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Workshop Proceedings

DISSOLVED OXYGEN PROBES: MAKING OXYGEN MEASUREMENTS ROUTINE LIKE TEMPERATURE

St. Petersburg, Florida

January 4-6, 2006

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

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An ACT 2006 Workshop Report

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

Dissolved Oxygen Probes: Making Oxygen Measurements Routine Like Temperature

St. Petersburg, Florida

January 4-6, 2006

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 University of South Florida (USF) College of Marine Science.

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.

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ACT WORKSHOP: *DISSOLVED OXYGEN PROBES: MAKING OXYGEN MEASUREMENTS ROUTINE LIKE TEMPERATURE*

EXECUTIVE SUMMARY

The Alliance for Coastal Technologies (ACT) Workshop "Making Oxygen Measurements Routine Like Temperature" was convened in St. Petersburg, Florida, January 4th - 6th, 2006. This event was sponsored by the University of South Florida (USF) College of Marine Science, an ACT partner institution and co-hosted by the Ocean Research Interactive Observatory Networks (ORION). Participants from research/academia, resource management, industry, and engineering sectors collaborated with the aim to foster ideas and information on how to make measuring dissolved oxygen a routine part of a coastal or open ocean observing system.

Plans are in motion to develop large scale ocean observing systems as part of the US Integrated Ocean Observing System (IOOS; see http://ocean.us) and the NSF Ocean Observatory Initiative (OOI; see http://www.orionprogram.org/OOI/default.html). These systems will require biological and chemical sensors that can be deployed in large numbers, with high reliability, and for extended periods of time (years). It is also likely that the development cycle for new sensors is sufficiently long enough that completely new instruments, which operate on novel principles, cannot be developed before these complex observing systems will be deployed. **The most likely path to development of robust, reliable, high endurance sensors in the near future is to move the current generation of sensors to a much greater degree of readiness**. The ACT Oxygen Sensor Technology Evaluation demonstrated two important facts that are related to the need for sensors. There is a suite of commercially available sensors that can, in some circumstances, generate high quality data; however, the evaluation also showed that none of the sensors were able to generate high quality data in all circumstances for even one month time periods due to biofouling issues.

Many groups are attempting to use oxygen sensors in large observing programs; however, there often seems to be limited communication between these groups and they often do not have access to sophisticated engineering resources. Instrument manufacturers also do not have sufficient resources to bring sensors, which are marketable, but of limited endurance or reliability, to a higher state of readiness. The goal of this ACT/ORION Oxygen Sensor Workshop was to bring together a group of experienced oceanographers who are now deploying oxygen sensors in extended arrays along with a core of experienced and interested academic and industrial engineers, and manufacturers. The intended direction for this workshop was for this group to exchange information accumulated through a variety of sensor deployments, examine failure mechanisms and explore a variety of potential solutions to these problems. One anticipated outcome was for there to be focused recommendations to funding agencies on development needs and potential solutions for O2 sensors.

Workshop participants established that dissolved oxygen sensor technologies can provide reliable data in the absence of biofouling. Advancement in dissolved oxygen technology depends on improving the accuracy, endurance, and response time of existing sensors. **The main impediment to making long-term dissolved oxygen measurements in the open ocean and coastal environments is biofouling**. Additionally, participants agreed that standardized calibration procedures should be developed and implemented by skilled personnel. Participants thoroughly discussed issues with instrument drift, calibration, long-term instrument stability, and instrument accuracy and precision. Both open ocean and coastal environmental users found that sensor accuracy in suboxic waters needs to be improved. Potential solutions addressing several of these issues include: establish standardized calibration protocols for manufacturers, establish calibration facilities with skilled personnel, develop in-situ samplers for data verification, develop the ability to see data in real time in order to monitor instrument performance. Participants also agreed that it is necessary to overcome the issue of biofouling, thereby reducing the costs of operating a long-term network by reducing the required maintenance, ship costs, and man-power required to maintain the instruments. Several biofouling prevention remedies were suggested and the main recommendation is to perform a verification of biofouling prevention technologies in a controlled environment.

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.

OCEAN RESEARCH INTERACTIVE OBSERVATORY NETWORKS

The Ocean Research Interactive Observatory Networks (ORION) is a program that focuses the science, technology, education and outreach of an emerging network of science driven ocean observing systems. Building on the heritage of the ship-based expeditionary era of the last century, oceanography is commencing a new phase in which research scientists increasingly seek continuous interaction with the ocean environment to adaptively observe the earth-ocean-atmosphere system. Such approaches are crucial to resolving the full range of episodic and temporal change central to so many ocean processes that directly impact human society, our climate and the incredible range of natural phenomena found in the largest ecosystem of the planet.

The National Science Foundation formed a Cooperative Agreement with the Joint Oceanographic Institutions (JOI) to establish the ORION Project Office (PO), in order to promote the development and oversee the design, construction, installation and eventual operation of the ORION Program. To date the PO has developed the ORION Science Plan, is presently developing the overall conceptual network design, and will ultimately be responsible for generating the project execution plan and overseeing the installation and operations of this new infrastructure. The PO is advised by an extensive community-based advisory committee structure. The membership of the advisory committees come from academic, industry, government, and the international community, and includes scientists, engineers, and educators with broad, interdisciplinary expertise in ocean-related issues. For more information about the ORION Program, please visit www.orionprogram.org.

WORKSHOP GOALS

The underlying goal of the ACT/ORION workshop on making dissolved oxygen measurements routine like temperature was to identify the challenges and potential solutions that would enable users to obtain consistent, high quality data under a variety of different environmental conditions, much like temperature. Specifically, the participants were charged with the following tasks:

1) Catalogue the strengths and weaknesses of different types of oxygen sensors and their use under different environmental conditions and types of platforms

2) Provide recommendations on lessons learned and alternative solutions

3) Discuss potential solutions for impediments in existing sensors

4) Discuss other promising new technologies that are on the horizon

ORGANIZATION OF THE WORKSHOP

The workshop's organizing committee included Drs. Kendra Daly (USF/ORION), Michael DeGrandpre (UM), Holly Greening (TBEP), Ken Johnson (MBARI), Mark Luther (USF/ACT), and Scott McLean (Satlantic/ACT). **Participants represented researchers, engineers, federal/state/regional environmental managers, and industrial representatives interested in the development of more practical and robust dissolved oxygen sensors.** A list of participants is included at the end of the workshop proceedings.

The two and half day workshop commenced on the evening of January 4, 2006, where Dr. Mark Luther summarized ACT's missions and goals to the invited participants. The following morning opened with presentations from Charles Roberston from Skidaway Institute of Oceanography, Dr. Chris Langdon from RSMAS, Dr. Nancy Rabalais from LUMCON, and Dr. Arne Kortzinger from the University of Kiel all summarizing particular sensor performance obtained from their research studies or monitoring programs. After lunch, participants were then divided twice into two groups. The first division was based on the participants' area of research: coastal or open ocean. The purpose was to facilitate focused discussions on the common issues among their area of expertise regarding the charges of the workshop. Later in the afternoon, the participants separated into two mixed groups (coastal and open ocean combined). For both breakout sessions, attendees with engineering backgrounds were evenly distributed throughout the two groups. During brunch on the morning of January 6th, a chairperson from each breakout group gave a short presentation summarizing responses to the charges.

Results from the two afternoon breakout discussions led to several commonly mentioned impediments. These issues can be categorized as: *biofouling, accuracy/calibration, stability of sensor, and standardization*. Later that morning, the workshop concluded with a prioritized ranking of specific action items.

OVERVIEW OF MAKING DISSOLVED OXYGEN MEASUREMENTS

The purpose of this workshop was to build upon three previous ACT hosted functions. The first was an ACT workshop hosted by Skidaway Institute of Oceanography, January 12-14, 2004, entitled "State of Technology in the Development and Application of Dissolved Oxygen Sensors". For more information on this workshop, please visit http://www.act-us.info/workshops_reports.php where you can download the full workshop report. The second was a pilot "Dissolved Oxygen Training Workshop" co-hosted by the University of South Florida and Skidaway Institute of Oceanography, December 14-16, 2005. Additionally, ACT completed its first test and verification in the summer of 2004 on dissolved oxygen sensors. It is the hope of the community that a "best-practices" type manual come out of these functions, a first step in making dissolved oxygen measurements like temperature.

The unit of measurements referenced in the summaries below are kept in the unit quoted by the users. However if the reader would like to convert between units, the following conversion factors are given:

Oxygen	mL/L	ì mol/L=ì M	mg/L
ml/L	1	44.615	1.4276
ì mol/L = ì M	0.0224	1	0.0320
mg/L	7.005	31.251	1

I. OPEN OCEAN AND CONTINENTAL SHELF

It is impossible to give an overview of how dissolved oxygen is measured in the open ocean without discussing the issue of biofouling. The Mid-Atlantic partner of ACT, Chesapeake Biological Laboratories, hosted a workshop in November of 2003 where participants were charged with identifying problems and limitations with biofouling prevention systems that are currently available. For more information on this workshop, please visit http://www.act-us.info/workshops_reports.php where you can download the full workshop report.

The open ocean group discussed three main applications for making dissolved oxygen measurements. Each of these applications requires different specifications from the sensor and sensor platform. These are summarized below.

➢ Moorings at fixed depths
- Endurance: 6 months to 1 year
- Precision: 0.2 - 0.3 μM, this is achieved by most existing sensors
- Accuracy: <2 μM, not achieved by any existing sensor
- Long-term drift: <1 μM/year
- Response time: minutes
- Biofouling protection in euphotic zone

➢ Profilers (Argo, gliders, AUVs, moorings)
- Endurance: >2 years
- Precision: 0.2 - 0.3 μM, this is achieved by most existing sensors
- Accuracy: <2 μM, not achieved by any existing sensor
- Long-term drift: <1 μM/year
- Response time: 10-20s or better for 90% response, 1s for ship-based profiling for 99% response
- Large dynamic range: 0-700 μM
- Pressure limitations of sensor must be addressed

➢ Sediment profiling
- Microelectrodes
- High mechanical robsustness
- Precision: <1 μM
- Accuracy: not as high requirements if referenced against bottom water

Participants also discussed the need for improved sensor accuracy in low oxygen (hypoxic) waters for all applications. In suboxic waters the limit of detection needs to be less than 1 μM.

Ideas on how to meet these specifications were discussed and then classified into three main topics: biofouling, accuracy and calibration, and other. The summary of suggested biofouling preventions will be discussed separately since it was a major factor impeding the ability to measure dissolved oxygen long term in the open ocean, as well as short term in the coastal environment.

➢ Accuracy/Calibration
- Establish standardized calibration protocols for manufacturers (i.e. Winklers, calibration cells)
- Establish calibration facilities with skilled personnel

- Use O_2-free nitrogen (liquid N_2 blow off) or O_2 free seawater (NaSO3) for a zero-point check and verify Winkler titration performance at 3 μM
- Manufacturers can provide better documentation on sensor characteristics and testing
- Users should always read the manuals

➢ Other
- Manufacturers should make platforms that are suitable for biochemical sensor packages
- In situ samplers for O_2 data verification
- Make sulfide based electrolyte for O_2-depleted environments

II. COASTAL ENVIRONMENT

In this context, we are defining "coastal" as the region from the landward most extent of tidal marine influence to as far out as the outer edge of the Exclusive Economic Zone. This includes sensors affixed to a dock out to sensors incorporated into a coastal buoy system. This encompasses a wide range of environments and each of these environments poses its own obstacles in measuring dissolved oxygen. The issues that were discussed in this session are summarized below.

➢ Regulatory Agencies
- Accuracy: 0.3 to 0.5 mg/L tolerance for post-calibration, most sensors currently have: 0.2 mg/L
- Response time: minutes
- Deployment length: 60 days, biofouling limiting factor
- Limitations: manpower, translates to $$

➢ Research Institutions
- Accuracy: 0.3 to 0.5 mg/L tolerance for post-calibration, most sensors currently have 0.2 mg/L
- Response time: variable
- Deployment length: 60 days, biofouling limiting factor

➢ Calibration Issues
- In situ calibration capabilities
- Long term stability of factory ready calibration
- Temperature coefficients to determine sensor response to drastic temperature changes

Measuring water temperature in the coastal environment is currently viewed as being straightforward. Attempting to make oxygen measurements fall into the same category may require some modifications. First, the ability to see sensor data in real time can let the user know when deterioration of data quality starts and can reduce the occurrence and length of data gaps in the record. Additionally, having a spatially dense network of deployed sensors can allow intercomparisons, identify malfunctioning sensors, and also give information about larger scale variability. Unavoidably, the major obstacle to overcome is biofouling. In the absence of biofouling, users would be able to let more time lag between site visits, reducing operating costs (personnel, maintenance, ship time, etc.), leading to the ability to purchase more sensors, extending the end-user network.

The participating manufacturers were interested is standardizing instrument specifications for all users' applications. **Once the community agrees on standard specifications, manufacturers can begin to develop either more robust technologies with a factory calibration that lasts for up to one year at a higher cost, or smaller, less expensive sensors that may be less precise**. At present, the community is dealing with this issue by having different manufacturers specialize in different applications. Manufacturer participation identified the need for a market analysis to give them a sense of assurance that if they spend time and energy to meet the specific needs of the community, it will be both cost effective and useful for the maximum number of customers.

III. BIOFOULING

Marine growth on sensor heads, bodies, and on the biofouling prevention mechanism itself has been the main impediment in taking long-term dissolved oxygen measurements in both the open ocean and in coastal environments. **If the community wants to measure dissolved oxygen like we measure temperature, the biofouling issue needs to be overcome**. In all of the breakout sessions, discussions invariably turned to biofouling and the following suggestions were made.

- Sensors should be confined in pumped mode with a combination of different antifouling measures (copper tubing for sampling lines, tributyltin (TBT) cartridges, coatings, etc.)
- Generate chlorine for flushing
- Make sensors that are small so as to minimize flushing requirements
- Optimize flow-through cell design
- Develop/use miniature pumps for flushing
- Ultrasonic technologies
- Pulsed voltage
- Ultra smooth surfaces (polyetheretherketone polymer, PEEK)
- Chemicals that are time released or leach slowly over time

WORKSHOP RECOMMENDATIONS

As stated previously, we have a unique opportunity here as being the second ACT DO workshop to look at the state of dissolved oxygen sensing technology. Recommendations were made at the close of the first DO workshop as well as the Biofouling Workshop that were also brought up at the close of this workshop. Thus, we would first like to review the status of those recommendations before we summarize the recommendations from our ACT/ORION workshop.

STATUS OF PREVIOUS RECOMMENDATIONS FROM "STATE OF TECHNOLOGY IN THE DEVELOPMENT & APPLICATION OF DISSOLVED OXYGEN SENSORS"

- Provide a mechanism for objective, testing of DO sensor technology across a variety of field conditions.

ACT responded to this recommendation by performing a sensor test and verification of dissolved oxygen sensors. Four manufacturers submitted a total of eight sensors to be tested in a wide range of environmental conditions. The instruments were deployed for a 30-day test and data collected by the instruments were compared with Winkler titrations at each ACT partner site. Please visit the ACT website to download these verification statements.

- Become an 'honest broker' of the results of the technology testing and transferring the information to the broad user community.

ACT accomplished this by making the dissolved oxygen sensor verification statements publicly available for the users.

- Encourage and facilitate interactions between managers and industry to improve the dialogue to get the appropriate sensors developed.

ACT workshops are designed to create a forum for both users and manufacturers to discuss sensor requirements. Two ACT partners, SkIO and USF, held a DO Training session in Orlando, Florida December 14-16, 2005 where five manufacturers had the opportunity to speak with trainees to discuss current available technologies and catalogue user needs.

- Work with regulators and managers to determine the level of precision that is required in DO measurements, with the aim of working with industry to develop a cheaper, disposable (but less precise) DO sensor technology and to compile specifications required for different applications.

The goal of this current workshop report is to summarize the level of precision required by particular applications.

STATUS OF PREVIOUS RECOMMENDATIONS FROM "BIOFOULING PREVENTION TECHNOLOGIES FOR COASTAL SENSORS/SENSOR PLATFORMS"

To date, ACT has not become involved in tackling any of the proposed suggestions from this previous workshop.

RECOMMENDATIONS FROM "MAKING DISSOLVED OXYGEN MEASUREMENTS ROUTINE LIKE TEMPERATURE" WORKSHOP

At the close of the workshop, the participants constructed an itemized list of recommendations that would facilitate advances in making routine measurements of dissolved oxygen. These recommendations were prioritized in order of importance by vote of all participants, with each participant having 5 votes to cast.

General Recommendations:

1. Perform side by side biofouling prevention test in matrix of environmental conditions (eg. Surface roughness technologies, time released chemical compounds) in order to evaluate the effectiveness of these biofouling technologies. Perhaps this could be funded by NOPP. (22)
2. Locate funding for new technologies. (18)
3. Develop sensors and instrumentation that provide in situ calibration. (13)
4. Generate standard operating procedures (SOP) or a best practices manual that can be distributed to a wide audience. This could be an ACT/CSC/ORION responsibility. (11)
5. Create more training opportunities. (9)
6. Perform long term study on stability of sensor in absence of biofouling. (7)
7. Create standardization of manufacturers' specifications. (5)
8. Develop sensors with faster response time (0.5 seconds) for eddy flux studies. (5)
9. Manufacturer to provide accuracy of at least 2 ?M with factory calibration. (5)
10. Encourage more manufacturers to use flow through or pumping technology. (4)
11. Develop disposable dissolved oxygen heads. (3)
12. Create ante chamber prototype for biofouling technique development. (3)
13. Encourage EPA approval for new technologies. (3)
14. Facilitate more communication and collaboration between end user and manufacturer. (1)
15. Synthesize user needs. (0)

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