

Workshop Proceedings



State of Technology in the Development and Application of Nutrient Sensors

*Savannah, Georgia
March 10-12, 2003*



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

An ACT 2003 Workshop Report

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

***State of Technology in the Development and
Application of Nutrient Sensors***

Savannah, Georgia
March 10-12, 2003

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

Hosted by Skidaway Institute of Oceanography (SkIO).

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

TABLE OF CONTENTS

Table of Contents	i
Executive Summary	1
Alliance for Coastal Technologies	2
Goal for the Nutrient Sensor Workshop	3
Organization of the Nutrient Sensor Workshop	3
Nutrient Enrichment in Coastal Waters, Statement of Problem	4
The Need for In Situ Nutrient Monitoring	5
Nutrient Sensor Technology	6
Recommendations	8
Conclusions	9
Appendix I. Workshop Participants	A-i
Appendix II. Available Technology for Nutrient Sensing	B-i

ACT WORKSHOP: STATE OF TECHNOLOGY IN THE DEVELOPMENT AND APPLICATION OF NUTRIENT SENSORS

EXECUTIVE SUMMARY

The Alliance for Coastal Technologies (ACT) convened a Workshop on the Development and Application of Nutrient Sensors in Savannah, GA on March 11 to 13, 2003. The workshop was designed to summarize the state of Nutrient Sensor technology and to make strategic recommendations for the future development and application of nutrient sensors for coastal environmental research and monitoring. The workshop was focused primarily on sensors for the major plant nutrients nitrate, phosphate, ammonia and silicate. Participants (Appendix I) included researchers responsible for nutrient sensor development, nutrient sensor industry representatives, researchers using nutrient sensors in oceanographic studies in the coastal zone and environmental managers involved in nutrient monitoring programs.

Discussion focused on the types of nutrient sensors that were available, including strengths and weaknesses, impediments, if any, to the use of nutrient sensors in coastal monitoring programs, desirable features in new sensor developments, and additional infrastructure that adoption of sensor systems will require.

Five general recommendations were made:

- Increase outreach efforts to coastal managers regarding the benefits of in situ nutrient sensors. While it is clear that current sensor systems may not be able to meet all goals in monitoring programs, it is also clear that sensors represent a very significant improvement in our ability to monitor nutrient fluxes and loading that cannot be achieved in manual sampling programs.
- ACT could facilitate sensor development by providing a defensible assessment of the potential market. Commercialization of sensor systems requires a large capital investment by private industry. Such investments are difficult to obtain, in part because there is not a clear assessment of the market potential for nutrient sensor systems.
- Encourage development and availability of nutrient standards. A major impediment to all nutrient monitoring programs is the lack of nutrient standards that can be used to intercalibrate the results from different laboratories or on different instruments.
- An important function for ACT could be to serve as a central point of contact for sensor funding announcements. Funding mechanisms for sensor R&D are found in a variety of agencies. While announcements are frequent, there is no central repository for such information.

- Finally, ACT should convene a second, more focused nutrient sensor workshop. It is clear that the development of nutrient sensors has been driven primarily by the research community rather than by environmental resource managers. The market survey, recommended above, could provide a better understanding of the needs of this latter group and provide the basis of the focus of a second workshop which would likely include just manufacturers and managers. Follow-up workshops or training sessions for managers that involve experienced sensor users may help spread expertise and speed the adoption of sensor technology.

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 and predicting the state of coastal waters. The workshop goals are to both help build consensus on the steps needed to develop useful tools while also facilitating the critical communications between the various groups of technology developers, manufacturers, and users.

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.actonline.ws.

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 NUTRIENT SENSOR WORKSHOP

The ACT Workshop on Nutrient Sensors was convened on March 11 to 13, 2003 in Savannah, GA to summarize the state of Nutrient Sensor technology and to make strategic recommendations for the future development and application of nutrient sensors for coastal environmental research and monitoring. The workshop was focused primarily on sensors for the major plant nutrients nitrate, phosphate, ammonia and silicate.

Workshop attendees were given the following charges to address:

- (1) What types of nutrient sensors are presently available and what are their strengths and weaknesses regarding application to coastal environmental research, monitoring and management?
- (2) What are the major impediments to the application of nutrient sensors?
- (3) What is the nutrient sensor tool needed for coastal environmental resource monitoring and management?
- (4) What are the technology, infrastructure and other needs necessary to encourage and enhance the application of nutrient sensors in coastal resource surveillance and management programs.

ORGANIZATION OF THE NUTRIENT SENSOR WORKSHOP

The workshop was sponsored by ACT and hosted by the Skidaway Institute of Oceanography, one of ACT's Partner Institutions. The workshop was organized by Dr. Herb Windom, Skidaway Institute of Oceanography and Dr. Ken Johnson, Monterey Bay Aquarium Research Institute, served as Facilitator. Participants arrived on Monday afternoon, March 10, and gathered that evening for a reception and dinner during which a presentation was given to introduce them to the ACT program. The workshop commenced on the next day beginning with an introduction to the Workshop goals followed by three breakout group discussions to address the first two charge questions. The first groups were organized according to the professional background of the participant. Afternoon breakout groups, to discuss the remaining charge questions were arranged to mix participants of differing professional backgrounds. This allowed for a greater perspective of the application of nutrient sensor technology. The final day was devoted to identifying common issues and organizing recommendation for the future.

NUTRIENT ENRICHMENT IN COASTAL WATERS, STATEMENT OF PROBLEM

Plant nutrients such as nitrate, phosphate, silicate and ammonia play a key role in controlling coastal ecosystems. These chemicals are essential nutrients that are required by phytoplankton and benthic plants for growth. In natural coastal ecosystems, a lack of these nutrients is generally the factor that limits the accumulation of plant biomass.

Nutrient inputs to coastal waters have increased rapidly in the past 50 years due to man's activities. Production of fixed nitrogen, primarily as fertilizers, has increased to the point where it now equals the natural production rate over the entire globe.

Anthropogenic inputs of nutrients to coastal waters come from a variety of sources including fertilizer in runoff from agricultural and urban lands, atmospheric deposition of nitrogen oxides produced when fossil fuels are burned and waste-water from sewage treatment plants. The flux of nitrate through the Mississippi River to the Gulf of Mexico has increased 3-fold since 1970 as a result of these processes. In some estuaries and bays, the input of nutrients from land is elevated more than 10-fold over natural levels. These findings are reported in numerous papers in the scientific literature.

The increased flux of nutrients has led to a number of negative impacts on coastal ecosystems. Elevated concentrations of plant nutrients cause eutrophication, or the increased production of plant organic carbon. This, in turn, leads to a variety of deleterious effects. Accumulation of phytoplankton in the water column may reduce light at the bottom and prevent benthic plants from growing. This leads to the loss of key habitat for animals. Eutrophication drives an increased demand for oxygen in subsurface waters as plant material sinks to the bottom and decomposes, resulting in hypoxic and even anoxic conditions. This loss of oxygen frequently leads to greatly reduced oxygen concentrations (hypoxia) or anoxia when oxygen loss is complete. Biological resources in bays (e.g., Chesapeake Bay) and open coastal regions (Gulf of Mexico) have been negatively impacted by the loss of oxygen produced by nutrient enrichment and eutrophication of surface waters.

The increase in nutrient concentrations may also lead to a shift in ecosystem structure. These shifts occur due to a variety of causes. Some plants, which are more tolerant of low nutrient concentrations, are replaced as nutrient inputs increase. In other cases, ecosystem structure shifts because of a change in the relative abundance of different nutrient elements. For example, enrichment of coastal waters with nitrate and phosphate is often accompanied by a loss of diatoms, a major phytoplankton group in unperturbed coastal waters. Diatoms require Si to grow, while other phytoplankton do not. Silica is seldom enriched in runoff because it is not as widely used as a fertilizer. Long-term observations in nutrient-enriched coastal waters often show a striking population shift from diatoms to dinoflagellates. Finally, the ecosystem shifts may be driven by indirect effects, such as a loss of benthic filter feeders that consume phytoplankton.

Rapid shifts in ecosystem structure may favor increases in the concentration of phytoplankton that produce toxic compounds. These Harmful Algal Blooms (HAB's), or "Red Tides", impact the environment in a number of negative ways. The toxins may kill or impair finfish, shellfish, birds and mammals. Thus HAB's can have a significant economic impact on commercial fisheries and recreational amenities. While the connection between inputs

of nutrients and HAB's has not been shown directly, abundant indirect evidence comes from strong correlations between increased nutrient concentrations and the frequency of HAB events.

THE NEED FOR IN SITU NUTRIENT MONITORING

Accurate assessments of nutrient loading are required to determine the impacts of nutrient enrichment on coastal ecosystems and to determine the efficacy of management actions that are designed to regulate nutrient enrichment. Effective monitoring programs must sample at time and space scales that capture the major variability found in coastal systems to provide accurate assessments of loading. Coastal and estuarine water quality monitoring programs, however, usually consist of sampling at fixed sites on a monthly or bimonthly frequency. Such programs can result in severe misinterpretation of nutrient dynamics of coastal systems.

Processes such as tidal flushing, runoff following storms and wind-driven upwelling all cause large and rapid oscillations in nutrient concentrations of coastal systems. It is unlikely that monitoring programs based on manual sample collection can routinely sample at the rates required to assess such processes. For example, a time series of nitrate and phosphate concentrations measured with experimental sensor systems in the Moss Landing Harbor during the fall of 2002 are shown in Figure 1. This data set shows the rapid change in concentration that follows the first large rain event of the year. Nitrate concentrations increase rapidly as a low salinity pulse of fresh water runoff from the extensive agricultural lands of the lower Salinas River valley flows through the harbor to Monterey Bay. The low salinity water is then flushed from the Harbor on each rising tide. It would be fortuitous to capture the runoff event in a monthly sampling program and the tidal oscillations could not be detected without high frequency sampling.

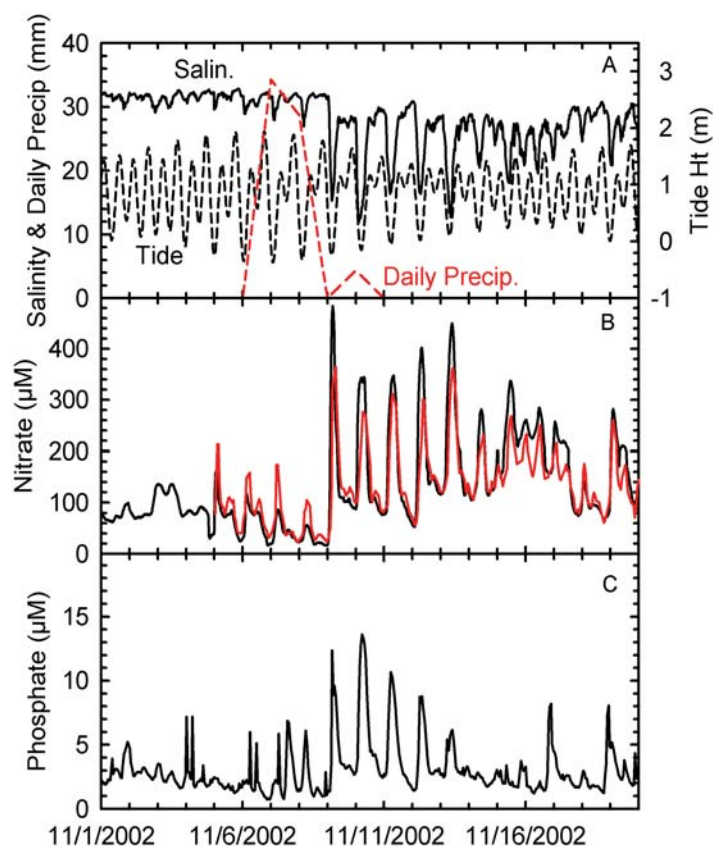


Figure 1. A) Salinity (solid line) and tide height (dashed line) in Moss Landing Harbor, California. Daily precipitation measured at a weather station 15 km distant in Pajaro, California is also shown (red line). B) Nitrate concentration measured in Harbor waters with two different in situ nitrate sensors suspended at 1 m depth and sampling at hourly intervals. C) Phosphate concentration measured in Harbor waters with an in situ sensor operating as in (B). Courtesy of Ken Johnson, MBARI.

In the open coastal waters of Monterey Bay, nutrient concentrations are also extremely variable as upwelling favorable winds bring cold, nutrient-rich waters to the surface (Figure 2). These pulses of nitrate then disappear as winds relax and surface water down-wells or phytoplankton consume the nutrients.

Nutrient sensors have become accepted for use in research projects, but there are few cases where they are being used for regulatory monitoring. A variety of reasons were discussed concerning why in situ nutrient sensors have not become more widely used in the regulatory arena. Regulatory programs often have a requirement to monitor a broad range of chemicals, while nutrient sensors may be available for only one or a few chemicals, thus they cannot completely replace a manual sampling program. Nutrient sensors often require a highly trained operator, while personnel without formal analytical training may be used to collect samples and return them to a central laboratory.

Finally, despite the fact that manual sampling often provides a very flawed perception of nutrient distributions, it is a legally defensible strategy that, if properly implemented, can provide a clear chain of custody from the sample to the final measurement. Such a chain of custody may be more difficult to implement with a sensor deployed in the field. However, the widely deployed system of breathalyzers, which are used to determine blood alcohol levels, is a chemical sensor network that provides legally defensible data. This could be viewed as a model for instigating acceptance of a nutrient sensor network that must provide some chain of custody.

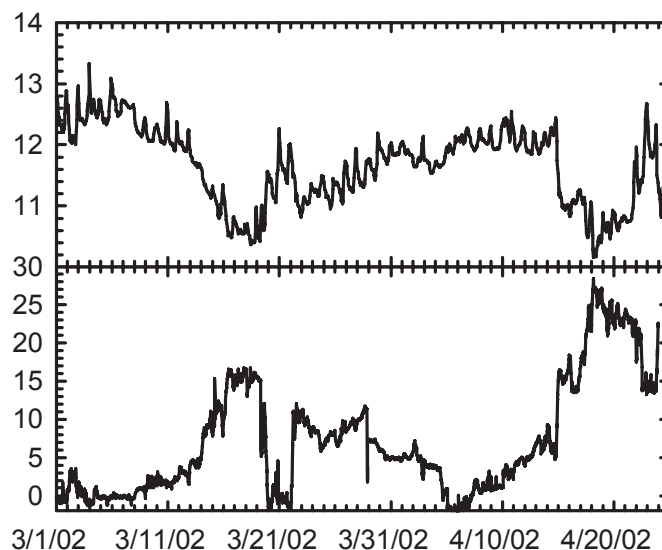


Figure 2. Temperature and nitrate concentrations measured hourly on the MBARI M1 Mooring in Monterey Bay, California. Measurements were made in situ at 2 m depth. Data courtesy of Ken Johnson, MBARI.

NUTRIENT SENSOR TECHNOLOGY

A variety of in situ nutrient measurement methods have become available within the past five years. Instruments are now in or near production by at least four companies (Appendix II) that are capable of measuring nutrient concentrations in coastal waters. Three of these systems are automated analyzers that perform colorimetric chemical analyses based on standard "wet-chemical" methods used in the laboratory. Such systems are often adaptable to monitor a variety of different chemicals by changing the chemical reagents that are used in the analysis. The fourth system is a nitrate sensor based on direct optical measurements of the nitrate UV absorption spectrum. Ion sensitive electrodes are also available for in situ measurements of nutrient concentrations. However, electrodes are not widely used in marine or brackish water environments due to large interferences from salt ions and these systems were not discussed extensively at the workshop.

Nutrient sensors that are used for research or monitoring may be deployed in a variety of environments and for a variety of reasons. Each of these applications may impose different requirements that are unlikely to be met by a single type of sensor system. Surveys of broad areas of the coastal ocean or embayments may require a sensor capable of making measurements at a high response rate ($\sim 1/s$), but long-term stability may not be a requirement. Long-term monitoring of the nutrient concentrations requires a sensor that can be placed on a mooring and return accurate data for months at a time. However, the sampling frequency may be less than that required for a sensor used in a spatial survey (~ 1 sample/hour vs. ~ 1 sample/second). Instruments used in research projects may be used by more highly trained operators than those used for monitoring and need not be as robust. Finally, cost is a major factor for monitoring projects that require large numbers of sensors. These factors all suggest that a variety of nutrient sensor types will be required by the coastal research and monitoring community.

These considerations led to a discussion of the characteristics of an "ideal" nutrient sensor properties, which should be considered in sensor development and operation.

- Sensors should be self calibrating to provide traceability of the observations.
- Ideally, a sensor system provides data for a suite of nutrients, such as nitrate, phosphate, silicate and ammonia.
- Sensors used for long-term observations must be immune or highly resistant to biofouling, which can be one of the major impediments to successful sensor deployments.
- Total Lifecycle Cost, which is often more important than the initial capital cost, is an important factor in sensor selection and operation.
- Reliability should be $>90\%$ in field deployments.
- Sensor systems should be capable of real-time data transmission.
- Instruments used in monitoring programs should operate without service for at least several months.
- Instruments used for spatial surveys must provide data that is integrated with other sensors such as a CTD and should accept data from global positioning devices.

In addition, participants also identified issues that can make sensor systems difficult to use. These include:

- Steep learning curves for sensor systems can greatly inhibit their adoption and often lead to improper use that impacts the image of sensor systems.
- Complexity of instruments that contribute to low reliability or difficult operation is clearly undesirable.
- Waste disposal and storage in wet chemical analyzers can be an issue that impacts their operation in the field.

- Problems can arise during reagent preparation in wet chemical analyzers and manufacturers should consider steps to alleviate this issue.
- Standardization in variable environments typical of the coastal zone (large salinity, color, and turbidity gradients) can be difficult.
- High instrument costs clearly are an issue with users.
- Large instrument size can make deployments difficult.

RECOMMENDATIONS

Five general recommendations were made by the workshop participants:

- Increase outreach efforts to coastal managers regarding the benefits of in situ nutrient sensors. While it is clear that current sensor systems may not be able to meet all goals in monitoring programs, it is also clear that sensors represent a very significant improvement in many areas. Sensor systems have primarily been used in research projects and there are few, if any, cases where they are being used for regulatory monitoring. However, the examples obtained with sensor systems demonstrate that episodic processes dominate nutrient flux. Accurate estimates of flux are not possible, in many cases, with manual sampling efforts. ACT must encourage the adoption of these instruments in monitoring programs.
- ACT could facilitate sensor development by providing a defensible assessment of the potential market. Commercialization of sensor systems requires a large capital investment by private industry. Such investments are difficult to obtain, in part because there is not a clear assessment of the market potential for nutrient sensor systems. It was noted that the major market may not yet exist because sensors are not yet considered "Best Available Technology" that must be used in many cases.
- Encourage development and availability of nutrient standards. A major impediment to all nutrient monitoring programs is the lack of nutrient standards that can be used to intercalibrate the results from different laboratories or on different instruments. Biases introduced by undersampling in programs based on manual sampling may obscure the problems introduced by a lack of standards. However, in situ sensors are capable of generating sufficient data to alleviate many of the undersampling problems. As they become more widely used, problems due to poor calibrations and lack of comparability will become more apparent. Efforts to develop a widely distributed nutrient in coastal seawater standard should be undertaken.
- An important function for ACT could be to serve as a central point of contact for sensor funding announcements. Funding mechanisms for sensor R&D are found in a variety of agencies. While announcements are frequent, there is no central repository for such information.
- Finally, ACT should convene a second, more focused nutrient sensor workshop. It is clear that the development of nutrient sensors is been driven primarily by the research community rather than by environ-

mental resource managers. The market survey, recommended above, could provide a better understanding of the needs of this latter group and provide the basis of the focus of a second workshop which would likely include just manufacturer and managers. As sensors become available, there is often a barrier to their initial acceptance due to unfamiliarity and the large commitment of time that it may take to become adept at operating sensor systems. Therefore follow-up workshops or training sessions for managers that involve experienced sensor users may help spread expertise and speed the adoption of sensor technology. Workshops might also be conducted to facilitate the familiarization of the community with emerging or existing technologies outside the marine/aquatic arena.

In addition to these five specific recommendations, there were a number of additional comments made related to the use and development of nutrient sensors. These include the following.

- Sensor developers, both researchers and industry, should not lose sight of the need to develop sensors for a wide range of users. This might include the development of simple, stand-alone sensors for resource managers that need not be deployed autonomously.
- ACT should maintain User contacts associated with a "sensor clearinghouse" on the ACT website .
- ACT could encourage more interaction between developers and users. One such interaction might involve identifying identify beta testers.
- Finally, the community must begin to develop support for the large quantities of data that will be generated by sensor systems. There is a large difference between dealing with data that is generated once a month and values that are generated at hourly intervals. These differences impact archiving, visualizing, interpreting and quality controlling the data.

CONCLUSIONS

In situ nutrient sensor technology has progressed rapidly in the past decade. Commercial units are now widely available and they are being used in a variety of research programs. Data collected with this technology has demonstrated large variability in nutrient concentrations that would be difficult to quantify with manual sampling programs that are typical of most environmental monitoring programs. It is clear that our understanding of natural and anthropogenic flows of nutrients through coastal systems will be greatly improved by the widespread use of in situ sensor technology.

Adoption of in situ nutrient sensors by coastal monitoring and management programs will be the next major hurdle. This will involve, in part, continued refinement of instruments by manufacturers to resolve concerns such as those identified at the Nutrient Sensor Workshop. Perhaps more importantly, though, acceptance of in situ nutrient sensors requires more communication between the research and the monitoring communities. ACT can play a major role in this regard.

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APPENDIX II. AVAILABLE TECHNOLOGY FOR NUTRIENT SENSING

MANUFACTURER	TYPE	BASIC DESCRIPTION
EnviroTech (www.n-virotech.com)	Wet chemical analyzer	The NAS-2E has been adapted to perform nitrate, phosphate, silicate and ammonia analyses in all of these environments. The system utilizes a syringe pump and novel rotary valve to acquire and react discrete water samples. Flexible user programmable controls make the system versatile. A macro language allows the operator to easily reprogram the complete chemistry analysis and sequencing. The NAS-2E is extremely resistant to the effects of biofouling and high turbidity.
Satlantic (www.satlantic.com)	Optical nitrate sensor	The MBARI-ISUS is a novel optical approach to measure nitrate concentrations in situ in a wide range of oceanographic and fresh water applications. Using UV absorption spectroscopy, the ISUS measures nitrate without the need for any reagents or manipulation of the water sampled. By simply turning the system on and immersing it in water, ISUS automatically starts to compute the nitrate concentration in real time, continuously, at a rate of 1-2 measurements per second.
SubChem Systems (www.subchem.com)	Wet chemical analyzer	SubChemPak Analyzer is a four channel, real-time profiling analyzer for dissolved inorganic nutrients (nitrate, nitrite, phosphate, silicate, ammonium and iron). Unique features include multi-chemical adaptability, analytical chemical simplicity, continuous measurements (seconds), and low detection limits (nanomolar). The company has also now offers a line of autonomous submersible chemical analyzers, with smaller size and lower power requirements, for deployment on autonomous underwater vehicles and profiling moorings.
YSI Environmental (www.ysi.com)	Ion Selective Electrodes (ISE)	As a part of YSI's nutrient sensor line, YSI provides Nitrate and Ammonia Ion Selective Electrodes (ISE) that may be integrated into a sensor package. Currently, YSI is in the final development stages of a wet-chemistry nutrient analyzer for nitrate and phosphate. YSI will be looking for Beta test sites beginning in summer 2003.

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