

Workshop Proceedings



**State of Technology in the Development and
Application of Dissolved Oxygen Sensors**

*Savannah, Georgia
January 12-14, 2004*



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

An ACT 2004 Workshop Report

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

State of Technology in the Development and Application of Dissolved Oxygen Sensors

Savannah, Georgia
January 12-14, 2004



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 Skidaway Institute of Oceanography (SkIO), University System of Georgia in Savannah, Georgia.

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: STATE OF TECHNOLOGY IN THE DEVELOPMENT
AND APPLICATION OF DISSOLVED OXYGEN SENSORS**

EXECUTIVE SUMMARY

The Alliance for Coastal Technologies (ACT) convened a Workshop on the Development and Application of Dissolved Oxygen Sensors in Savannah, GA on January 12 to 14, 2004. The workshop was designed to summarize the state of technology and make strategic recommendations for the future development and application of dissolved oxygen (DO) sensors for coastal environmental research and monitoring. The workshop focused on the available DO technology and newer developing technology, including strengths and weaknesses, desirable features for DO sensor technology and *in situ* measurements, technological needs for reliable and accurate DO measurements, and mechanisms for overcoming barriers to development of adequate DO sensors and their incorporation into routine monitoring strategies. Participants (Appendix I) included researchers using DO sensors in studies of oxygen dynamics of estuarine and coastal waters, coastal water quality managers, and industry representatives.

The value of DO measurements is well accepted by researchers and managers, who are currently making these measurements as (1) point measurements, at a specific location and depth, (2) profiles of continuous change in DO with depth through the water column, or (3) continuous measurements at a specific location and depth in a deployed mode. Vertical profiles may take the form of (a) vertical casts from a CTD deployed shipboard, (b) undulating horizontal and vertical mode from a towed or autonomous vehicle, or (c) continuous vertical profiling at a single location according to an automated system with a predetermined temporal sequence. Despite the need for long-term *in situ* DO measurements to understand oxygen dynamics and overall water quality conditions in estuarine and coastal waters, few local and state agencies use moored DO sensors for their routine monitoring. DO sensors are considered to be unreliable for long-term deployments, can be difficult to maintain and calibrate, and require a significant effort in personnel to manage moored observational programs. Part of this perception is due to real technological issues with the commercially available DO sensors. Part of this, however, comes from the inherent inertia on the part of monitoring programs that results in resistance to change.

Two general recommendations concerning needed technological advances for DO sensors and one for the role of ACT in facilitating the development of technology and application of DO sensor technology were made. Details for each recommendation follow in the report.

- The use of electrochemical probes will likely continue, because many local, state, and federal agencies have invested in this type of instrumentation. While there remain problems, technological improvements can reduce the amount of biofouling, extend

battery life for longer deployments, improve response time, and develop technology for internal compensation for drift.

- The relatively new and developing luminescence technology of optical probes addresses several of these problems, but others remain, or new ones become relevant, such as: verification of reliability of long-term data (e.g., 6 months to 1 year), need for improved response time, development of technology for internal compensation for drift, and ease of use and integration with other parameters.
- ACT can serve as an active promoter of increased use of in situ DO sensors, a communicator of unbiased specifications and comparative test results, a facilitator for bringing industry and users together to develop DO sensor technology that suits the needs of the users yet maintains a healthy income for the manufacturers, and promoter and facilitator for standard DO sensor data format.

ALLIANCE FOR COASTAL TECHNOLOGIES

There is widespread agreement that an Integrated Ocean Observing System 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 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.

GOAL FOR THE DISSOLVED OXYGEN SENSOR WORKSHOP

The ACT Workshop on Dissolved Oxygen Sensors was convened on January 12 to 14, 2004 in Savannah, GA to summarize the state of technology and make strategic recommendations for the future development and application of dissolved oxygen sensors for coastal environmental research and monitoring.

Workshop attendees were given the following charges to address:

- (1) What are the commercial-ready technologies for dissolved oxygen (DO) sensing and what are their strengths and weaknesses regarding application to coastal environmental research, monitoring and management?
- (2) What are the major impediments to the deployment of DO sensors?
- (3) What are some of the emerging technologies for DO sensing and how do they address weaknesses of existing technologies?
- (4) What are the characteristics of an ideal DO sensor for application to coastal environmental resource monitoring and management? And what are technology, infrastructure and other limitations that impede the development of such sensors?

ORGANIZATION OF THE DISSOLVED OXYGEN SENSOR WORKSHOP

The workshop was sponsored by ACT and hosted by the Skidaway Institute of Oceanography, one of ACT's Partner Institutions. Dr. Herb Windom, Skidaway Institute of Oceanography, Dr. Nancy Rabalais, Louisiana Universities Marine Consortium, and Dr. Richard Burt, Chelsea Instruments organized the workshop. Dr. Rabalais served as Facilitator and drafted the report. Participants arrived on Monday afternoon, January 12, and gathered that evening for a reception and dinner during which a presentation by Dr. Mario Tamburri was given to introduce the ACT program. The workshop commenced with an introduction to the problem by Dr. Nancy Rabalais followed by three breakout group discussions to address the first two charge questions. The first groups were organized according to researchers, managers, and industry representatives. Afternoon breakout groups to discuss the remaining charge questions were mixtures of the morning breakout groups. The final half-day was devoted to identifying common issues and developing recommendations. Participants provided a representation among research scientists, water quality managers, resource managers, and industry representatives. It should be noted that some information regarding certain technologies was not available to the workshop participants because key industry representatives were not present.

DISSOLVED OXYGEN CONDITIONS IN COASTAL WATERS, STATEMENT OF PROBLEM

There is little doubt that human population growth and its associated activities have increased the flux of nutrients essential for plant growth to coastal waters at accelerating rates during the last half of the 20th century (Vitousek et al., 1997). There are thresholds of nutrient loading above which the nutrient inputs no longer stimulate entirely positive responses from the ecosystem, such as increased fisheries production. Instead, land- and air-based sources of nutrients are causing problems, for example, poor water quality, noxious algal blooms, oxygen depletion and in some cases, loss of fisheries production. While hypoxic (low oxygen) environments have existed through geologic time and are common features of the deep ocean or adjacent to areas of upwelling, their occurrence in estuarine and coastal areas is increasing, and the trend is consistent with the increase in human activities that result in nutrient over-enrichment. No other environmental variable of such ecological importance as dissolved oxygen has been so drastically changed by human activity, in such a short period of time (Diaz and Rosenberg, 1995). Within the last 40 to 50 years, the oxygen conditions of many major estuarine and coastal ecosystems around the world have been adversely affected (Figure 1). Where oxygen deficiency was not present before, it is now a periodic or recurring event. Where present before, it is more severe, either in duration, intensity, or spatial extent than historically.

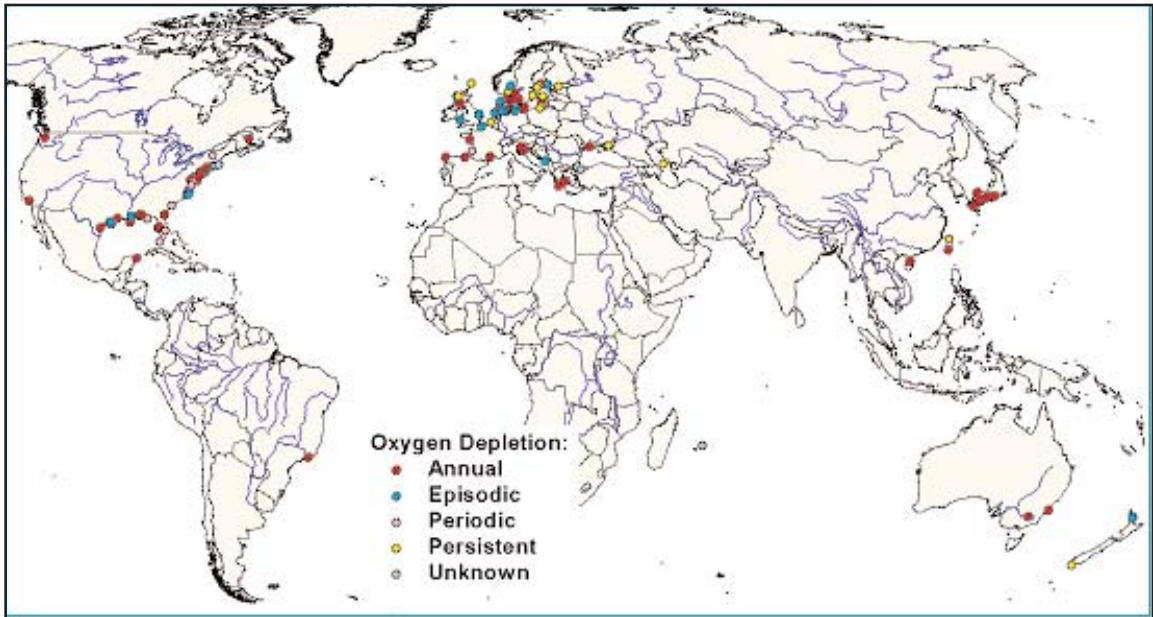


Figure 1. The global distribution of oxygen depletion events as summarized by Diaz et al. (in press), n = 146.

There is clear evidence for the increase or worsening of hypoxia (low-oxygen) in coastal waters worldwide, e.g. the northern Gulf of Mexico influenced by the Mississippi River discharge (Rabalais et al., 2002), coastal areas of the Baltic Sea (Rosenberg, 1985), the northwestern shelf of the Black Sea (Tolmazin, 1985; Mee, 2001), Chesapeake Bay (Officer et al., 1984; Cooper and Brush, 1991), the German Bight and the North Sea (Dethlefsen and von Westernhagen, 1983), and Long Island Sound (O'Shea and Brosnan, 2000). Oxygen deficiency is also a common event in estuarine waters throughout the U.S., with the occurrence being more prevalent in estuaries of the southeastern and Gulf coasts (Figure 2).

The measurement of DO over time provides the evidence that oxygen conditions have worsened in estuarine and coastal waters. These data are often supplemented with paleoindicators of increased primary production and worsening oxygen conditions that follow a similar time line. Measuring DO provides an integrative measurement of community metabolism, and thus an overall 'health' status of the community. Research on the dynamics of oxygen deficiency aim to provide a better understanding of the physical, chemical, and biological processes that lead to its development, maintenance, and abatement. Low DO environments also provide unique areas to study biogeochemical processes under reduced, minimal, or no oxygen conditions. DO measurements provide data to develop standards for water quality criteria that are protective of designated uses, assessment of compliance to the subsequent water quality criteria, standards for development of TMDLs (total maximum daily loads that maintain water quality standards), and information to develop mitigation measures to improve oxygen conditions.

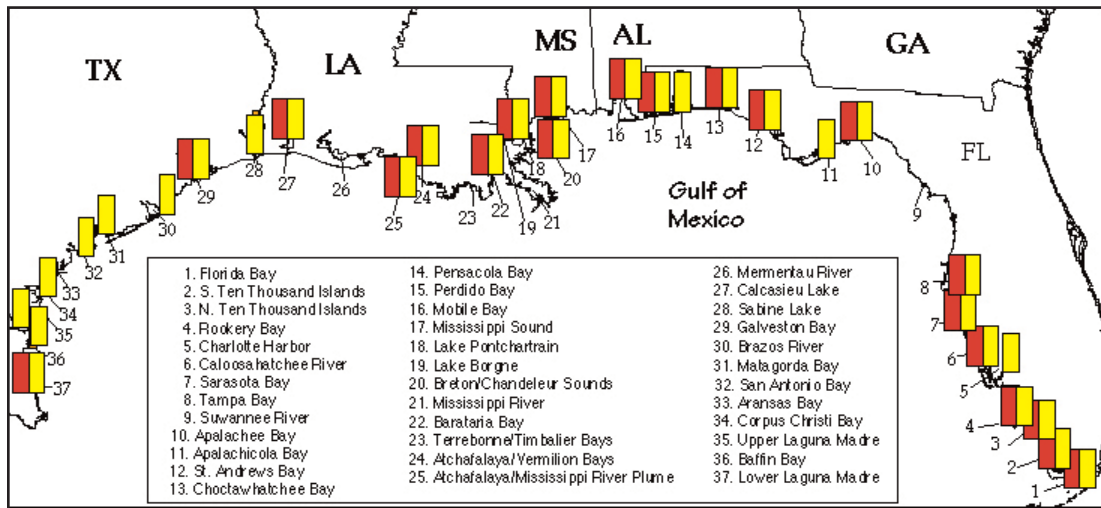


Figure 2. Distribution of estuaries in the Gulf of Mexico that periodically experience hypoxia (yellow) or anoxia (red) at some time during the year (Bricker et al., 1999)

THE NEED FOR *IN SITU* DISSOLVED OXYGEN MONITORING

The concentration of dissolved oxygen, in water at any particular place or time, integrates community metabolism (the oxygen present as a result of both photosynthetic and respiratory processes) and can be used to characterize a water body as autotrophic (oxygen producing) or heterotrophic (oxygen consuming). DO, as an integrative measurement, is useful for understanding the dynamics of an aquatic community, comparing water bodies (temporally and spatially), and assessing their suitability for support of living resources. DO measurements across a range of physical and chemical parameters are necessary for the development of appropriate DO criteria for water quality conditions that will support and sustain living resources. Long-term measurements of DO in conjunction with field surveys, behavioral observations, and physiological measurements are needed to develop these criteria. More recent water quality criteria consider the frequency and duration of DO concentration fluctuations on various life stages or organisms rather than a fixed minimum concentration [Ambient Water Quality Criteria for Dissolved Oxygen (Saltwater): Cape Cod to Cape Hatteras (EPA 822-D-99-002)]. The ability to reliably monitor DO is key to the development of criteria, AND the subsequent assessments as to whether the criteria are being met.

DO measurements can be (1) point measurements, at a specific location and depth, (2) profiles of continuous change in DO with depth through the water column, or (3) continuous at a specific location and depth in a deployed mode. Vertical profiles may take the form of (a) typical vertical casts from a CTD deployed shipboard, (b) undulating horizontal and vertical mode from a towed or autonomous vehicle, or (c) continuous vertical profiling at a single location according to an automated system with a predetermined temporal sequence.

Characteristics of coastal waters compared to open oceanic systems make the measurement of DO more problematic. Coastal waters vary in salinity from the fresh end member at head of tide to saline conditions of continental shelves and have a greater range in temperature than more stable oceanic waters. The amount of oxygen dissolved in water (percent oxygen saturation) is dependent on both temperature and salinity, and thus availability of oxygen levels for organisms will vary according to these parameters. Gradients in salinity, temperature, and DO in coastal systems may be abrupt on horizontal, vertical, and temporal scales. The ability to record these changes is a desired feature of DO sensor technology.

Improved DO sensor technology that provides accurate and reliable data over long-term deployments is critical to the development of DO criteria, which are currently problematic because of lack of standardization and inherent system-specific variation. Interpretations of DO measured horizontally (station 'representativeness'), vertically (change, or not, with depth) and temporally (during a diel or seasonal cycle) are required for a synthetic understanding of the oxygen dynamics of a water body (Figure 3).

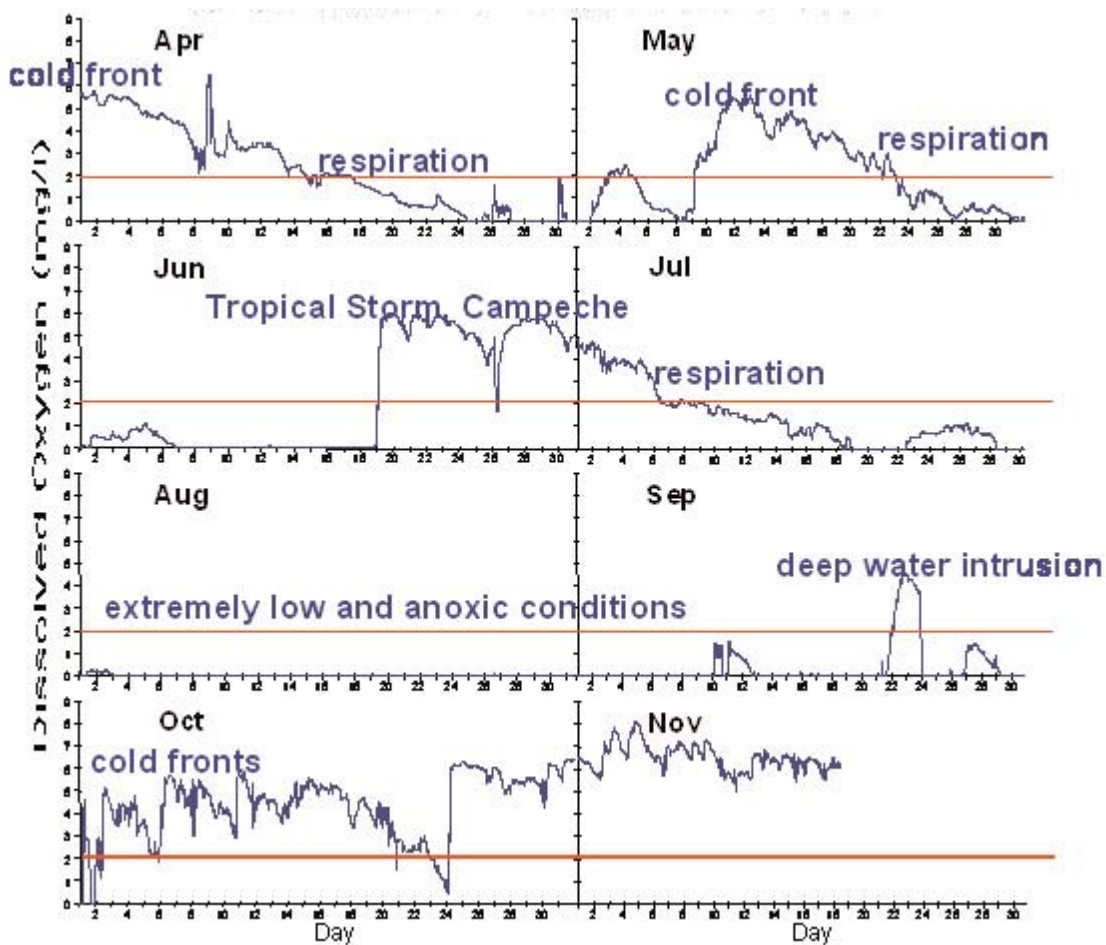


Figure 3. Long-term bottom-water DO in 20 m water depth on the continental shelf west of the Mississippi River can be coupled with meteorological, current, temperature and salinity data to identify the interaction of physical and biological processes that lead to low DO. The data are

from Apr - Nov 1993. The red line defines hypoxia as 2 mg/L ($\approx 20\%$ oxygen saturation). Wind mixing from cold fronts and tropical storms disrupts stratification and hypoxia. As stratification reforms, respiration during decomposition of organic matter in bottom waters occurs at a rate faster than DO can diffuse from surface waters across a strong pycnocline. Bottom current direction and colder, saltier water in late Sep indicated that higher DO was advected across the oxygen meter from deeper water. Data source: N. Rabalais, LUMCON.

The value of DO measurements is well accepted by managers and researchers; many are making these measurements in one form or another already. Cost is always an issue for water quality managers, both in the instrumentation and the personnel to calibrate, maintain, and deploy instruments and to manage, analyze, and synthesize DO data. Few state agencies use moored DO sensors for their long-term monitoring, but rather for special studies. The major impediment is the large degree of servicing that is required, which represents costs and a dedicated workforce. Secondly, an impediment is data comparability, data quality assurance, and data reliability. Technological advances that address these issues in DO measurements will further our ability to understand the oxygen dynamics of coastal systems and to develop and assess suitable water quality criteria based on DO.

The ability to measure the flux of DO across the sediment-water interface in in situ benthic flux chambers requires similar sensor technology as profiling or deployed DO sensors. However, this avenue of inquiry, as opposed to DO monitoring in coastal environments, is not a focus of this report. Similarly, gradients in DO with depth in sediments require more specialized microprobes, which, while intriguing, are not the types of DO measurements addressed here.

STATE OF DISSOLVED OXYGEN SENSOR TECHNOLOGY

- Available technologies

Many oceanographers have worked their way through the ranks titrating chemicals to determine dissolved oxygen concentration by the Winkler redox method. This method or modifications of it (Mettler, 1888; Parsons et al., 1984; WOCE standard protocol by Culberson, 1991, for dissolved oxygen that follows Carpenter, 1965) has been the standard since the 19th century, and has provided consistently derived values for determination of ecosystem-level change in many coastal environments. For example, Justic et al. (1987) and Justic (1988, 1991) used Winkler data from the early 1900s through 1984, coupled with Secchi disk depth and nutrient loads, to document eutrophication and worsening bottom-water hypoxia in the northern Adriatic Sea. Gone are the days of careful dripping of titrant for a visual starch endpoint. Automatic titrators (e.g., Mettler Metrohm potentiometric titrator) now provide an accurate (± 0.03 mg/L) and fairly rapid chemical measurement, which serves as the reference against which the accuracy of DO sensors is compared.

The commercially available sensor technologies that measure dissolved oxygen are galvanic, polarographic, and optical. These are all proven technologies currently available on a commercial basis.

- Galvanic sensors produce a millivolt output proportional to the oxygen present in the medium in which it is placed. The galvanic probe principle was introduced by Macreth in 1964. The main advantage of a galvanic probe is that it does not need an external power supply to provide polarization as required by the Clark Cell (see below). This is achieved by using two dissimilar metals. In the presence of an electrolyte, there is an electromotive voltage produced between the two metals. At approximately 800 mV, this is large enough to reduce the oxygen at the cathode. If lead and gold or lead and silver is used, the differential voltage is approximately 800 mV. Hence, a galvanic probe is really a self-polarizing amperometric cell. The biggest advantages are that the cell is always ready and that there is no warm up time.
- There are many manufacturers of galvanic cells for field and lab bench applications; among them are: Hach 5740, OxyGuard 2710, Sentek Model 650, Dryden Aquay, Eutech Instruments, General Cybernetics.



Figure 4. Example of galvanic cell for dissolved oxygen.

- Polarographic sensors are electrochemical detectors that are polarized and depolarized so that oxygen is reduced in the electrolyte separated from the medium by a membrane. The electron flow rate (coulombs) is proportional to the oxygen partial pressure in the medium. The electrochemical method of measuring DO requires a cathode, anode, electrolyte solution and a gas permeable membrane. The material of the membrane is specially selected to permit oxygen to pass through. Oxygen is consumed by the cathode that creates a partial pressure across the membrane. Oxygen then diffuses into the electrolyte solution. Dr. Clark first discovered the cell to measure oxygen in 1956. This is basically an amperometric cell that is polarized around 800 mV. This cell is built around the popular Ag/AgCl half-cell and a noble metal such as gold, platinum or palladium. Reduction of oxygen is achieved between 400 to 1200 mV, hence a need for a voltage of around 800 mV. This is provided externally by a battery source. The polarization sequence may be steady-state or pulsed. Factory-calibration is required for some; others can be calibrated in the laboratory. Verification of calibration by Winkler titration is often part of the process.

- Examples are Hach/Hydrolab, SeaBird, Beckman, Stevens/Greenspan, YSI, Orion, and LaMOTTE for the steady-state, and YSI 6000 series for the pulsed.

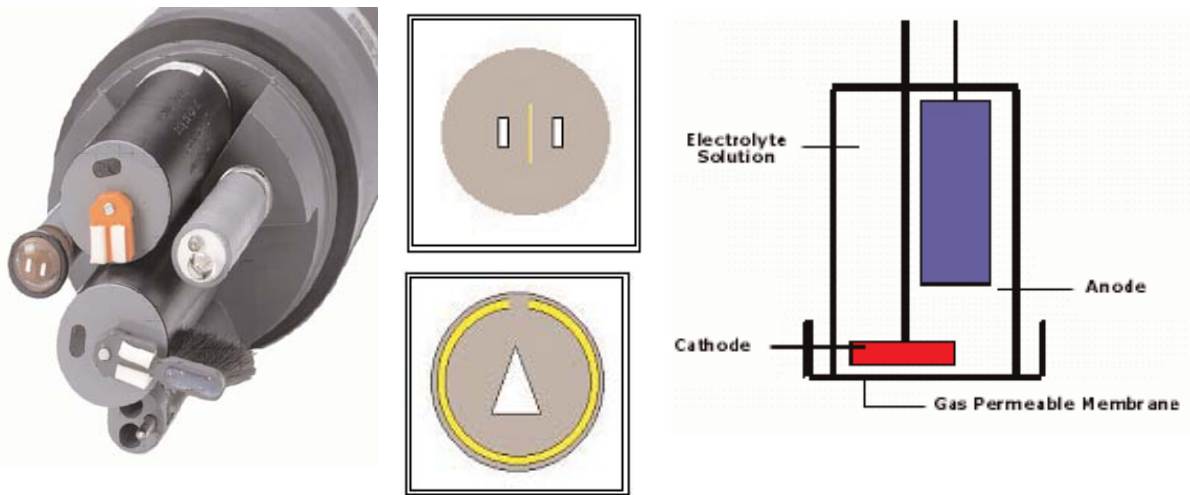


Figure 5. Left: Polarographic probe in a YSI6600 EDS sonde (clockwise from bottom), temperature/ conductivity, turbidity, Rapid Pulse™ dissolved oxygen sensor, chlorophyll, and pH/ORP; Clean Sweep™ universal wiper assembly cleans all by conductivity. Center upper: anode and cathode configuration in YSI 6600 DO sensor. Center lower: anode and cathode configuration in Hydrolab 4a. Right: diagram of Clark cell.

- Optical sensors are based on dynamic fluorescence quenching. When a specially-designed chemical complex is illuminated with a blue LED, it will be excited and emit back a red luminescent light with a lifetime that directly depends on the ambient oxygen concentration. Linearizing and temperature compensation determines absolute oxygen concentration in the medium. Probes are factory calibrated.
- Examples are Aanderaa RCM MkII, Hach LDO, Environ Systems, VanEssen marketed in North America under Solinst, and FOXY Fiber Optic Oxygen Sensor.



Figure 6. Two examples of optical probes: left, Aanderaa optode; right, Hach LDO.

- Strengths and weaknesses

Differences in technology for measuring DO leads to variability in several characteristics necessary for use in coastal and oceanic systems. Polarographic sensors reduce the concentration of dissolved oxygen during the polarization/depolarization process, and therefore are flow-dependent. To avoid DO depletion at the membrane, a flow must be created across the membrane by pumping, stirring, or manual agitation of the medium. A pulsed probe rapidly polarizes ('on' for 40 msec) and depolarizes ('off' for 3960 msec) during a measurement sequence, and thus avoids the continual local depletion of oxygen at the membrane surface of a steady state sensor. The membrane technology prevents long-term deployment (limited life of probe reliability before recalibration is required), especially where biological fouling is a problem. There is also a limited life of a polarographic probe. Galvanic and polarographic probes are less stable over long periods than optical probes. Galvanic sensors have low flow dependence; optical sensors have none since they do not consume oxygen. Variability in the response time ranges from slow for galvanic to medium for polarographic and fast for optical. Galvanic and polarographic probes measure DO more accurately in the high range than optical probes do, while the opposite is the case for optical sensors in the low range. Optical sensors, while offering better accuracy and less maintenance, are not presently integratable with common CTDs; salinity is a necessary measurement for determination of percent oxygen saturation. The reliability of long-term measurements from optical probes is not yet proven.

Variable	Galvanic	Polarographic Steady State	Polarographic Pulsed	Optical Steady State	Optical Life
Flow dependence	Low	High	Low	None	None
High pressure hysteresis (over 500 m)	Yes	Yes	Yes	No	No
Response time (to 90%)*	Slow	Medium	Medium	Fast	Fast
Range (0-2008)	Yes	Yes	Yes	Yes	Yes
low end (0-1 ppm)	+	+	+	++	++
high end (20 ppm)	++	++	++	+	+
Long term stability	+	+	+	++	++
Frequency of maintenance	High	High	High	Low	Low
Calibration					
zero point required	No	No	No	No	No
factory or labor atory	F	F/L	F/L	F	F
difficulty	N/A	Medium	Medium	N/A	N/A

*Slow ≈ 7 minutes, Medium < 1 to 3 minutes, Fast < 1 minute

++ indicates better performance than +

The performance of current, available technology is often mixed. Manufacturers can achieve good results in the laboratory and as a sensor and sensor-package are produced. The subsequent

performance and reliability may degrade once delivered dependent on the reliability of the instrument and the skills of the customer. The standard operating procedures and the training of the individual following those procedures for calibration of the DO sensor are critical to how successful the calibration and subsequent data collection will be. How the instrument is handled in the field and whether proper field procedures are followed will also influence the quality of data collected. Some are well-versed in the use of DO sensors; others are not. The results in the latter case are often poor data.

- What is needed in DO sensor capabilities?

Many of the requirements for a DO sensor are the same as required for any other sensor, but some are specific to DO measurements:

- accuracy (± 0.04 mg/L)
- precision (± 0.004 mg/L)
- qualified over -5 to $+35$ °C, 0 to 65 psu salinity
- minimal drift in measurement
- adequate response time for rapidly changing conditions
- data output rate that can be set by the user and/or polled
- standard data transmission protocols, such as RS-235, RS-485
- ability to telemeter data for real-time capabilities
- ease of calibration
- ease of maintenance
- internal performance diagnostics
- adaptability to incorporate in modular systems, i.e. 'plug and play'
- standard data formats in addition to existing proprietary data formats for raw oxygen, temperature, and salinity data; corrected oxygen value as mg/L, μ M/L, and percent saturation; data logger or post processing performs all calculations
- smaller is always better, especially for incorporation into larger packages (e.g., AUVs, autonomous underwater vehicles)
- reliability of maintenance and service from supplier
- technical support from supplier

- What is needed for the long-term deployment of DO sensors?

Many of the requirements for deployment of DO sensors are similar to that required for the deployment of other physical, chemical, or biological sensors:

- adequate power for long-term deployments
- adequate data storage for long-term deployments
- reliability for long-term deployments (6 months to 1 year), OR
- 'self-correcting' performance test circuitry to compensate for drift (internal standard)
- less than 2% drift over a 6-mo deployment in coastal/estuarine waters, and a 1-yr deployment in the open ocean
- reasonable cost per unit so that multiple units can be deployed
- resistance to biofouling
- rugged

- reasonable logistical costs (platforms, personnel) for deployment, recovery, maintenance

- Emerging technologies that address existing limitations

Most of the technologies that address the limitations of existing DO sensors are currently employed in various instruments. The rapid achievement of an equilibrium reading after a step change in DO concentration (i.e., fast response time for profiling instruments) is currently available in optical sensors. For polarographic sensors, there are software routines that can be applied to vertical profiling data that can accommodate the delay in response of the DO sensor to the temperature and salinity sensors. While this is not a solution to rapid response, it is a mechanism for generating adequately paired, discrete depth data.

The pulsed polarographic probes require less power and extend the time period of accurate determinations. Combinations of (1) wipers across oxygen sensor membranes of polarographic probes, (2) the use of antifouling agents on probe bodies, membranes, wiping mechanisms, and housings, (3) reducing the exposure of the DO probe to the environment and fouling organisms by pumping water across the probe, and (4) encasing of probes in copper hardware have provided mechanisms for extending the life of a single DO sensor deployment due to the effects of biofouling. Fortunately, biofouling is not an issue for the reliability, accuracy, and limited drift of temperature and salinity sensors that are a necessary component of a DO 'package.'

Technology that currently exists but which is not yet incorporated into many DO sensor deployments is the optical or luminescence quenching-based technology. These sensors have no membrane, no electrolyte, no cathode or anode, and are not flow-dependent or susceptible to H₂S poisoning. They are resistant to common modes of degradation from biofouling. Hysteresis as a function of pressure is obviated by the optical sensors, but this is not an issue in the coastal waters. The response time is ~ 10 sec to 90%. There is a single replacement 'part' that is quickly interchangeable. These sensors respond best at low DO concentrations, which is a positive feature when studying hypoxia, but the lack of a similar response at high DO concentrations makes them less suitable for studying the oxygen dynamics of high productivity in surface waters. Both measurements are required for determining the metabolic state of the water body and its change over time. The long-term stability of the optical sensor can be compromised with the intensity method due to bleaching of the foil substrate. Technologies developed for DO sensors that were destined for application in other markets than profiling or *in situ* DO measurements (e.g., wastewater monitoring in fresh water systems) can be converted to coastal and marine applications. As such, these would correct some of the shortfalls of current coastal and marine DO sensors. The technology of optical luminescence is seen as the most likely candidate for reliable, long-term DO measurement. However, the development of long-term data sets that support this observation is required.

- Other impediments

Impediments to new sensor technology development for improved DO measurement are not just improved sensing technologies. There are factors that relate to the customer (water quality managers and researchers) and manufacturers. There may be funding limitations for expansion

of programs or purchase of new or upgraded equipment purchases. Agencies are often limited to approved vendor lists or require special appropriations for large equipment purchases. The customer could aid by (1) expressing the market needs more clearly, (2) consolidating purchases and demonstrating longer-term equipment needs, and (3) reducing change inertia. These changes with the customer would attract industry and thus provide incentive to industry for innovation. Industry could also assist by (1) making it less expensive to trade in or upgrade existing equipment and (2) facilitating the education of technicians in calibration and operational procedures.

Water quality and resource managers are not using DO sensor technology to the extent possible. Managers' needs depend more on regulatory requirements and the monitoring needed to assess compliance. There remain many water quality monitoring programs based on grab samples that are chemically titrated or minimal measurements in time and space with probes. States are required through the Clean Water Act to assess the quality of their waters on a regular basis. EPA issues guidelines to states on how to assess and prepare 305b reports biannually that are then consolidated into a report to Congress on the status of the Nation's waters. Limited temporal and spatial monitoring is less costly, but does not provide data necessary to properly characterize a water body. Recent guidance that emphasizes a statistical approach to randomly sample various resources types should be re-assessed with regard to the significance and benefits of time series monitoring versus discrete sampling for improving ecological assessments.

CONCLUSIONS/RECOMMENDATIONS

The value of DO measurements is well accepted by researchers and managers, who are currently making these measurements in one form or another, and there are both similarities and differences in the needs for DO sensors between researchers and managers. Research tends toward more application-specific configurations, tailored for sampling requirements of a particular study, and water quality managers' instrumentation and monitoring needs are tailored for assessment and management. Accuracy and dependability are needed by both researchers and managers. The desired dependability is on the order of present conductivity sensors, with a reduction in the requirement for validation sampling. This is a long-standing need that has had slow progress to date. To improve the quality of DO measurements and broaden their use in water quality monitoring, both industry and the user communities can contribute to future improvements. Improved technology should promote broader use. Instrumentation needs to reduce drift from calibration, be capable of longer deployments, be easier to calibrate and maintain, and cost less. Cost savings from reliable long-term DO sensor deployments could easily offset personnel and travel costs used to collect discrete samples that reveal little about variability.

The use of electrochemical polarographic probe technology will likely continue, because many local, state, and federal agencies have invested in this instrumentation. While there remain problems, technological improvements can

- reduce amount of biofouling for longer deployments

- extend battery life for longer deployments
- verification of reliability of long-term data (e.g., several months) before users can be assured to commit to long-term deployments
- improve response time
- ease of calibration and maintenance
- develop internal compensation for drift

The new luminescence technology of optical probes addresses many of these problems, but others remain to be addressed, such as

- verification of reliability of long-term data (e.g., 6 months to 1 year) before users can be assured to commit to long-term deployments
- internal compensation for drift
- ease of data translation and intercomparability
- integration with other parameters, e.g., salinity, in vivo fluorescence, turbidity, in sensor packages

ACT can play an active role in the advancement of technology through

- Providing a mechanism for objective, comparative testing of DO sensor technology across a variety of field conditions.
- Being an 'honest broker' of the results of the technology testing and transferring the information to the broad user community.
- Developing an ACT 'Performance Verification' as a potentially important step in getting DO sensors and newer technologies accepted for broad use and adoption as approved standard methods, starting the adoption process.
- Encouraging and facilitating interactions between managers and industry to improve the dialogue to get the appropriate sensors developed.
- Working 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.
- Compiling specifications required for different applications, e.g., time-series, profiling, and continuous undulating spatial sampling.

The role of ACT is in the development and implementation of sensor technologies for monitoring and studying coastal systems. Several concerns raised at the workshop, however, might benefit from ACT's facilitation of communication.

- Adequate time scales are not being used for water quality assessment.
- Managers and researchers that are involved in monitoring fresh water, estuaries and coastal waters need standardized QA/QC procedures for data collection and reporting.
- Federal agencies, such as NOAA, USGS, and EPA should coordinate where possible to establish compatible standard QA/QC and reporting formats.
- The existence of standard data output formats for dissolved oxygen probes would make them easier to incorporate into data logging systems and distributed networks. A standard data format would greatly advance the modularity of a dissolved oxygen sensor and its usage.

- Considerable DO data exist that document rate of change over time. These data can be used for more than just documentation of conditions, such as use in determining net ecosystem metabolism and oxygen and carbon budgets. As more and better DO data are collected, it is imperative that managers know how to interpret and use these data for assessing water quality.

Beyond the scope of sensor technology and development, ACT can be an active communicator and facilitator of information exchange by

- Encouraging EPA and other monitoring agencies to develop a standard for data collection, quality, and assurance for DO measurements. Involve the industry in these standard developments.
- Serving as an interface between users and industry in the development of a standard DO sensor data format.
- Being a source of example DO data (obtained with specific technology) that spans a range of conditions (abrupt changes, strong gradients, variable temperature and salinity, broad range of DO values, etc.).
- Designing and conducting workshops for managers on the appropriate applications of time series data from DO sensors.
- Educating managers at the state and federal agency level to affect a shift from discrete to time series sampling.

SUMMARY

The value of DO measurements is well accepted by researchers and managers, who are currently making these measurements as (1) point measurements, at a specific location and depth, (2) profiles of continuous change in DO with depth through the water column, or (3) continuous measurements at a specific location and depth in a deployed mode. Vertical profiles may take the form of (a) vertical casts from a CTD deployed shipboard, (b) undulating horizontal and vertical mode from a towed or autonomous vehicle, or (c) continuous vertical profiling at a single location according to an automated system with a predetermined temporal sequence. Despite the need for long-term *in situ* DO measurements to understand oxygen dynamics and overall water quality conditions in estuarine and coastal waters, few local and state agencies use moored DO sensors for their routine monitoring. DO sensors are considered to be unreliable for long-term deployments, can be difficult to maintain and calibrate, and require a significant effort in personnel to manage moored observational programs. Part of this perception is due to real technological issues with the commercially available DO sensors. Part of this, however, comes from the inherent inertia on the part of monitoring programs that results in resistance to change.

Two general recommendations concerning needed technological advances for DO sensors and one for the role of ACT in facilitating the development of technology and application of DO sensor technology were made.

- The use of electrochemical probes will likely continue, because many local, state, and federal agencies have invested in this type of instrumentation. While there remain problems, technological improvements can reduce the amount of biofouling, extend battery life for longer deployments, improve response time, and develop technology for internal compensation for drift.
- The relatively new and developing luminescence technology of optical probes addresses several of these problems, but others remain, or new ones become relevant, such as: verification of reliability of long-term data (e.g., 6 months to 1 year), need for improved response time, development of technology for internal compensation for drift, and ease of use and integration with other parameters.
- ACT can serve as an active promoter of increased use of in situ DO sensors, a communicator of unbiased specifications and comparative test results, a facilitator for bringing industry and users together to develop DO sensor technology that suits the needs of the users yet maintains a healthy income for the manufacturers, and promoter and facilitator for standard DO sensor data format.

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