An autonomous indicator-based pH sensor for oceanographic research and monitoring

Annual report for period Dec. 1, 2009 to Nov. 30, 2010

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LONG-TERM GOALS

This project, funded under NOPP Topic 3A *Sensors for Measurement of Biological, Bio-Optical or Chemical Properties of the Ocean,* uses NOPP/NSF funding to commercialize an autonomous, in situ indicator-based pH sensor that was developed in the PI's lab. The long-term goal of the project is to make more autonomous chemical and biological sensors available to the oceanographic research community. These autonomous sensors will enable researchers able to more effectively study processes such as natural CO_2 sequestration and ocean acidification.

OBJECTIVES

The objective is to commercialize the autonomous pH sensor, SAMI-pH, through Sunburst Sensors, LLC. Studies conducted in the PI's laboratory found that the original SAMI-pH design had excellent precision, accuracy, and long-term stability. However, this design was complex with high power requirements and primitive software. The goal of this project is to improve upon the strengths of the existing sensor, while making the instrument more commercially attractive.

The specific objectives of this project, as originally stated in the proposal, are to:

- Implement design improvements established during redesign of the autonomous sensors SAMI-CO_2 including the optical detection system, control and data acquisition electronics, fluidics, and user software.

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- Redesign the features that are specific to the SAMI-pH, focusing on optimizing the mixing technique, power consumption, ease of troubleshooting, and expanding deployment versatility.
- Establish rigorous manufacturing quality control criteria to verify absorbance and pH precision and accuracy prior to shipment.
- Extensively field-test the new design.
- Implement in situ data validation using pH certified reference materials (CRMs) made by Andrew Dickson's laboratory.
- Commercialize the sensor through Sunburst Sensors, LLC.

APPROACH AND WORK PLAN

We have based the SAMI-pH redesign on Sunburst Sensors' recently redesigned SAMI-CO_2 (v2.0), a project that was supported by a previous NOPP grant. This portion of the project, which has now been completed, required changes in the electronics and optics, changes in the fluidics design, and new software. During this reporting period, our focus has been to further optimize the design based on continued laboratory and field evaluations. An in situ quality control procedure is also being implemented.

At Sunburst Sensors, Dr. Reggie Spaulding continued work on establishing long-term stability of mCP. Jim Beck coordinated improvements to the design of the software and hardware to support external serial instruments, such as GPS and CTDs. Data handling and display were also greatly improved. Jenny Newton has investigated methods for improving data filtering, working with UM post-doctoral researcher Tommy Moore. Dr. Moore has also been coordinating a number of collaborations aimed at further field-testing of the SAMIs. Katherine Harris, a 3rd year graduate student in the DeGrandpre lab, has been working with Dr. Moore on these field tests. Our other NOPP partner, Andrew Dickson, has been developing and testing tris CRMs for spectrophotometric pH validation. All of these activities are described in more detail below.

Our efforts in the coming year will focus on further field-testing and optimization of the instrument. These tests will include testing a different pH indicator (thymol blue) that can be purchased in higher purity than the current indicator, meta-cresol purple. Implementation of in-situ quality control using tris CRMs will be completed (see below). Further fine-tuning of the electronics and software will also be undertaken. Field tests are continuing off the Oregon coast and we will pursue other deployments and testing with interested parties as we have done during the previous years of the grant.

WORK COMPLETED

In the past year, progress was made on many fronts. We have continued to improve the electronics and software. Manufacturing quality control criteria have been established and implemented. The shelf-life of the pH indicator has been tested using tris CRMs. The in situ tris validation method has been tested in the laboratory. Two deployments were made with this configuration but no data were obtained due to technical problems that are now being addressed. We have also completed design of a benchtop version of the SAMI-pH. Field-testing has continued with our collaborators including deployments off the coast of Oregon (Burke Hales, OSU), Mexico (Adina Payton, UC Santa Cruz), and during an Arctic cruise (Wei-Jun Cai, U. Georgia). We also participated in a pH sensor intercomparison on a mooring in Monterey Bay organized by Ken Johnson (MBARI). The latter three field efforts are very recent and results have not yet been analyzed.

RESULTS

Hardware and software: Since the last report, there have been many changes made to the SAMI-pH (Figure 1) hardware and software that have led to improved functionality including:

- easier assembly of the electro-optical board and pump/valve housing.
- the instrument can now read the output from up to two other serial devices and can communicate with other data loggers and telemetry systems. Users now have the option to log salinity data needed for calculation of pH.
- the software has a super-user interface for high-level troubleshooting, improved graphing for data visualization (Figure 2), and an automated check for software updates.

Figure 1: The new SAMI-pH design (dimensions are 62 cm long x 15 cm diameter). The lower housing contains the pH indicator, tris CRM and pump housing. The upper chamber contains the batteries and electronics. The sensor flow cell is located between the two housings.

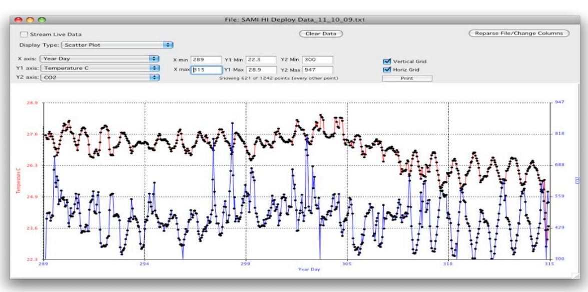


Figure 2: New data visualization software for the SAMI-pH.

Laboratory testing: The following laboratory tests have been conducted:

- Testing is underway to further optimize the indicator and sample mixing configuration including mixing coils of different diameters. Some promising results have recently been obtained using a small section of large bore tubing. This mixer will simplify assembly and is lighter weight and lower cost than the existing mixer.

- Long-term tests of the indicator stability have found no change in indicator total concentration or pH performance after more than 100 days of indicator storage (at room temperature).
- Analysis time has been minimized by optimizing the number of pumps pulses needed per measurement and the on/off time of the pump. At the optimized pumping rate we can make 1 measurement every 2.5 minutes.
- Temperature tests found that the indicator solution can operate at the freezing point of seawater (-2^{o}C) and so no modifications are needed for cold water deployments.
- A pH buffer, tris certified reference material (CRM), can now be measured when the SAMI-pH is deployed. A month long laboratory test was conducted in a variable temperature water bath (13-18 °C) sampling seawater every hour and the tris CRM every day (Figure 3). The seawater pH showed the expected variability with temperature, and declined over time during the experiment due to the respiration of organic carbon. The tris CRM accuracy and precision is ~0.001 pH units.

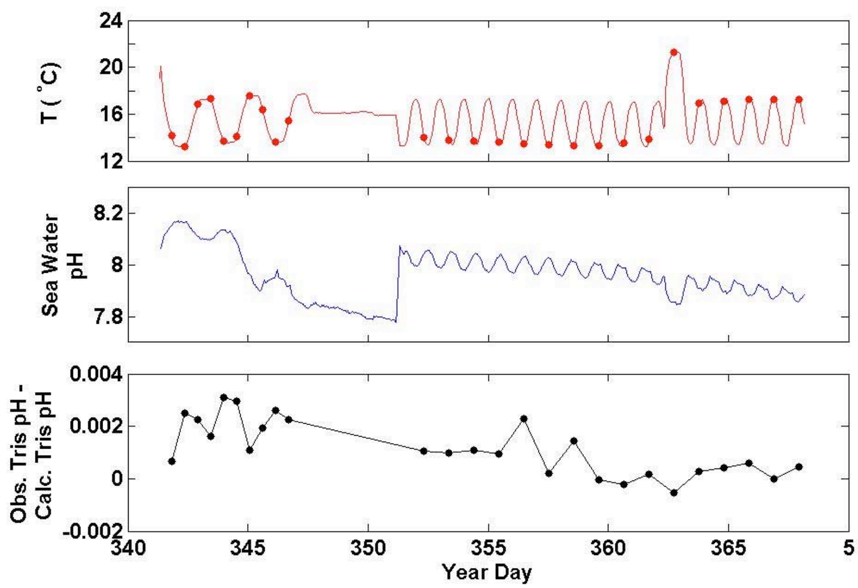
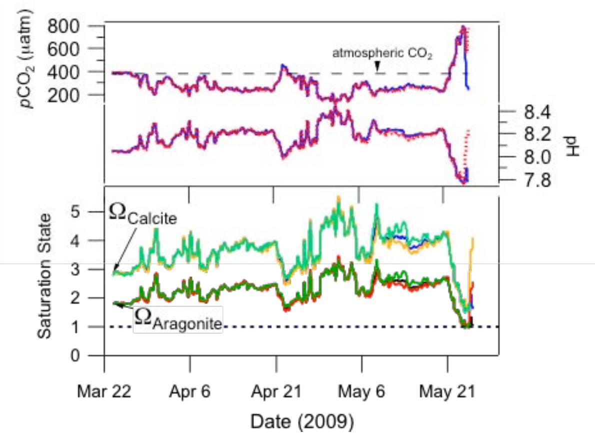


Figure 3. Data collected by the SAMI-pH sensor in a variable temperature water bath. The sensor sampled seawater hourly and a tris CRM every day. The temperature during the tris measurement is indicated by the red circles. The pH offset is the difference between the sampled tris and the calculated pH based upon the temperature relationship provided by Andrew Dickson.

Field studies: As stated above, we have collaborations that are enabling us to extensively test the SAMI-pH in the field. The most recent results have not been analyzed and we focus here on a 2009 deployment off of the Oregon coast. A SAMI-pH was deployed with a SAMI-CO_2 in surface water at the OSU NH-10 mooring. The high temporal resolution of the SAMIs (measurements every 30 minutes), captured the high pH and pCO_2 variability of the site (Figure 4). During strong upwelling events, when CO_2-rich water upwells onto the coastal shelf, pH shows sharp decreases of up to 0.4 pH units over a period of only two days, compared to much smaller changes of around 0.04 pH units during times of no upwelling. In addition to monitoring natural changes in pH and pCO_2, another objective of this field study was to further test the accuracy and utility of tandem pH and pCO_2 measurements. Using a geochemical CO_2 model, we are able to calculate pCO_2 from SAMI-pH data and alkalinity. Alkalinity was calculated from salinity measured on the NH-10 mooring using a relationship derived for California coastal waters. As can be seen in Figure 4, the calculated pCO_2 show no drift from the SAMI-CO_2 data over time. The data can also be used to calculate saturation states, important for ocean acidification studies (Figure 4).

Figure 4: Top: SAMI-CO_2 and SAMI-pH time-series (blue lines) from a mooring deployment off the Oregon coast. Using salinity-derived A_T (A_{Tsalin}) with either parameter allows calculation of the other parameter (red dotted). Bottom: saturation states calculated from the A_{Tsalin}-pH (blue, black), A_{Tsalin}-pCO_2 (orange, red) and pH-pCO_2 (light green, green) combinations.



IMPACT AND APPLICATIONS

National Security

The sensor will enable scientists to better understand the ocean carbon cycle and ocean acidification and this understanding will be used to develop future energy policy. Anything related to energy policy has implications for national security because of our dependence upon foreign petroleum and natural gas. Alterations of energy usage by U.S. and foreign governments based on scientific research enabled by our technology will be important for future national security decisions.

Economic Development

Although a small market, the SAMI-pH is the only system available and therefore we are able to dominate this market. Commercialization of the SAMI-pH has direct economic benefits for Missoula, Montana and the United States. Sales and service revenue from the instrument generate income from outside the state of Montana. Moreover, ~50% of the sales are to other countries so the product is helping to reduce the trade imbalance. Small businesses such as Sunburst Sensors are critical for economic development.

Quality of Life

Ocean acidification has the potential to affect marine ecosystems at all levels. Continuous in situ observations of the pH of the oceans will provide a comprehensive understanding of the changes caused by ocean acidification, which can then be used to inform policy makers and the public about the state of our oceans.

Science Education and Communication

As this project is a joint effort between academia and industry, it has served as a tool to educate undergraduate, graduate students and post doctoral researchers in the PI's lab. These personnel have learned about instrument design, testing, and marine science applications.

RELATED PROJECTS

A NOPP award (NSF OCE-052955) led to commercialization of an autonomous sensor for quantifying seawater pCO_2.