6252 and/or LI-820 CO_2 sensor. The precision of the system is ± 1 ppm. Preparation consists of calibration and replacement drying and CO_2 stripping reagents. About four hours is needed for routine operation. Most mooring deployments last for 12 months.

A complete dissolved inorganic carbon measurement system

Robert Byrne and James Patten

University of South Florida

The experimental system developed by Robert Byrne is designed to measure three of the four components of the dissolved inorganic carbon system: $p\text{CO}_2$, pH, and total dissolved inorganic carbon (DIC). All of these measurements are made spectrophotometrically with different indicator dyes being used for each of the different parameters. The measurement accuracies are ± 2 mM for DIC, ± 1 ppm for $p\text{CO}_2$, and ± 0.001 for pH.

Aqueous $p\text{CO}_2$

Harvey Bootsma

University of Wisconsin at Milwaukee

The experimental system developed by Harvey Bootsma at the University of Wisconsin at Milwaukee is designed on the premise of pumping the water across a gas-permeable membrane and measuring the resulting flux of CO_2 gas with a LI-COR LI-820 CO_2 gas analyzer. The long-term precision and accuracy of the instrument are ± 3 ppm and ± 5 ppm, respectively. The unit is currently used for ship-based measurements, however, a modified unit is being developed for deployment on a great lakes mooring.

Flow injection analysis system for measuring Total Alkalinity

Andrew Steven

Queensland Environmental Protection Agency

The design, construction and validation of a compact, portable flow injection analysis (FIA) instrument for underway analysis of phosphate in marine waters is described. This portable system employs gas pressure for reagent propulsion and computer controlled miniature solenoid valves for precise injection of multiple reagents into a flowing stream of filtered sample. All the components are computer controlled using software developed using the LabVIEWTM graphical programming language. The system has the capacity for sample throughput of up to 380 phosphate analyses per hour, but in the mode described here was operated at 225 analyses per hour. The system was evaluated for the mapping total alkalinites in the Yarra River and Port Phillip Bay, south eastern Australia. In general, good agreement was observed between analyses obtained using the portable FIA system and those obtained from manual sampling followed by standard laboratory analysis.

**BREAKOUT SESSION #1: DISCUSSION OF DISSOLVED
INORGANIC CARBON MEASUREMENT TECHNOLOGIES**

In addition to summarizing existing technologies designed for the measurement of dissolved carbon species, the second purpose of the morning session was to identify strengths and weaknesses for different applications and to further articulate some of the important motivations for *in situ* DIC measurement. There were two breakout sessions, one with scientists and managers, the other with industry representatives and developers of technologies.

Scientists and Resource Managers Breakout Session #1

There were three broad areas in which the measurement of DIC parameters were discussed: compliance issues, carbon budgets and direct measurements of CO₂ gas flux. Although compliance issues are not based on scientific questions, they are important to managers for monitoring the quality of natural waters. pH is often a standard parameter for characterizing water quality. A measurement precision of ± 0.1 pH units is usually sufficient for water quality monitoring, but many natural waters can have ranges in pH for which a precision of ± 0.01 pH would be better.

A precision of ± 0.1 pH resolution is *not* useful for DIC measurements. As yet, TA, DIC and pCO₂ content of natural waters are not regulated because inorganic carbon is not considered a pollutant. It is likely, however, that carbon dioxide emissions will be regulated on regional and global scales through a currency of carbon dioxide 'credits.' Carbon budgets and CO₂ gas flux of various regions and countries will be monitored. When this occurs it is expected that regulatory measurement of the full suite of dissolved inorganic carbon parameters will become standard protocol. At present, pCO₂ is already routinely monitored at a number of terrestrial sites within continental US, but is not monitored in the coastal zone where the effluxes of CO₂ can be comparably large.

Carbon budgets of coastal ecosystems are presently mostly performed by scientists, but will move to management and monitoring, as stated above. Participants agreed that for estimating and modeling carbon biogeochemical fluxes, accuracies of dissolved inorganic carbon species should be ± 0.001 for pH, $\pm 1 \mu\text{equiv L}^{-1}$ for TA, $\pm 1 \mu\text{M}$ for DIC, and ± 1 ppm for pCO₂. If the effort is to determine carbonate mineral saturation states, however, and its effect on inorganic carbon fluxes, the required accuracies may be 5 times less.

Summary:

1. An accuracy of ± 0.1 pH is inadequate for assessing the dissolved inorganic carbon speciation in either fresh or marine waters, but is adequate for regulatory and compliance issues. A precision of ± 0.01 pH would improve general compliance issues.
2. There was some concern for the stated accuracies in the measurement of pCO₂ concentrations. Participants suggested that developing some real inter-calibration efforts would help to verify the claims made for existing pCO₂ measurement technologies.

3. Coastal waters are typically very dynamic in their dissolved inorganic carbon speciation and abundance. It was suggested that real-time spatial and temporal measurements of TA and DIC in addition to pCO₂ are needed.

Industry Representatives and Developers of Sensor Technologies Breakout Session #1

Industry representatives considered limitations to existing technologies for coastal moorings. As similarly stated in other ACT workshops, biofouling was a major factor in maintaining moorings. Typical open-ocean mooring deployments for these technologies are about a year, with little drift occurring within the instrument (see summary of existing technologies) and little susceptibility of the CO₂ sensor itself to biofouling (due to its physical separation from the sampled water by the water-impermeable, gas-permeable membrane). The gas equilibrators themselves, however, can be susceptible to fouling through clogging of organic and inorganic debris. One suggestion for combating the potential problem of biofouling within the gas exchangers was to use all-copper equilibrators, which would be cleaned or replaced following a year-long deployment. It was also pointed out, however, that existing pCO₂ sensors have demonstrated adequate performance in turbid, productive, coastal waters.

Additional concerns were that of power requirements. Power consumption depends on sampling frequency - a reasonable sampling rate of once an hour (24 times per day) was suggested. It may be possible to supplement the power needed to run these sensors with solar panels to reduce the weight of required batteries; however, at the time of the workshop, designs involving solar panels are not yet been developed.

Summary:

The participants agreed upon the following points for the development of existing and new sensor technologies:

1. These technologies should be easy to use, thus minimizing the costs associated with training of research and management personnel.
2. The costs of the technologies should also be minimized to maximize the number users, data collection, and applications.
3. The size and weight of self-contained sensor technologies is always an issue with respect to the range of applications for which they can support.
4. Existing, commercially available pCO₂-sensing technologies for moorings meet necessary precision requirements.
5. *In situ* measurements of pH, TA, DIC are not yet ready for moored applications.
6. Use of technologies will require money for training to ensure proper use and application of the technologies (see point #1).

**BREAKOUT SESSION #2:
DIRECTED QUESTIONS FROM SESSION #1**

Question #1

What are the major impediments to transform existing shipboard $p\text{CO}_2$ systems for use on cost-efficient moorings?

The measurement of $p\text{CO}_2$ 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 and biofouling - the system is designed as a number of components all of which have error and intrinsic limitations.
2. Software should be designed for 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 and portable.
5. Provide venues for training people to not only use the technologies, but on how to understand and interpret the data.

Question #2

What are the major technical hurdles for in situ TA and DIC measurements?

At present, self-contained systems for the measurement of DIC and TA are not available for use on moorings, although it appears the measurement of TA is closer than that of DIC. Additional efforts to develop these technologies could pay off depending on the purpose of such measurements and the measurement accuracies required. More precise quantification of basic dissolved inorganic carbon equilibrium constants and solubility constants of carbonate minerals are needed for estuarine waters of intermediate salinities.

Question #3

What specific information do we need to coordinate efforts for the 'proof of concept' testing of existing and new technologies, intercalibration of those technologies, better software

development, and more precise knowledge quantifying the geochemistry of dissolved inorganic carbon species in order to develop an observing system for dissolved inorganic carbon?

1. Proof-of-concept demonstrations involving multiple representatives from research science and industry are still needed. Synthesis of the results from such demonstrations could be used to provide resource managers with meaningful data acquisition strategies.
2. Algorithms for data synthesis and management, identifying the meaning of each of the measured parameters need to be developed.
3. More people need to be trained in the measurements of dissolved inorganic carbon species in natural waters, facilitating the flow of information and expertise from researchers to managers. Provide supplemental education on the importance of carbon biogeochemical cycles.

ACTION ITEMS

Near the closing of the workshop, participants recommended the following actions. The order of each action item reflects their general importance to all participants based on voting process.

1. More detailed measurements of the carbonate system (e.g., carbonate ion activities, mineral saturation states, total DIC abundance) are needed.
2. In accordance with #1, the further development of self-contained, *in situ* TA measurements systems should be continued. The precise spectrophotometric measurement of pH may provide an alternative or complementary constraint to *in situ* TA measurements.
3. More measurements of pCO₂ in coastal waters are needed to better quantify CO₂ fluxes in coastal environments, not just open-ocean environments. These data need to be coordinated with other spatially dependent physical and biogeochemical information.
4. Facilitate the training and education of future users of dissolved inorganic carbon measurement technologies.
5. Create collaborative, multi-investigator programs to evaluate measurement accuracies, processing and analysis of data, and presentation of the meaning of the data generated.
6. Work on the portability and packaging of sensor technologies.

7. Establish possible regional proxy measurements for components of dissolved inorganic carbon.
8. Verify that *in situ* pCO₂ sensing works within a broad range of environments as prescribed with comparison and availability. Companies working with Euro-ACT should be involved.
9. Identify necessary target accuracies required to answer specific scientific and management questions so that industry can respond with the development of appropriate technologies.
10. Stability of the data output is determined by stability of the entire system. System stability must be evaluated.

WORKSHOP CONCLUSIONS

The recommendations made by all participants within the workshop can be summed by the following. First, scientists must re-visit the fundamental issues that need to be addressed and articulate these issues to government agencies - global carbon cycles, productivity of coastal ecosystems, the health of calcifying organisms and communities, etc. The community of research scientists should also decide the technical requirements for the measurement of dissolved inorganic carbon abundance and speciation needed to address these issues, both in terms of frequency of measurement in both space and time as well as in terms of measurement precision and accuracy. Some general programs for the development of scientific technology exist at present (e.g., STTR, SBIR, MRI, OTIC, NOPP, etc.) and could already provide avenues for the necessary technology development. However, the implementation of focused RFPs would prevent efficient development of needed technologies by commercial enterprises without industry facing the severe financial risks of misjudging their markets. Government agencies should also focus efforts to properly train personnel to use these technologies as well as to interpret the data so as to meet the scientific and regulatory goals established by consensus between government agencies and the research community. Such education could occur through evaluation and demonstration projects such as ACT. Thus, a proper flow of direction and guidance would occur between the research science community, government agencies, and the small businesses developing and manufacturing technologies aim for the measurement of dissolved inorganic carbon species in natural waters.

WORKSHOP PARTICIPANTS

Jim Amen
LI-COR Biosciences, Inc.
4421 Superior St.
Lincoln, NE, 68504
Email: jamen@licor.com

Marlin Atkinson
Professor
Hawaii Institute of Marine Biology
PO Box 1344
Kaneohe, HI, 96744
Email: mja@hawaii.edu

Harvey Bootsma
Great Lakes Water Research Institute
University of Wisconsin - Milwaukee
600 E Greenfield Ave.
Milwaukee, WI, 53204
Email: hbootsma@uwm.edu

Alberto Borges
University of Liege
Interfaculty Center for Marine Research
Chemical Oceanography Unit
Institut de Physique (B5)
B-4000 Liege, BELGIUM
Email: alberto.borges@ulg.ac.be

Michael DeGrandpre
Associate Professor
Department of Chemistry
The University of Montana
Missoula, MT 59812
Email:
Michael.DeGrandpre@umontana.edu

James Falter
Assistant Researcher
Hawaii Institute of Marine Biology
PO Box 1344
Kaneohe, HI, 96744
Email: falter@hawaii.edu

Gernot Friederich
Research Specialist
Monterrey Bay Aquarium Research
Institute
7700 Sandholdt Rd.
Moss Landing, CA, 95039
Email: frge@mbari.org

June Harrigan-Lum
State of Hawaii
Department of Health
P.O. Box 3378
Honolulu, HI 96801
919 Ala Moana Blvd., 3rd Floor
Honolulu, HI 96814
Tel: (808)-586-4337
Email: jharrigan@eha.health.state.hi.us

Bruce Johnson
Pro-Oceanus Systems
1721 Lower Water St.
Halifax, Nova Scotia
B3J 1S5, CANADA
Email: johnson@pro-oceanus.com

Paul Jokiel
Professor
Hawaii Institute of Marine Biology
PO Box 1344
Kaneohe, HI, 96744
Email: jokiel@hawaii.edu

WORKSHOP PARTICIPANTS (CONTINUED)

Ilsa Kuffner
Ecologist
USGS Center for Coastal & Watershed
Studies
600 Fourth Street South
St. Petersburg, FL 33701
phone: 727-803-8747 ext. 3048
fax: 727-803-2032
Email: ikuffner@usgs.gov

Fred MacKenzie
Professor
Dept. of Oceanography
University of Hawaii
1000 Pope Road
Honolulu, HI, 96822
Email: fredm@soest.hawaii.edu

Daniel Merritt
Pacific Islands Fisheries Science Center
2570 Dole Street
Honolulu, HI 96822-2396
Phone: (808)-983-5300
Fax: (808)-983-2902
Email: dmerritt@mail.nmfs.hawaii.edu

Darius Miller
Sea-Bird Electronics
1808 136th Pl. NE
Bellevue, WA, 98005
Email: dmiller@seabird.com

Casey Moore
WetLabs
620 Applegate St.
Philomath, OR, 97370
Email: casey@wetlabs.com

David Murphy
Sea-Bird Electronics
1808 136th Pl. NE
Bellevue, WA, 98005
Email: dmurphy@seabird.com

Janet Newton
University of Washington
214 NW 62nd St.
Seattle, WA, 98107
Email: newton@ocean.washington.edu

Tamotsu Oomuri
Dept. of Chemistry, Biology, and Marine
Sciences
Faculty of Science
University of the Ryukyus
Nishihara, Okinawa
903-0213, JAPAN
Email: oomori@nirai.ne.jp

James Patten
University of Southern Florida
470 South Lime Ave.
Sarasota, FL, 34237
Email: jpatten@marine.usf.edu

Frank Sansone
Professor
Dept. of Oceanography
University of Hawaii
1000 Pope Road
Honolulu, HI, 96822
Email: sansone@hawaii.edu

WORKSHOP PARTICIPANTS (CONTINUED)

Dan Schar
Junior Researcher
Hawaii Institute of Marine Biology
PO Box 1344
Kaneohe, HI, 96744
Email: schar@hawaii.edu

Tanvir Shah
LI-COR Biosciences, Inc.
4421 Superior St.
Lincoln, NE, 68504
Email: tdshah@licor.com

Andrew Steven
Manager-Waterways Science
Queensland Environment Protection Agency
80 Meiers Rd.
Indooroopilly, 4068
AUSTRALIA
Email: andy.steven@epa.qld.gov.au

Ken Tenore
Director
UMCES-Chesapeake Biological Laboratory
Post Office Box 38
Solomons, MD, 20688
Telephone: 410 326 7385,
Fax: 410 326 7428
Email: tenore@cbl.umces.edu

Yoshimi Suzuki
Professor
Shizuoka University
836 Ohya
Shizuoka, JAPAN 422-8529
Email: seysuzu@ipc.shizuoka.ac.jp



Ref. No. [UMCES] CBL 05-076

Copies may be obtained from:
ACT Headquarters
c/o University of Maryland Center of Environmental Science
Chesapeake Biological Laboratory
Post Office Box 38
Solomons, Maryland 20688-0038
Email: info@act-us.info