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Workshop Proceedings

Recent Developments in In Situ Nutrient Sensors: Applications and Future Directions

Savannah, Georgia
December 11-13, 2006

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

An ACT Workshop Report

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

Recent Developments in In Situ Nutrient Sensors: Applications and Future Directions Workshop

Savannah, Georgia
December 11-13, 2006

Hosted by Alliance for Coastal Technologies (ACT) and the Skidaway Institute of Oceanography (SkIO)

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EXECUTIVE SUMMARY

The Alliance for Coastal Technologies (ACT) convened a Workshop on "Recent Developments in In Situ Nutrient Sensors: Applications and Future Directions" from 11-13 December, 2006. The workshop was held at the Georgia Coastal Center in Savannah, Georgia, with local coordination provided by the ACT partner at the Skidaway Institute of Oceanography (University System of Georgia). Since its formation in 2000, ACT partners have been conducting workshops on various sensor technologies and supporting infrastructure for sensor systems. This was the first workshop to revisit a topic area addressed previously by ACT.

An earlier workshop on the "State of Technology in the Development and Application of Nutrient Sensors" was held in Savannah, Georgia from 10-12 March, 2003. Participants in the first workshop included representatives from management, industry, and research sectors. Among the topics addressed at the first workshop were characteristics of "ideal" in situ nutrient sensors, particularly with regard to applications in coastal marine waters.

In contrast, the present workshop focused on the existing commercial solutions. The in situ nutrient sensor technologies that appear likely to remain the dominant commercial options for the next decade are reagent-based in situ auto-analyzers (or fluidics systems) and an optical approach (spectrophotometric measurement of nitrate). The number of available commercial systems has expanded since 2003, and community support for expanded application and further development of these technologies appears warranted. Application in coastal observing systems, including freshwater as well as estuarine and marine environments, was a focus of the present workshop. This included discussion of possible refinements for sustained deployments as part of integrated instrument packages and means to better promote broader use of nutrient sensors in observing system and management applications. The present workshop also made a number of specific recommendations concerning plans for a demonstration of in situ nutrient sensor technologies that ACT will be conducting in coordination with sensor manufacturers.

ALLIANCE FOR COASTAL TECHNOLOGIES

The Alliance for Coastal Technologies is a NOAA-funded partnership of research institutions, resource managers, and private sector companies dedicated to fostering the development and adoption of effective and reliable sensors and platforms. ACT is committed to providing the information required to select the most appropriate tools for studying and monitoring coastal environments. Program priorities include transitioning emerging technologies to operational use rapidly and effectively; maintaining a dialogue among technology users, developers, and providers; identifying technology needs and novel technologies; documenting technology performance and potential; and providing the Integrated Ocean Observing System (IOOS) with information required for the deployment of reliable and cost-effective networks.

To accomplish these goals, ACT provides these services to the community:

- Third-party testbed for quantitatively evaluating the performance of new and existing coastal technologies in the laboratory and under diverse environmental conditions.

- Capacity building through technology-specific workshops that review the current state of instrumentation, build consensus on future directions, and enhance communications between users and developers.

- Information clearinghouse through a searchable online database of environmental technologies and community discussion boards.

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's goal is to help build consensus on the steps needed to develop and adopt useful tools, while facilitating critical communication among 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 organized to ensure geographic and sector involvement:

- Headquarters is located at the UMCES Chesapeake Biological Laboratory, Solomons, MD.

- Board of Directors includes Partner Institutions, a Stakeholders Council, and NOAA/CSC representatives to establish ACT foci and program vision.

- There are currently eight ACT Partner Institutions around the country with coastal technology expertise 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.

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.

CHARGE QUESTIONS FOR THE WORKSHOP

Based on the deliberations of the first nutrient sensor workshop (March, 2003) it appeared likely that further development of in situ nutrient sensors would proceed along two paths:

1) Inexpensive less sensitive sensors for the riverine, estuarine, and coastal resource management communities;

2) Continued development of sensor systems required for real-time coastal ocean observing systems.

At the March 2003 workshop, it was recommended that ACT should convene future workshops to assess progress along these two paths. Given recent developments, it was felt that it was appropriate to revisit the nutrient sensor topic in the context of coastal ocean observing system (COOS) applications. Since 2003, there has been progress in planning the basic architecture of a national Integrated Ocean Observing System (IOOS; see *www.ocean.us*), and regional coordination efforts are being conducted by various Regional Associations (RAs; see *www.usnfra.org*). There has also been the growing experience among a number of regional and sub-regional pilot programs, some of which have included deployments of in situ nutrient sensors, and there have been introductions of new commercial in situ nutrient sensors systems since 2003. Compared to the first nutrient sensor workshop, this follow-on workshop emphasized requirements for sustained in situ measurements as part of integrated sensor packages (i.e., an observing system context) and had a somewhat broader environmental scope, including consideration of the general requirements for observations in the Great Lakes and other freshwater systems, as well as estuarine, coastal, and continental shelf environments.

For this workshop, participants were presented four sets of charge questions:

1) What are the nutrient parameters that are of greatest importance to coastal observing systems? What are the quality objectives required of the measurement methods and sensor technologies?

2) What sensor technologies presently exist to make these measurements? What are their weaknesses and strengths? What are the lessons learned regarding their application?

3) How can the existing technologies be improved? Are there other approaches and/or technologies that are worth pursuing?

4) What should be included as part of a basic protocol for the ACT demonstration of in situ nutrient sensors?

The first three sets of charge questions considered application areas for nutrient sensors as part of observing systems and the requirements for sustained deployment in such systems. A number of the workshop participants had first-hand experience deploying nutrient sensors in coastal monitoring and observing programs and thus provided a valuable perspective on operational considerations, including servicing and personnel training requirements. As noted above, while participants at the first nutrient sensor workshop discussed basic specifications for "ideal" sensors (i.e., what ultimately is desired by various users of the technology), the focus of discussion at this workshop was on the existing technologies and how these might be improved for observing system applications.

The fourth charge question was intended to generate input for the ACT Nutrient Analyzer Demonstration colloquium. This represents a somewhat new role for ACT in promoting adoption of sensor technologies by management, research, and observing system communities. The prior ACT evaluations of oxygen, chlorophyll-a, and turbidity sensors emphasized verification of the manufacturer's stated performance specifications, with ACT in an independent, third-party role. During the Nutrient Analyzer Demonstration colloquium, deployments will be coordinated with manufacturers to demonstrate the capabilities of these technologies; however, the overall objective of this event aims to promote wider acceptance of in situ nutrient sensors in a range of observing system and monitoring applications. The workshop discussion of the fourth charge question was intended to provide a starting point for a subsequent focused meeting where specific protocols for the Demonstration colloquium would be defined.

Finally, workshop participants were asked for input on other aspects of the ACT program that relate to promoting the development of technologies and furthering their acceptance and application. This includes the web-based information ACT provides through its sensor database and the Customer Needs and Use Assessments (CNUA), which has included surveys regarding nutrients sensors.

ORGANIZATION OF THE WORKSHOP

The Workshop was hosted by the local ACT partner, the Skidaway Institute of Oceanography, and co-chaired by Jan Newton (University of Washington, Applied Physics Laboratory), Casey Moore (WETLabs, Inc.), and Jim Nelson (Skidaway Institute of Oceanography). Participants met for a reception and dinner on the evening of December 11th, at which Herb Windom (Skidaway Institute of Oceanography) provided an update on the ACT program and an overview of the workshop goals. The formal workshop commenced the following morning with three introductory presentations:

-- Jim Nelson presented a review of the workshop charge questions and summary of recommendations made at the first Nutrient Sensor Workshop (March, 2003);

-- Jan Newton provided an overview of Applications of in situ Nutrient Sensors;

-- Allan Devol (University of Washington, School of Oceanography) reported on results obtained with nutrient sensors deployed on a profiling buoy system in Hood Canal, Washington and some of the practical "lessons learned" from this experience.

For the remainder of the morning, participants addressed the first two charge questions in two breakout groups; one composed of the industry participants, and the second composed of participants from research and management. Following lunch, the morning discussions were summarized, and Tom Johengen (University of Michigan, CILER) presented an overview and introduction to the ACT Nutrient Analyzer Demonstration project, which was the focus of charge question four. Participants from industry, research, and management were mixed in two afternoon breakout groups to address Charge Questions three and four, with a major objective being to provide ACT with an initial set of recommendations for the protocols for the proposed Nutrient Analyzer Demonstration project. These will be finalized in a separate meeting to be held in late winter 2007 at ACT Headquarters, Solomon, MD.

APPLICATIONS OF IN SITU NUTRIENT SENSOR TECHNOLOGIES

Jan Newton summarized the basic requirements for nutrient sensors in several application areas. The following summarizes points made in her introductory presentation in the initial plenary session of the workshop:

There are a number of challenges in assessing nutrient concentrations in aquatic systems that point to the value of sustained in situ observations. High spatial horizontal variability is typical of many coastal, estuarine, and fresh water systems, as are strong depth gradients. High temporal variability in natural background concentrations are typical of many locations, often in response to short-term forcing (e.g., vertical mixing) or input events (e.g., runoff, river discharge). A lack of consistent relationships to other variables often makes inferences regarding nutrient-related impacts from other more easily measured proxies (such as chlorophyll-a fluorescence) problematic. In many aquatic ecosystems, assessing responses to nutrient inputs from various sources will also require monitoring of multiple nutrient species.

In terms of application needs, Jan Newton pointed out differences in the requirements for management, observing systems, and basic science. It was recognized that this is really more of a continuous spectrum and that, in a COOS context, there will be a blending of applied and basic science applications. However, in general, these requirements can be categorized as follows:

MANAGEMENT APPLICATIONS

- typically requires many units (for multi-site monitoring)
- decent accuracy/precision (as opposed to the highest quality possible)
- ease of use
- low cost
- reliable

Examples of Management Applications include monitoring programs established to document compliance to the Clean Water Act. Key requirements for such applications include establishing background concentrations, especially for ammonium, nitrate, and phosphate, and deployments in a range of environments (coastal ocean, estuaries, and freshwater).

OBSERVING SYSTEMS APPLICATIONS

- requires sustained deployment of many units
- robust sensor systems
- consistent accuracy/precision of reasonably high quality
- consistent use among system operators
- medium cost
- typically involves evaluation of nutrients in relation to other variables and system responses

Improved nutrient sensor capabilities in observing system applications can contribute to several of the broad goals that have been set for the Integrated Ocean Observing System (IOOS), including detecting and forecasting oceanic components of climate variability, managing resources for sustainable use, preserving healthy marine ecosystems, and ensuring public health. Examples of observing system applications related to nutrient impacts on aquatic ecosystems include: evaluation of eutrophication and associated hypoxia, harmful algal blooms (detection and tracking blooms, characterizing stimuli and improving predictive capabilities); microbial contamination; and stimuli for blooms of submerged aquatic vegetation (SAV), which are often localized responses that have been referred to as “green tides.” Key needs for observing system applications include compatibility with other sensors, data acquisition, communications systems, and the potential for event-driven or “trigger sampling.”

BASIC SCIENCE / RESEARCH APPLICATIONS

- typically fewer units (a limited number of locations of focused study)
- high accuracy/precision
- sensitive
- flexible use (adaptable to various specific project objectives)
- relatively high cost is justifiable (based on the research requirements)

Examples of general research topics needing high quality time series information on nutrient concentrations include: evaluating new/regenerated production; defining nutrient ratio effects on species composition; estimating benthic-pelagic fluxes; evaluating transport between and within ecosystems; food web dynamics; and small-scale physical-chemical-biological interactions. Needs for basic science applications include: high precision and accuracy and the means to assess these through field deployments; and flexibility of use (configurations are often user-specific).

CASE STUDIES – EXAMPLES OF APPLICATIONS OF IN SITU NUTRIENT SENSORS

As is evident from the preceding summary, nutrient sensors can play an important role in a range of regulatory and applied observing system and basic research applications. This section provides a set of "case study" examples that illustrate the value of high frequency, sustained time series measurements of nutrients with in situ systems. Workshop participants were asked to provide examples or solicit these from colleagues. The three case studies, which follow, provide examples from an in situ autoanalyzer and optical nitrate sensor in estuarine and coastal ocean environments. Cited references are listed in the Reference section.

Case Study 1: The Role of Nutrients in Harmful Algal Blooms in the Chesapeake Bay

(Contributed by Mark Rawlinson, EnviroTech LLC)

A classic dilemma in assessing nutrient stimulation of Harmful Algal Blooms (HABs) is that reporting and sampling of the bloom generally occurs after the HAB has developed. By that time many nutrients are consumed, and this may lead to the erroneous conclusion that nutrients are unavailable and therefore unimportant. This brief case study demonstrates that the development of in situ nutrient analyzers has provided a tool to begin resolving the all important antecedent conditions for HABs and to provide sufficient resolution in the temporal scale for these conditions to be studied (see Glibert et al. (2005) for further details).

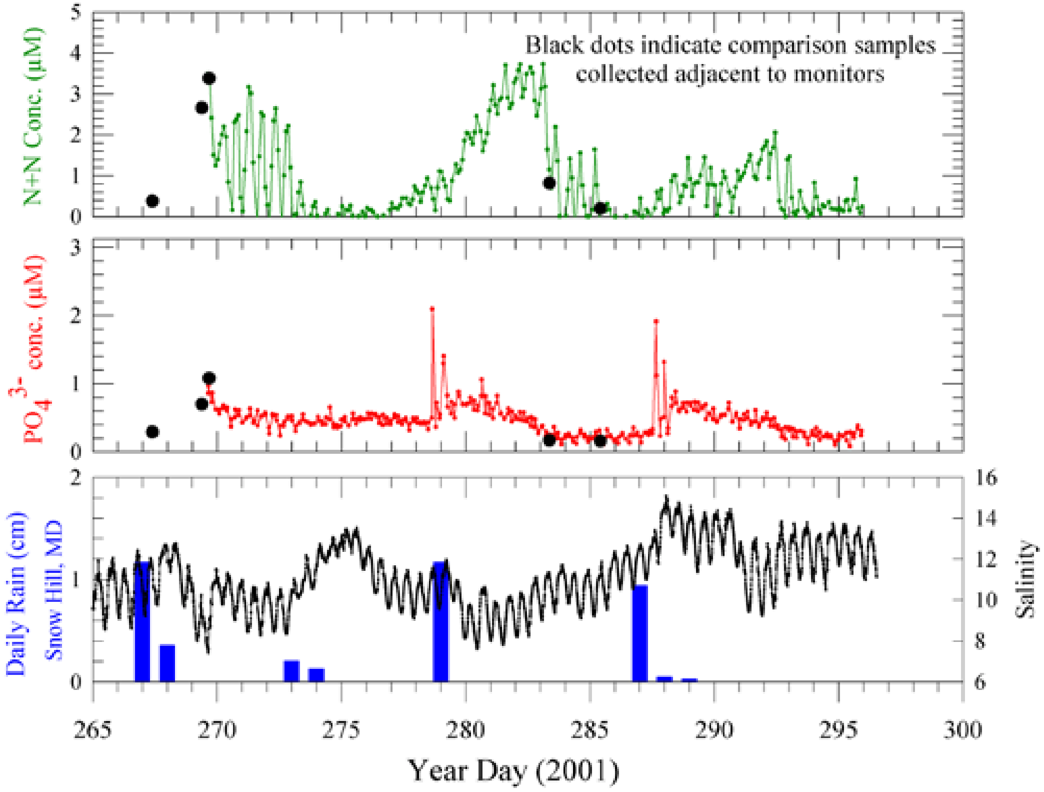


Fig. 1. Time series measurements from the Pocomoke River in 2001.

In situ nutrient monitoring equipment was deployed as part of a Harmful Algal Bloom (HAB) study in the Chesapeake Bay. This followed a number of fish kills and negative health effects reported by waterman in the area.

In the resulting data there is a strong influence due to heavy rainfall early in the record. The nutrient reveals several-day time scale increases in nutrient concentrations following rain events, as well as a strong tidal component. Most surprising were the high-frequency (minutes scale) several-fold increases in reactive phosphorus coincident with the rain events. These nutrient pulses were attributed to runoff from the heavily agricultural watershed of the system. More conventional sampling, with samples collected every few days, missed these pulses in phosphorus, particularly because the pulses occurred during storm periods that contributed to the longer-lived increases in nitrogen and phosphorus.

The charts above (Fig. 1) show time series of nitrate plus nitrite (upper), reactive phosphorus (middle), salinity, and daily total rainfall (lower) in the mouth of the Pocomoke River, a tributary of Chesapeake Bay. Nutrient data was collected with EnviroTech LLC in situ monitors, salinity was measured with a SeaBird MicroCAT, and rainfall data was collected at a USGS station in Snow Hill, MD. All instruments were mounted on a Chesapeake Bay Observing System Buoy (CBOS) at an approximate depth of 1m.

This work was performed by Professor Lou Codispoti's research group and the Horn Point Laboratory, University of Maryland Center for Environmental Science as part for their AIMS initiative. AIMS is an Adaptive and Integrated Nutrient Monitoring and Sampling System developed by Vince Kelly at HPL. Further information such as real-time and archive nutrient data from this and other investigations can be found at the AIMS website - http://www.hpl.umces.edu/aims/

Case Study 2 -- Using In Situ Nitrate Sensors to Measure New Production in the Coastal Oceans

(Contributed by Ken Johnson, Monterey Bay Aquarium Research Institute)

In situ measurements of nitrate concentration have been made on the MBARI M1 and M2 moorings, which have been stationed 20 and 50 km offshore Monterey Bay since 2002. The nitrate variability in these observations is dominated by the approximately 7 to 20 day cycle of upwelling and relaxation that occurs along the Central California coast (Fig. 2). There is also a high frequency component of variability in this data with a distinct diel frequency (Fig. 3). Nearly every day, nitrate concentration decreases during daylight. This drop is due to uptake of nitrate by phytoplankton and the amplitude can be used to estimate new primary production (primary production fueled by nitrate). The daily changes in new production have been used to construct a 3-year long time series of monthly mean primary production in the waters near the M1 and M2 moorings (Fig. 3 D). The variability in primary production is closely linked to the rate of upwelling. For further details see Johnson et al. (2006).

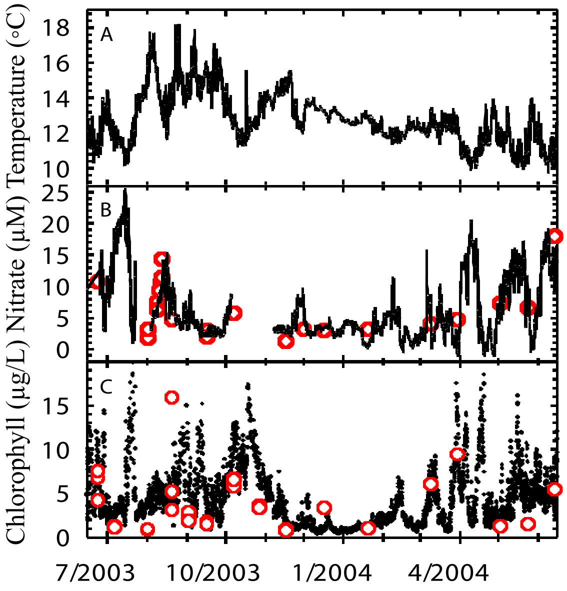


Fig. 2 One year of temperature (A), nitrate (B) and chlorophyll (C) measurements at the M1 mooring. Nitrate was measured using an ISUS optical sensor and chlorophyll was determined from the attenuation of sunlight at 490 nm. Red circles are measurements in samples collected from ships and analyzed in the laboratory using standard methods. Adapted from Johnson et al., 2006.

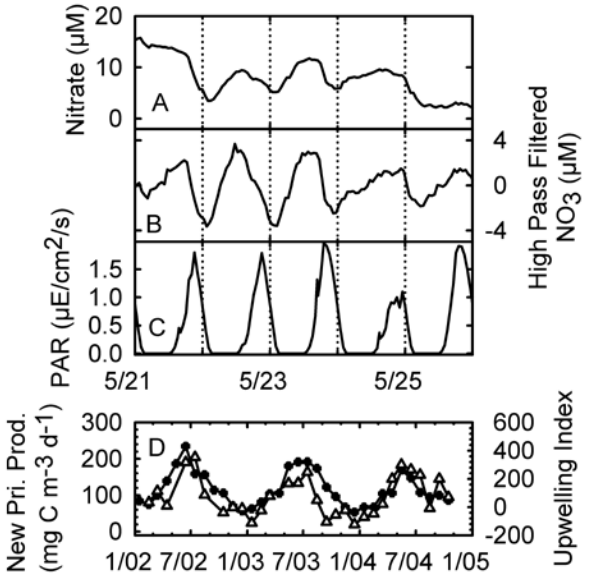


Fig. 3 Five days of nitrate concentration (A), high-pass (33 hr) filtered nitrate concentration (B) and Photosynthetic Available Radiation (PAR) (C) at the M1 mooring in 2004. A three-year record of new primary production at M1 inferred from daily observations of the diel nitrate cycle (triangles) and the upwelling index (m^3 water upwelled/100 m coastline/d) for the same period (D). Adapted from Johnson et al., 2006.

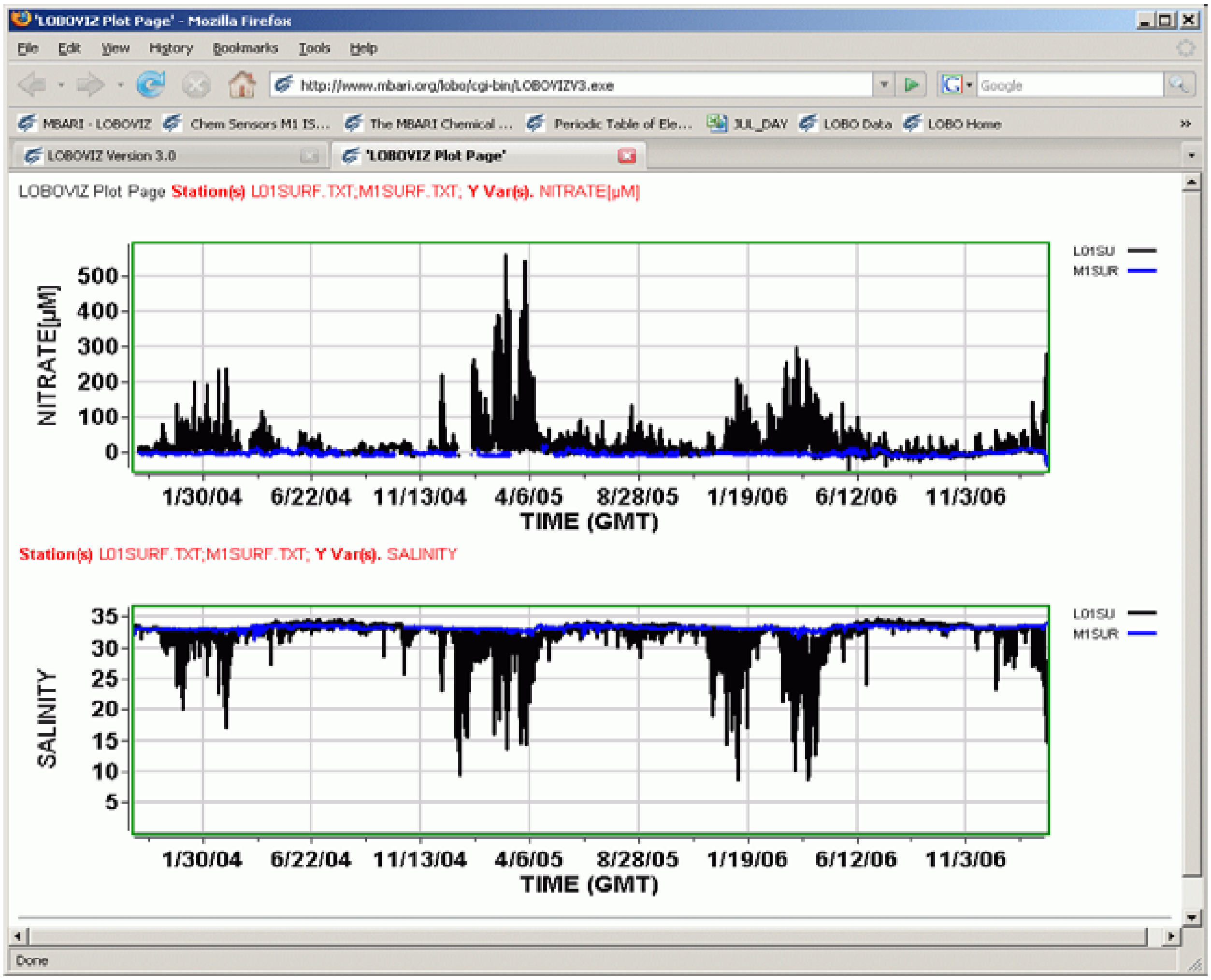
Case Study 3 -- Using Nitrate Sensors to Track the Coupling of Agricultural Fertilizers with the Coastal Ocean in Elkhorn Slough (California)

(contributed by Ken Johnson, Monterey Bay Aquarium Research Institute)

The Land/Ocean Biogeochemical Observatory (LOBO – http://www.mbari.org/lobo) is a network of chemical sensors installed in the Elkhorn Slough at the head of Monterey Bay on the California coast (Johnson et al., 2007). Five moorings with nitrate sensors are installed in Elkhorn Slough. Measurements are made hourly, and data are telemetered directly to the Internet (*http://www.mbari.org/lobo/loboviz.htm*). Observations of nitrate from the M1 and M2 Monterey Bay moorings are also available.

The watershed of Elkhorn Slough is heavily farmed. In the Mediterranean climate of Monterey Bay, rain falls almost exclusively in the months from November to April. A three-year record of nitrate and salinity (Fig. 4) at the L01 mooring in the LOBO array and at the M1 mooring in Monterey Bay shows the impacts of the coupling between rainfall and the nitrogen cycle in Elkhorn Slough. Concentrations of nitrate in the Slough approach those of Monterey Bay during the dry season in summer and early fall. However, during the wet winter months, large amounts of freshwater are transported from land (Fig. 4B), and nitrate concentrations increase to levels that may be

50 times higher than in Monterey Bay. The moored measurements also clearly resolve inter-annual variations in nitrate, which are driven by the amount and timing of rainfall. See Johnson et al. (2007) for additional information.



http://www.mbari.org/lobo/cgi-bin/LOBOVIZV3.exe

LOBOVIZ Plot Page **Station(s)** L01SURF.TXT,M1SURF.TXT, **Y Var(s).** NITRATE[μM]

Station(s) L01SURF.TXT,M1SURF.TXT, **Y Var(s).** SALINITY

Fig. 4. ***A screen grab of data downloaded from the Internet using the "LOBOViz" application. This figure shows data from November, 2003 to February, 2007 for nitrate and salinity at the L01 mooring in Elkhorn Slough (black line) and the M1 mooring in Monterey Bay (blue line). Large drops in salinity and increases in nitrate are observed each winter as rain water runoff transports nitrate from farms to the Slough waters.***

Discussion of Charge Questions #1 and #2

For the discussion of Charge Question sets #1 and #2, two breakout groups were formed; one composed of the industry representatives attending the workshop; the second composed of researchers and managers. The reports from the two groups had somewhat different but complementary areas of emphasis.

The industry group initially focused on defining the commercial systems presently available, the nutrients these measured, and the configuration ("platform") options that can be accommodated. The initial discussion in the research/management group emphasized priority measurements (which nutrients are of greatest interest) and the desired quality (e.g., precision, limits of detection, response time) for various applications, as well as for a "second tier" of desired nutrients. Other desired variables were also noted (e.g., total dissolved nitrogen) for which there are not presently commercial in situ sensor systems. Both groups considered perceived strengths and weaknesses of the existing nutrient sensor technologies, including potential interferences that will vary in significance with both locations and time. Since a number of the workshop participants had considerable experience with field deployments of various commercial systems, a separate subsection for some general "lessons learned" is also presented below.

Priority Nutrients for Research and Management Applications

There was consensus that the priority nutrients and desired level of precision and limits of detection for a broad range of applications can be defined as follows:

Priority Nutrients	Desired Precision	Desired Limit of Detection
Nitrate (NO_3^-)	0.1 µM	0.1 µM -- oligotrophic -- rate measurements 1 µM -- non-oligotrophic
Ammonium (NH_4^+)	0.1 µM	1 µM
Phosphate (PO_4^{-3})	10 nM	100 nM

It is recognized that requirements for precision and detection limits will vary greatly between applications. The preceding list also took into consideration what might be realistically achieved with the existing technologies. A "second tier" of desired nutrients would include:

Iron (Fe)	sub-nM	20-50 pM (open ocean) 200-500 pM (coastal) 100 nM (freshwater)
Silicate (SiO_4)	0.25 µM	0.25-2.5 µM (depending on the system)

Other nutrient-related properties of interest were noted without trying to necessarily define desired levels of precision or limits of detection. For many of these variables, there are not presently in situ measurement systems. For example, measurements of Total Dissolved Nitrogen (TDN) and Total Dissolved Phosphorus (TDP) are of broad interest for both EPA-mandated monitoring and research purposes. Also of interest are in-water measurements for Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON), Particulate Organic Phosphorus (POP), and Carbon dioxide (CO_2). (*Note*: In situ measurement of dissolved inorganic carbon species was the subject of an ACT workshop held in February, 2005 in Honolulu, Hawaii. See that workshop report for further information.) Atmospheric delivery of nutrients is also significant in many environments, and thus a desire for improved systems for quantifying aerosol and air-borne particulate concentrations of various nutrients was noted, including ammonium (NH4), nitrogen oxide species (NO_X), sulfate (SO_4^{-3}), and sulfide (HS^-).

Other performance qualities required for management, observing system, and research applications include means to assess accuracy (= calibration) and to compensate for drift in calibration response factors. Calibration was seen as a "user responsibility"; that is, the users must employ a calibration protocol to ensure that the sensors are responding reliably. Compensation for drift was seen primarily as a "manufacturer responsibility"; that is, it is desired that the sensor systems incorporate some means for drift correction while deployed. Desired response times vary with applications and instrument configurations (see configuration list below), but for profiling applications, it was thought that a response time of 10 seconds, and preferably less, would be needed to adequately resolve vertical gradients when sensors are incorporated into standard profiling packages. Much higher frequency response would be required for packages that undergo more rapid vertical excursions (e.g., towed undulating vehicles). A number of management and research users also expressed interest in capabilities for "burst sampling" in response to defined thresholds or events detected by other environmental sensors.

Commercially Available Systems

The industry group at the workshop compiled a list of presently available commercial in situ nutrient sensors and soon-to-be-released systems. The following tables summarize their basic attributes, including nutrients measured, sampling frequencies that can be achieved for sustained deployments, and deployment platforms for which these systems can be configured. Further information can be obtained from the ACT web site and manufacturer web sites listed in Appendix B.

Table 1. Summary of commercially available (or soon to be available) in situ nutrient sensor systems.

	NO_3	PO_4	NH_4	NO_2	Si	Fe
SubChem SubChemPak	X	X	X	X	X	X
TriOS ProPS	X					
Envirotech ECOLAB	X	X	X	X	X	X
YSI 9600	X (NO_3+NO_2)			X		
Satlantic ISUS	X					
EcoTech 1000		X				
WET Labs CYCLE-P		X				
Systea DPA	X	X	X	X	X	X

Table 2. Deployment platforms for which various commercially available nutrient sensors can be configured.

	Sampling Frequency	Profiler	AMP[1]	Buoy	AUV[2]	Glider	Flow-through	Towed Vehicle
SubChem SubChemPak	20 sec	X	X	X	X	(in development)	X	X
TriOS ProPS	1-2 Hz	X			X		X	X
EnviroTech ECOLAB	10-15 min		X	X	X		X	X
YSI 9600	10 min		X	X			X	
Satlantic ISUS	1-2 Hz	X	X	X	X		X	X
ECOTECH 1000	30 sec	X	X	X			X	
WET Labs CYCLE-P	10 min		X	X			X	
Systea DPA	15 min							

[1] "AMP" = Automated Moored Profiler; [2] "AUV" = autonomous underwater vehicle

Strengths and Weaknesses of Existing Systems

In discussion in the breakout sessions, the strengths and weaknesses of existing in situ nutrient systems were summarized in terms of what applied specifically to reagent (or fluidics) systems and to the optical nitrate system. There was considerable overlap in the perceived strengths and weaknesses between the two sessions and what are considered to be the key sources of interference with nutrient sensor performance. The input from each group is combined here. Note that these are generalizations, and actual performance features and limitations may differ from manufacturer to manufacturer.

Reagent-Based Systems (fluidics or wet chemistry systems)

Strengths
-- Systems are self-calibrating.
-- The in situ analyses are based on established, standard methods (EPA-accepted laboratory methods).
-- Nanomolar detection limits can be achieved.
-- System configurations can be customized with respect to nutrients and with respect to the range of nutrient concentrations expected for a given locale.

Weaknesses
-- The systems are resource intensive (initial costs, personnel time for servicing).
-- These include moving parts.
-- Reagent waste is generated.
-- The systems include fluidics components (and thus require accurate pump calibrations, consistent performance under variable environmental conditions, etc.)
-- There are a relatively slow response and analysis times.
-- The weight and bulk of the sensor packages can be considerable.
-- A reagent payload is required. Servicing requires replacement of reagents. Degradation of reagents in extended deployments can be a concern. (Also, in some configurations reagents are in exposed plastic bags – loss of reagents apparently due to fish bites was noted for one location).

Optical Nitrate System

Strengths
-- There is a comparative ease of use.
-- High frequency measurements are possible (1-2 Hz).
-- Post-processing of data is possible (i.e., later corrections based on discrete samples).
-- The instruments size allows incorporation into many packages.
-- Operational costs are relatively low.
-- There are no moving parts.
-- There are no waste reagents.

Weaknesses
-- The ultraviolet spectral measurements detect Nitrate only.
-- The detection limit is µM.
-- Calibration can be an issue (e.g., baseline drift over deployments).
-- This is not a standard method, thus there can be issues with acceptance by regulatory agencies.
-- There are a number of potential interferences with the optical measurements (see below).
-- Biofilm build-up (bio-fouling) affects the UV spectral measurements and data quality.

It was felt that either class of in situ nutrient systems can have notable advantages over standard manual sampling/monitoring programs, but there were also several factors that have impeded wider application of the technologies.

Advantages over the sampling and laboratory analysis approach include:
-- The elimination of storage artifacts.
-- Once deployed, it is easier to obtain data than by water sampling.
-- The cost per sample is lower than sampling programs.
-- Greatly improved temporal resolution is possible.
-- Data accuracy can be improved (i.e., resolution of gradients, events).
-- Data can be acquired in near-real time.

> <u>Impediments to broader application in monitoring and observing programs include</u>:
> -- The need to integrate the nutrient sensors with other instruments and data systems (interoperability issues). Issues associated with standardization for observing system applications include defining the required performance specifications to be met by manufacturers, the communications protocols needed for integration into multi-parameter observing system packages and software issues (e.g., the operating systems among existing systems are diverse and are not always readily integrated with other systems).
> -- Unit costs are relatively high.
> -- The level of power consumption is relatively high compared to many other instruments.
> -- Fouling compromises data quality and imposes the need for regular maintenance.
> -- There are "ease of use" issues associated with deploying and maintaining systems.
> -- The level of technician training required for reliable operation and to ensure good data quality is significant.

Product acceptance was also identified as a challenge by the manufacturers. This has several aspects. For example, while funds for sensor development have been available, funding opportunities for wider application of the in situ sensor systems has been limited. From the manufacturers' point of view, it was also felt that the time required to achieve broad market acceptance of a new sensor system must be shortened if further development is to be supported. A prolonged transition from research to operational status for a given sensor type limits the ability of manufacturers to bring new products to market.

Promoting the perception of value by potential users was also discussed. One important point of reference for this would be to define the real costs of existing nutrient monitoring programs based on point sampling and laboratory analyses. Managers and other potential users may also need to be convinced of the value of continuous in situ measurements; this is why they should be concerned with the capability to characterize the variability of nutrient signals in the environment. This strength of the in situ approach may need to be better emphasized to those presently using point sampling as the basis for their monitoring strategies.

In summary, there are a number of commercial solutions for in situ nutrient measurements for three macronutrient ions that are typically among the top concerns for nutrient monitoring and observing programs (nitrate, phosphate, and ammonium). However, there are presently no in situ systems that measure total dissolved nitrogen (TDN) or total dissolved phosphorus (TDP), which are often key parameters for water quality and regulatory compliance monitoring programs. Two basic technologies presently available commercially include the reagent-based or fluidics approach and the optical nitrate sensor. These share some positive attributes, including capabilities for deployment on a variety of platforms without modification and demonstrated value for the data acquired through continuous in situ measurements. However, the cost of ownership is significant for either class of in situ nutrient sensor, and as noted above, there remain a number of challenges to be addressed for these systems to achieve a broader acceptance and routine application in monitoring and observing programs. Users and potential users felt that additional information from manufacturers and user groups would be quite useful, including operational recommendations for various environments, information on post-processing procedures, advice on appropriate ancillary measurements, and how to interpret these in relation to the nutrient sensor signals.

Lessons Learned

As noted above, a number of the workshop participants had considerable experience with extended field deployments of in situ nutrient sensors. “Lessons learned” from these experiences fall into several broad categories:

Applications and Available Configurations

- Some systems are more easily integrated with other sensor systems.
- Some sensors are better suited for particular habitats or ecosystem applications.

Operational Considerations

- It takes more time and effort than anticipated to get to a reliable operational status. These are generally not "plug & play" systems. Users must commit sufficient time to develop the procedures for their particular application and locale. However, the consensus from the experienced users has been that it has been worth the effort.
- Data volumes are relatively high compared to what is obtained with point sampling programs, and users must be prepared to handle the data.
- Given the current state of development, it is important for users to recognize that the technologies and applications are evolving and that customers are part of the development process.

Building Market Acceptance / Perceived Value of In Situ Nutrient Sensors

- Committing to the purchase of in situ nutrient sensors is a significant "investment decision" for many potential users. There are potential users (including workshop participants) who have been in a "waiting" mode, hoping for the introduction of better and cheaper systems. Broader application of the in situ nutrient technologies will require convincing these potential users that the capabilities meet their requirements and budgets.
- It was suggested that confidence-building measures that could expand the present markets could include: availability of demonstration units; established users groups that can provide information and advice to new or potential users.
- Present users felt that their results can demonstrate the importance of temporal and spatial scales of variability that would not likely have been detected with standard discrete sampling and laboratory analyses. In situ sensors can detect "real events" of significance, confirming the expected and revealing the unexpected, both of importance to understanding system dynamics. The acquisition of higher frequency nutrient data can also help to indicate which processes warrant further investigation.
- A broader application in research will in many cases be stimulated where it is seen that there is important information to be gained from linking the nutrient data with that obtained from other new technologies and analyses (e.g., molecular methods, community analyses, specific contaminant or toxin analyses).

DISCUSSION OF CHARGE QUESTION SET #3

How can the existing technologies be improved? Are there other approaches and/or technologies that are worth pursuing?

In the discussion of the third set of charge questions, it was again emphasized that two approaches for in situ nutrient systems for marine waters are likely to remain the leading commercially available technologies for the next decade. These technologies include <u>fluidics systems</u> (in situ auto-analyzers which employ "wet chemistry" colorimetric methods) and the <u>optical nitrate sensor</u> (which employs spectral absorption measurements in the ultraviolet to estimate nitrate concentrations)[1]. It was also emphasized that there has been a growing number of commercially available systems since the first ACT nutrient sensor workshop in 2003, and that the technologies continue to evolve. Thus for the near-term, users of the in situ nutrient systems must recognize that they are part of the evolution of the technology. It was felt that ACT can play a significant role in this process. One of the goals for ACT is to facilitate effective engagement across industry, management, and research sectors to help foster the technological evolution of environmental sensors, expand management and research applications of sensor technologies, and promote the development of viable commercial markets for these systems. The latter will thus further complement applications by providing a wider range of sensor configurations for users and ultimately lower the unit costs.

In terms of improvements of the existing technologies, the broader application of in situ nutrient sensors in coastal ocean observing systems and agency-sponsored monitoring programs will generally require that these be incorporated into integrated environmental monitoring packages. Thus interoperability and compatibility with other sensor, data acquisition, and communications systems was among the consensus "desires" of the researchers and managers at the workshop. This applies to either the fluidics or optical nitrate approaches. Standardization of data systems is a general issue. To date, data acquisition systems used by the coastal research and observing communities have been dominated by non-standard, and often, in-house designs. It is likely that IOOS requirements will push many users toward more standardized data systems and output formats. Other important operational considerations noted by present users and potential users include lower power requirements, reducing the bulk and weight of the fluidics packages, introduction of non-toxic reagents (reagent waste disposal can be an issue), and extending the required servicing interval (longer deployments).

Personnel Training and Operational Requirements

Several general recommendations pertained to practical aspects of personnel training for operating the in situ nutrient sensor systems. An important consideration for broader application of in situ nutrient sensors is "ease of use." Users of existing systems reported that the time and level of hands-on experience required to deploy and maintain the existing commercial systems was typically well beyond what they had expected. Several suggestions were put forward regarding

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[1] As at the first ACT nutrient sensor workshop, the commercial availability of ion-selective electrodes was noted. However interferences from other ions in estuarine and seawater applications limit their applications in these environments. Thus, ion-selective electrodes were not discussed at the second nutrient sensor workshop.

personnel training and exchange of information between users of the sensors; a number of which ACT may help address:

- establishing recommendations for Standard Operating Procedures (SOPs);
- distributing information from the manufacturers regarding what they consider to be the training/experience requirements for users of their systems (i.e., statements of the "skill level" deemed necessary for successful deployments/maintenance of their systems);
- establishing "user groups" to exchange information and build on the experience being acquired by groups presently deploying in situ nutrient sensors;
- developing training workshops for the technical personnel responsible for deploying and maintaining the systems;
- providing information/feedback on the design of appropriate sampling strategies for application and validation of in situ nutrient sensors in various environments;
- organizing of "topical meetings" on nutrient sensor technologies and applications.

Calibration

Ensuring reliable calibration of the in situ sensors is critical to validating system performance and producing quality controlled time series data. There are three basic components for the calibration protocols required for sustained in situ deployments:

- Measurements with standard solutions (before and after deployment);
- Monitoring stability during deployments;
- Collection of validation samples and analyses by accepted methods.

Thus, there are both functional and procedural issues to consider with regard to calibration, including the source of standard solutions (see Appendix C); possible deterioration of in situ standards during deployments; and the analytical method to be used for laboratory analyses (e.g., options include established EPA and WOCE methods). Again, sources of information and guidance for users on these issues and accepted methodologies would be useful.

Trends in Development for In Situ Nutrient Sensors

Many of the issues and areas for desired improvements were also noted in the deliberations of the first ACT nutrient sensor workshop (March, 2003). In discussion of "ideal" sensors (compared to what is presently available), recurring themes expressed by researchers and managers included the desire for smaller, cheaper, and more reliable systems, as well as packages that are easier to deploy and maintain. The manufacturers are well aware of such concerns, and new system developments are intended to address a number of these areas.

For the in situ auto-analyzers, the trend in development is toward:

- application of micro-fluidics technologies;
- modularity;
- facilitating incorporation into integrated systems.

Micro-fluidics offers the potential to greatly reduce the size and bulk of sensor packages. A key challenge in this area is ensuring reliable, sustained, and calibrated performance of the micro-pumps that deliver samples and reagents. The vision for modularity includes use of reagent "cassettes" that would provide pre-packaged reagents in an easily exchanged package, simplifying servicing requirements for users.

For the optical nitrate approach, further developmental efforts include miniaturization of the system and integration into a variety of package configurations. Reducing size will allow the package to be incorporated into Autonomous Underwater Vehicles (AUVs), including gliders and autonomous profiling packages, as well as more easily incorporated ship-deployed CTD/rosette water sampler and towed package systems. Improvement in anti-fouling strategies remains a key area that is central to expanding use of the optical system in sustained deployments.

Further suggestions for improvements from workshop participants include:

- explore the possible introduction of non-toxic reagents for the wet chemistry-based systems;
- direct some development efforts toward software improvements for handling the data;
- ACT should consider generating a list of requirements for operation of in situ nutrient sensors, perhaps through a survey of manufacturers and present users.

Other Future Technologies That May Have Applications in COOS/Monitoring Settings

A focused effort to identify potential new technologies/approaches for in situ nutrient measurements was not undertaken prior to the workshop. Thus, the input in this area was limited to what workshop participants were aware of and is not proposed to be a full and complete assessment. As noted above, for the near-term (5-10 years), the workshop participants felt that the fluidics (in situ autoanalyzers) and optical nitrate approaches would likely remain the commercially available options. However, some other approaches and possible research and development level systems were noted:

- Through a National Oceanographic Partnership Program (NOPP) grant, SubChem (*www.subchem.com*) is developing the "ChemFin" system, a low-power, compact, single-channel unit intended for glider deployment, targeting a 3-month duration.
- TriOS (*www.trios.de*) has a membrane-type sensor for phosphate (similar in its basic features to the oxygen optode) that has been tested and proven in the laboratory but not yet commercially available for field deployments.
- Unisense (*www.unisense.com*) has developed a new nitrate biosensor, presently targeting industrial applications.
- At an R&D level, engineers at the Georgia Tech Research Institute have developed a waveguide interferometer technology (*http://gtresearchnews.gatech.edu/newsrelease/danger.htm*), using relatively low cost, off-the-shelf components that has potential for point measurements of a range of analytes in environmental monitoring applications, including nutrients. Commercial prototypes for nutrients have not been developed at this time.

THE ACT PERFORMANCE DEMONSTRATION FOR IN SITU NUTRIENT SENSORS

Charge Question 4: What should be included as part of a basic protocol for the ACT Demonstration of in situ nutrient sensors?

Introduction

Prior to discussion in two break-out sessions, Tom Johengen (University of Michigan, CILER; ACT Chief Scientist) provided background material relevant to Charge Question #4 and an initial list of discussion topics for the ACT Performance Demonstration for in situ nutrient sensors.

A point of emphasis for the initial discussion of the planned demonstration project is that, while the basic values and principles that guide ACT in conducting technology evaluations are to be followed, there are important differences between the Performance Demonstration and the Performance Verifications previously conducted by ACT. In both cases, ACT conducts an independent, third-party evaluation that provides relevant and reliable performance information to potential users and a level playing field among manufacturers. The evaluations are intended to enhance the ability of potential users of the technologies to identify the systems that are appropriate for their applications and to help accelerate the adoption of innovative technologies. In conducting both classes of evaluations, ACT seeks to provide a fair, credible, and responsive assessment with consistent methodologies and quality assurance across the diverse coastal and freshwater environments represented among the ACT partners. The results of these evaluations are released to the public as either Verification or Demonstration Statements.

There are, however, key differences between the two types of Technology Evaluations conducted by ACT. ACT Technology Verifications are rigorous third-party evaluations of commercially available instruments to verify manufacturers' performance specifications or performance claims. The Performance Verifications must be carried out at five or more (but typically at all) ACT Partner sites. ACT Technology Demonstrations are a less rigorous exercise where the performance and potential capabilities of existing and newly emerging technologies is documented by working closely with developers/manufacturers to field test instruments in diverse coastal waters. Unlike for previous Sensor Verifications, the manufacturers will work directly with ACT Technical Coordinators during the initial set-up and deployment of the instruments. Furthermore, the Demonstration will not involve any direct laboratory tests to test specifically for accuracy, precision, or performance against varying physical/chemical properties within the test environment.

Although all Partner Institutions will be involved in the upcoming nutrient sensor demonstrations, the field tests will be conducted at only two or three sites. The goal is to test all of the participating sensors in fresh, brackish, and saltwater environments. The decision to run this evaluation as a Demonstration is also predicated on the fact that there is a relatively high cost and significant technical requirements for operating several of the existing nutrient sensor systems, and, in some cases, systems are still undergoing prototype changes. Therefore, it was not appropriate to expect manufacturers to provide four systems simultaneously as needed to run the typical Verification study. Since training time with the manufacturers would likely be limited, it was questioned whether ACT personnel could be trained to a high enough level of competency to effectively operate the systems independently. Thus, while ACT will maintain the same level of objectivity and scientific rigor to conduct this Demonstration, the key objectives for the project are:

(1) to highlight the potential capabilities of in situ nutrient analyzers by demonstrating their utility in a broad range of coastal environments with varying nutrient concentrations;
(2) to promote the awareness of this emerging technology to the scientific and management community responsible for monitoring coastal environments;
(3) to work with manufacturers that are presently developing new or improved sensor systems by providing a forum for thoroughly testing their products in a scientifically defensible program but at relatively minor costs in time and resources.

The schedule for the ACT nutrient sensor Performance Demonstration calls for detailed protocols for the Demonstration to be specified under agreement between ACT personnel, the manufacturers, and an external Advisory committee. These protocols will be finalized at a joint meeting of these personnel in February 2007, to be held at ACT headquarters in Solomons, MD. It is envisioned that field deployments will take place between May to September 2007. The discussion of this topic at the Savannah workshop was intended to help set some basic parameters/guidelines for the demonstration and help ensure that expectations are consistent among the industry, management, and research sectors involved in nutrient sensor technologies.

The initial discussion in break-out sessions addressed a set of topics and associated questions presented by Tom Johengen in his introduction to the Performance Demonstration project:

- Available reference standards and methods
  - Should literature or agency-based methods be employed?
  - Should there be direct determination of the analytes or use of surrogates?
  - What are the basic recommendations for QA/QC (e.g., use of certified standards; a "round robin" design; protocols for storage and handling of samples)?
- Laboratory and Field Conditions
  - Should the demonstration include direct measurements of temperature and salinity?
  - Should there be an attempt to control for other known sources of interference/contaminants?
  - Should physical limits for the demonstration be defined in advance?
  - What are the appropriate concentrations of nutrients to be targeted for the demonstration?
- What are the performance characteristics to be determined in the demonstrations?
  - Examples include range of detection, accuracy, precision, duration of deployment of individual systems, and reliability over time.

Discussion – ACT Performance Demonstration

There was general agreement that the Performance Demonstration should include both moored and profiling instruments, with the qualification that the deployment configuration should be deemed appropriate by the manufacturer of any particular sensor package. There was consensus that the general characteristics of the deployment sites should be well known in advance and include a reasonably high level of spatial and temporal variability in nutrient concentrations, such that the response of the sensors to changes in ambient nutrient concentrations can be evaluated. It was thought that at least one site should provide access to nitrate concentrations from <1 µM to >30 µM, and up to >80 µM and phosphate concentrations from <1 µM to 10 µM. Separate laboratory tests of the sensors under controlled conditions (e.g., under a range of controlled temperature and salinity) were not considered necessary for the Performance Demonstration.

The Quality Assurance (QA) program for nutrient sampling, storage, and analyses must be well defined and approved in advance of the sensor deployments, with specified levels of precision and accuracy. It was felt that EPA-approved methods should be followed (as part of the engagement of managers). A "round robin" approach for inter-calibration between sites was preferred. The consensus was that adoption of such protocols would be sufficient to allow analysis of nutrient concentrations in field samples to be conducted by laboratories operated at Partner institutions versus having to submit samples to a certified contract laboratory.

At the planned Solomons, Maryland meeting (ACT Headquarters), sampling strategies must be defined, including the frequency and types of nutrient and ancillary samples to be collected. Appropriate ancillary measurements to be obtained during the Demonstration will need to be further defined, based on information from the deployment sites. A range of possible variables that could affect performance or that would be useful for interpretation of the nutrient sensor data were noted, including: temperature, salinity, depth (i.e., a CTD package), dissolved oxygen, *in vivo* chlorophyll fluorescence, turbidity, and colored dissolved organic matter (CDOM) absorption. Conducting a full suite of validation sampling for all of these sensors was considered to be beyond the scope of this project. However, it was felt that such information would be useful and should be acquired if possible as part of the environmental characterization of the test sites. For specific sampling and analyses during the Performance Demonstration, it was felt that ACT should focus on the validation measurements for nutrients.

A number of issues and questions raised in the group discussions will need to be considered in the planning leading up to the protocol meeting at ACT Headquarters. Possible problem areas associated with integrating individual nutrient sensors into packages with ancillary sensors include: designing interfaces between the nutrient sensors, ancillary sensors, and data acquisition packages; meeting power requirements for various components; compatibility of cables and connectors; and the physical size of the integrated package (a number of the in situ nutrient sensor systems are large).

The set-up time that would be required for ACT personnel to configure instrument packages prior to deployment was a factor that participants felt must be considered up-front in plans for the Performance Demonstration. The available time frame prior to the planned deployments imposes a significant constraint on the extent to which customized packages might be designed and assembled for the Demonstration. Given the concerns with the engineering requirements for an ACT-configured, multi-sensor package/data acquisition system, the question was raised as to whether the vendors should provide integrated packages or just the nutrient sensors. There was general agreement that if the manufacturers had integrated packages available, these should be employed in the Performance Demonstration.

Recommendations Regarding the ACT Performance Demonstration

Based on the discussions in two break-out groups and in the subsequent plenary sessions, a number of recommendations were put forward for ACT to consider in further planning of the Performance Demonstration for in situ nutrient sensors:

- In further planning for the project, ACT should emphasize that this is a Demonstration and not a Verification project.
- There was a strong recommendation that the demonstrations should be conducted in accordance with the manufacturers' intended applications and the stated capabilities of the commercial systems. It was felt that the manufacturers should be allowed to deploy their sensors as part of a packaged system (e.g., with other sensors and integrated data acquisition provided by the manufacturers) should they desire to do so.
- Include additional workshop targeted at regional managers to discuss and demonstrate the capability of the in situ nutrient sensors. It was suggested that this be conducted at 2-3 sites. This workshop might also feature presentations from existing users highlighting the potential of in situ nutrient data.
- Have available for the managers an information package (referred to as the "enlightenment brochure" at the workshop) that highlights the benefits of having sustained in situ nutrient measurements in the context of a coastal observing system (i.e., integrated, real-time, with established data management procedures and links to complementary modeling efforts). It was suggested that this should include a cost-benefit analysis comparing use of in situ sensors with traditional sampling/monitoring/laboratory analysis programs.
- Deploy the sensors at sites that will provide sufficient variability in both nutrient concentrations and possible interferences to demonstrate capabilities to resolve spatial gradients and variability over a range of temporal scales under a range of conditions.
- Sufficient environmental characterization (ancillary measurements) should be included, particularly for factors that may affect sensor performance or the interpretation of the nutrient data.
- It was felt that deployment of various configurations of in situ nutrient sensors are needed to demonstrate adequately the range of capabilities of the existing systems. Again, these deployments should be in accordance with the intended use of the systems. Profiling, moored (fixed depth), and dock-mounted flow-through systems should be accommodated.
- An adequate Quality Assurance (QA) plan must be specified prior to the deployments.
- If possible, plan for the duration of deployment to be on the order of one month.

WORKSHOP WRAP-UP AND CONCLUSIONS

In the final plenary session for the workshop, the participants addressed several topics. In addition to formulating and prioritizing a list of recommendations to ACT based on the workshop discussions (below), the recommendations from the first ACT Nutrient Sensor Workshop (March, 2003) were revisited to assess whether these have been or should be pursued further. Other aspects of the ACT program related to nutrient sensors were also considered, notably the “Sensor Database” on the ACT web site and the Customer Needs and Use Assessment (CNUA) that have been conducted by Responsive Management for ACT (reports are available on the ACT web site).

REVIEW OF RECOMMENDATIONS FROM THE FIRST NUTRIENT SENSOR WORKSHOP

The general recommendations made at the conclusion of the first ACT nutrient sensor workshop were:

1) Increase outreach efforts to coastal managers;
2) Facilitate sensor development by providing a defensible assessment of the potential market;
3) Encourage development and availability of nutrient standards;
4) ACT to serve as "central point of contact" for sensor funding announcements;
5) ACT should convene a workshop targeting environmental managers. Market survey could help assess needs of this group.

Other potential ACT roles in promoting use of the nutrient sensor technologies were noted in the report from the March 2003 workshop, including holding follow-up workshops and training sessions for managers, facilitating contacts between users and manufacturers, and playing a role in data management.

Regarding Recommendations (1) and (5), participants at the second (December, 2006) nutrient sensor workshop felt that outreach efforts to inform and engage managers and decision-makers (coastal and freshwater) must be continued. Some specific recommendations in this area regarding informational material in a real-time monitoring context and training workshops are among the recommendations from this workshop (below). It was felt that workshops exposing managers and decision-makers to the sensor technologies and applications would be most effective if conducted at the regional level. An initial workshop is planned for May 2007 as part of the Nutrient Sensor Demonstration Project.

For Recommendation (2), it was felt that such market assessment has been initiated but that this must also be an ongoing effort. The present workshop included specific recommendations regarding the Customer Needs and Use Assessment (CNUA) process (below).

Participants in the second Nutrient Sensor workshop felt that the issue of nutrient standards (Recommendation (3)) has been adequately addressed, with a number of suppliers of standards identified. As follow-up to this, it was suggested that the suppliers be identified in this Workshop Report (see Appendix 2), and the ACT web site should provide advice on how to obtain the standards and protocols for their use. It was also suggested that ACT might host a follow-up workshop addressing this topic.

It was felt that Recommendation (4) had been addressed to some extent, but it was acknowledged that organization and maintenance of a comprehensive "clearinghouse" for funding opportunities would likely require a dedicated person and is thus beyond the present scope of activities that can be supported with the available resources.

FEEDBACK ON OTHER ACT PROGRAM ACTIVITIES

Sensor Database

Many workshop participants felt that the utility of the ACT sensor database is presently being hindered by the limited range of web browsers supported. The present lack of compatibility with Mozilla “Firefox” in particular was noted (this appeared to be the “browser of choice” for a substantial portion of the workshop participants). There was also interest among the manufacturers in how the database is updated (and whether this can be automated).

Customer Needs and Use Assessments (CNUA)

A number of workshop participants were critical of aspects of the CNUA surveys that have been conducted by Responsive Management for ACT and felt that the present CNUA process should be reconsidered. In particular, it was questioned whether the surveys to date are providing appropriate information to help gauge interest and market potential for a given sensor type. A strong recommendation from the industry group was that industry should be engaged in the design of the surveys. Many of the industry representatives have experience in this area and have developed contact lists of potentially interested parties.

WORKSHOP RECOMMENDATIONS

Based on the input from workshop participants in the breakout and plenary sessions, several major recommendations were compiled and discussed further in the final plenary session. These are presented below in order of priority, based on votes for the top choice.

- ACT should help promote "compatibility" between in situ nutrient sensors and other instruments and data acquisition packages. It was generally acknowledged that the value of nutrient sensors is, and will continue to be, part of integrated packages with other physical, chemical, and biological sensors. Compatibility/interoperability as part of such multi-sensor packages was seen as essential for more widespread application of nutrient sensor technologies.
- ACT should conduct "topical user" workshops with a focus on real-time monitoring systems. These would include technical seminars, presentations on specific applications, demonstrations, and adequate time for discussion. A 1-2 day meeting was envisioned at a national level that would include both marine and freshwater monitoring and applications. A recent USGS-sponsored meeting on turbidity measurements (April 30 – May 2, 2002, Reno, Nevada) was noted as a possible model (for reports from that workshop, see *http://water.usgs.gov/osw/techniques/turbidity.html*).
- ACT should develop informational material (an "enlightenment brochure") that would help justify the investment in in situ nutrient sensors by potential users, particularly in a real-time monitoring context. It was suggested that this should include cost-benefit analyses.

- Formalize the Standard Operating Procedures (SOPs) from the planned ACT Nutrient Sensor Demonstration Project and post these on the ACT web site. This might include a FAQ section that could be updated as needed.
- The Customer Needs and User Assessment process should be revised to include better input from Industry. In particular, Industry should be involved in the survey design and provide input regarding survey participants. It was suggested that electronic surveys should be considered.
- ACT should seek input from other fields beyond the aquatic sciences and aquatic systems management communities.

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APPENDIX A. LIST OF ATTENDEES (CONTINUED)

APPENDIX B. WEB SITE INFORMATION FOR EXISTING COMMERCIAL INSTRUMENTS

Further information on the in situ nutrient sensor systems listed in Table 1 can be found on the manufacturers' web sites. In addition to specifications, many also provide application notes and examples of data records obtained with the instruments. A single representative product is listed here. Multiple products and configuration options are available in a number of cases, some of which combine the products of different manufacturers in integrated packages.

Manufacturer	Product	Manufacturer Web Site(s)
EcoTech	NUT1000	*www.americanecotech.com*; *www.ecotech.com.au*
EnviroTech	ECOLAB	*www.n-virotech.com*
TriOS	ProPS	*www.trios.de*
Satlantic	ISUS	*www.satlantic.com* *www.wetsat.com*
SubChem	SubChemPak	*www.subchem.com*
Systea	DPA	*www.easychem.com*
WET Labs	CYCLE	*www.wetlabs.com* *www.wetsat.com*
YSI	9600	*www.ysi.com*

APPENDIX C. NUTRIENT STANDARDS – SOURCES, INFORMATION

Prepared Standards (aqueous)

As noted above, a concern expressed at the first ACT Nutrient Sensor workshop was the availability of nutrient standards. The participants at the second workshop felt that there are now sufficient commercial options in this area. Packaged aqueous nutrient standard solutions are available from a number of suppliers, including Sprex (Certiprep standards; www.sprexcsp.com), YSI (www.ysi.com), and OSIL (www.osil.co.uk; www.seawatersolutions.com).

Seawater Standards

Since colorimetric nutrient analyses are sensitive to salt concentrations (e.g., color development and refractive index effects), standard solutions prepared in seawater are required for many coastal applications. OSIL (www.osil.co.uk; www.seawatersolutions.com) supplies concentrated nutrient standard solutions that are diluted to working calibration concentrations with Low Nutrient Seawater (LNS), which has defined maxima for nutrient concentrations (except ammonium, due to possible ammonia contamination from air).

Certified Reference Material

The “MOOS-1” is a reference material for nutrients in seawater matrix certified by the National Research Council (NRC) of Canada. A large volume of seawater collected from the Atlantic Ocean off Nova Scotia was mixed and packaged in 50 mL aliquots in sealed bottles. MOOS-1 samples were analyzed by a number of expert laboratories (colorimetric analyses) and data were returned to NRC Canada for evaluation. Certified values were calculated from the unweighted means of results. Independent methods developed at NRC were used to corroborate the colorimetric results. Certified values for the MOOS-1 reference material for nutrients are provided for orthophosphate, silicate, nitrite, and nitrate plus nitrite. Data sheets for the MOOS-1 certified reference material are available through the NRC Canada web site (http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html).

Certified Contract Laboratories

Another standard of interest with regard to environmental nutrient analyses is certification for contract analytical laboratories. A national accreditation program was recently established for environmental laboratories. The NELAC Institute (TNI) was formed in November, 2006 through the actions of the National Environmental Laboratory Accreditation Conference (NELAC) and the Institute for National Environmental Laboratory Accreditation (INELA). TNI is intended to foster the generation of environmental data of known and documented quality through an open and responsive process, with consensus definition of standards for environmental analyses. Further information about these organizations and lists of laboratories accredited for various environmental analyses can be obtained at www.nelac-institute.org.

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