Chemical Sensor Networks for the Aquatic Environment

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1. Introduction

A recent commentary speaks to a broad range of potential applications for autonomous chemical sensor networks, including systems that monitor the state of the environment in real time.[1] However, the authors of the commentary noted that existing sensor networks are "almost entirely restricted to transducers for detecting physical parameters such as temperature, pressure, light or movement". They termed this the "chemical sensor paradox", a condition that results because current technology "makes the realization of small, autonomous, reliable, chemo/bio-sensing devices impractical at present".

Rapid strides have been made toward autonomous chemical sensing capabilities in the past decade by the marine and aquatic chemistry communities. While chemical sensors are not at the same level of cost or reliability as physical sensors, a variety of chemical sensing systems are now continuously deployed in aquatic environments such as rivers, lakes, estuaries, and the open ocean. These chemical sensors are being operated, in some cases, for multiyear periods and in the ocean at thousands of kilometers distance from shore. Data from dozens of sensors are being delivered in near-real time directly to the Internet.

The primary emphasis of this review is focused on such chemical sensor networks that can be deployed on autonomous platforms in aquatic environments and then operated without significant human intervention for extended periods. The aquatic sensor networks that we consider have two essential characteristics: (1) chemical sensors are deployed in situ at multiple locations, and (2) the networks are operated for months to years. These observing systems are dedicated to observing environmental processes in real time. Much of this effort is quite recent, and this article serves as an introduction to this work, as well as a review.

We focus on observing systems that operate for extended periods for two primary reasons. Long-term observations of the environment are essential to understanding variability driven by natural and anthropogenic climate change. In situ sensors also provide the continuous data needed to characterize high-frequency signals that cannot be easily sampled by manual methods. Undersampling of time-varying environmental processes can result in aliasing of the observed signal. The variability that is driven by processes occurring at higher frequencies than the sampling frequency of the environment can appear as unrecognizable low-energy events.[2]

Environmental chemists have often avoided the questions related to undersampling time-varying signals by assuming that aquatic systems are in a steady state. With this assumption, a single set of observations then provides an adequate assessment of environmental processes. This assumption has been necessary because, until recently, nearly all observations of chemicals in the aquatic environment required that a sample be collected and returned to the laboratory, where a variety of sophisticated tools could be used for sample analysis.[3] Much of the ocean is sampled only a few times in a decade because of the long (weeks in some cases) transit times from seaports to mid-ocean regions. Even in the coastal ocean, or lakes and rivers, samples for chemical analysis are generally collected only at monthly intervals, if at all.[4] Such sampling rates are often inadequate to characterize the dominant seasonal, daily, or semi-diurnal processes, which occur at well-defined frequencies, as well as episodic events driven by storms or other processes. Even the signals of decadal-scale processes may be contaminated

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Stephen C. Riser studied physics, engineering, and oceanography at Purdue University and the Massachusetts Institute of Technology. He received his Ph.D. degree from the Graduate School of Oceanography at the University of Rhode Island in 1982. Since 1984 he has been at the School of Oceanography, University of Washington, in Seattle, Washington, where he is presently Professor of Oceanography. His work concerns the general circulation of the ocean and its interaction with the atmosphere and the ocean's role in climate change. He works extensively with marine instrumentation and new methods of observing the ocean circulation.

Bill Showers was born in St. Paul, Minnesota. He received a Bachelor degree in Geology from University of California, Santa Barbara in 1973, an MS in Geology from University of California, Davis in 1978, and a Ph.D. in Geological Oceanography in 1982 from the Hawaii Institute of Geophysics at the University of Hawaii. He has been a faculty member in the Department of Marine, Earth, & Atmospheric Sciences at North Carolina State University since 1982, where he is also the Director of the NCSU Stable Isotope Lab and the Director of the RiverNet Program. His research interests include paleoceanography and solar influences on climate, paleobiology of dinosaurs and flightless birds, groundwater pollution, and the flux of nitrogen in watersheds.

by variability that occurs at higher frequency. Interpretation of the linkages between processes is further obscured due to long-term lags between cause and effect.[5] As a result, we begin by arguing that observing the environment requires sustained, high-frequency observations.

1.1. The Sampling Problem

We illustrate the problems that arise in monitoring efforts that are based on manual sampling by considering nitrate in aquatic systems. Nitrate is the dominant source of fixed nitrogen for new plant growth in most aquatic ecosystems. Surface waters in the open ocean are depleted in plant nutrients, including nitrate. This depletion is a result of nutrient incorporation by photosynthetic organisms and subsequent sinking of organic material in fecal pellets and decaying organic matter. Deep waters are enriched in nutrients when heterotrophic organisms remineralize sinking particles. The low concentrations of nitrate in the sunlit surface waters limit the accumulation of plant biomass in many marine and freshwater systems.[6] Processes that add new nutrients, such as vertical transport (upwelling or diffusion) of essential nutrients from deep waters into the sunlit euphotic zone or nitrogen fixation, then become the rate-limiting step for primary production of new organic carbon.

Figure 1 shows nitrate measurements made on a mooring located 20 km off the central California coast at hourly intervals for 1 year[7] using an optical nitrate sensor[8] and nitrate

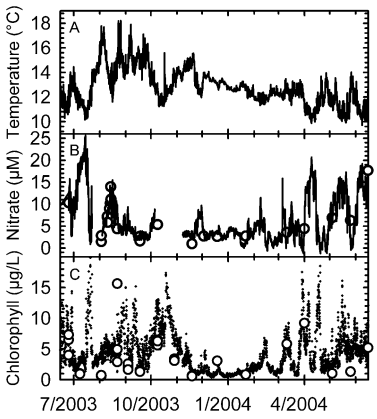

Figure 1. Measurements of temperature (A), nitrate (B), and chlorophyll (C) made at hourly intervals for 1 year on the M1 mooring 20 km offshore in Monterey Bay, California. Nitrate was measured with an optical nitrate sensor.[8] Chlorophyll concentration was calculated from the attenuation of sunlight at 490 nm between the surface and 10 m. Measurements of nitrate and chlorophyll in samples collected near the mooring at approximately 21 day intervals are shown as open circles. Adapted from ref 7, Copyright 2006, with permission from Elsevier.

measurements in samples collected near the mooring at ~21 day intervals. The annual cycle observed by the moored chemical sensor shows a series of events throughout the year with high (>10 μM) nitrate concentrations. These events are produced by upwelling of cold, nutrient-rich water, which is driven to the surface when the wind blows to the southeast in this region. Upwelling of cold, nutrient-rich deep water into warm, nutrient-poor surface water produces the anticorrelation in temperature and nitrate (Figure 1). The nutrients carried into sunlit surface waters during the upwelling events result in phytoplankton blooms that increase chlorophyll concentrations and deplete nitrate (Figure 1). This cycle of events, clearly seen in the hourly data, is not easily resolved in monthly monitoring data. A quantitative understanding of such processes has come from intensive field sampling campaigns. However, intensive field programs are difficult to sustain in the long-term. As a result, most aquatic environments are severely undersampled, long-term variations are not understood, and our understanding of environmental processes can be quite biased.

In addition to large temporal variability, there is also significant spatial variability in concentrations of chemicals that play important roles in regulating ecosystems. For example, the physical processes that reintroduce nutrients to the surface have high spatial variability. This may produce great spatial variability in the growth of phytoplankton populations. Thus, chemical sensors in this type of environment should, ultimately, be capable of characterizing high spatial variability, as well as temporal variability.

The undersampling problem, which is inherent in measurement programs that are based on manual sample collection, can be overcome either by using remote sample collection devices[9,10] or by making nearly continuous chemical measurements over long time periods on networks of unattended platforms. Here we focus on systems that make in situ measurements. Chemical sensors deployed in situ for extended periods have shown the impacts of events driven by storms,[11] eddies,[12,13] El Niño climate oscillations,[14,15] planetary (Rossby) waves,[16] tides,[17] upwelling,[7] and ice melting.[18]

1.2. Data at Global Scales

The need for a better understanding of the linkages between chemicals and environmental processes is driven by the globally significant scope of environmental change presumed to be occurring. During the past 100 years, concentrations of carbon dioxide in the atmosphere have increased 36%, industrial and agricultural processes that fix dinitrogen gas have grown to the point where their rates now exceed natural processes,[19] some 10−50% of the photosynthetic products on land are appropriated by processes controlled by humans,[20] and one-half of the accessible freshwater runoff is already utilized.[21] Such global scale processes necessarily require global observing systems.

The best example of the power of a global environmental chemical analysis network is the system of stations that collect atmospheric measurements of carbon dioxide and oxygen. These networks build on the pioneering work of the late Charles David Keeling, who started the time series of atmospheric carbon dioxide measurements at Mauna Loa in Hawaii. Keeling's CO_2 data from Mauna Loa have played a seminal role in identifying human perturbation of global chemical cycles, and it has been the most influential environmental data set now available. His results led to an expansion of the observing system, and there is now a network of stations around the world where samples for carbon dioxide and oxygen are collected.[22,23] The network measurements reveal distinct annual cycles in atmospheric oxygen and carbon dioxide concentrations. Further, there is a distinct geographic pattern to the variability that is related to differences in land and ocean areas in the Northern and Southern Hemispheres. The patterns of annual variation are driven by photosynthesis and respiration on land and in the sea and by differences in the rates at which these two chemicals equilibrate across the air−sea interface. These geographic and temporal variations in chemical properties of the atmosphere allow the long-term, network-based observations to be used to create estimates of global net primary production on land and in the ocean and to quantify the interannual change in these rates.[22,23]

Ultimately, monitoring aquatic biogeochemical cycles and their impacts on the environment and climate will require dense networks of chemical sensors that operate at global scales within the oceans, lakes, and rivers, as well as in the atmosphere. While there are no direct examples operating at a global scale today, there are a variety of in situ chemical sensor networks operating at smaller scales. Further, there are examples of global aquatic sensor networks that illustrate the potential for the development of networks that sense chemical properties. For example, we describe in section 3.2 chemical sensor measurements from the Argo array of profiling floats.[24] These platforms have become an important tool for observing the large-scale ocean circulation. Profiling floats typically drift passively with the flow at depths of 1000 or 2000 m in the ocean and then cycle at 7−10 day intervals away from their parking depth by inflation of a bladder, which increases float volume without changing mass. This causes the float to rise. During the ascent to the surface, the floats collect measurements of oceanic variables such as temperature and salinity at 50−75 different pressure levels. The floats transmit their data to orbiting satellite communication networks while on the surface and then descend back to their parking depth to begin another cycle.

A map of seawater salinity at a depth of 200 m based on in situ salinity measurements that were made by ~1200 Argo

floats in the Pacific Ocean during the first two weeks of December 2005 is shown in Figure 2 (35 on the IAPSO

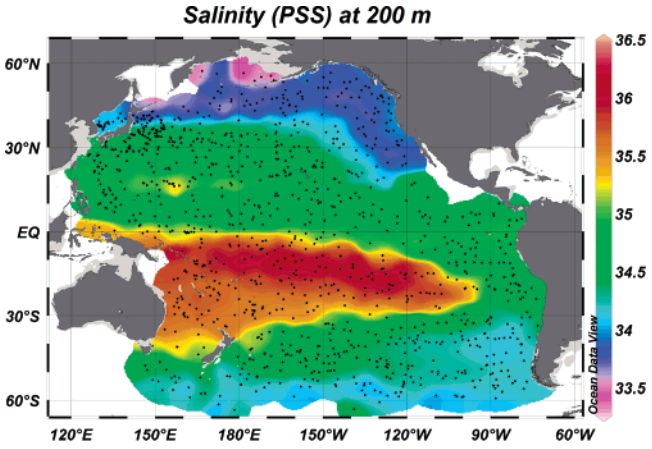

Figure 2. Salinity measured on the Practical Salinity Scale[25] at 200 m depth in the Pacific Ocean. The map was contoured using the program OceanDataView[26] after importing vertical profile data for ~1200 Argo floats from the Argo data center (ftp://ftp.ifremer.fr/ifremer/coriolis/global_profile/pacific_ocean/). Data was collected during the first two weeks of December 2005. The location of each vertical profile is shown as a black dot.

Practical Salinity Scale[25] is nearly equal to 35 g of salt/1000 g of seawater). The program OceanDataView[26] was used to read the data and create the map. The Argo array illustrates the potential for operating global sensor networks within the aquatic environment. Further, profiling floats are now being equipped with chemical sensors.[27]

The Argo array is building onto a sustained set of 3000 floats, approximately one per each 3° longitude by 3° latitude box in the ocean. Given the richness of biological and chemical processes, that produce distributions with greater complexity than temperature or salinity, we will need sensor arrays with equivalent, if not greater, sampling density to be able to resolve important biological processes in the ocean. On continents, one might expect that chemical sensor networks designed to monitor transport of nutrient elements from land to the coastal ocean would require sampling densities similar to that used to assess water flow in streams. There are presently some 3600 real-time stations operated by the United States Geological Survey to monitor stream flow in the USA.

2. In Situ Chemical Sensors and Analyzers

There has been an extensive effort to design chemical sensors and analyzers that are capable of operating in situ. Much of this work has been recently summarized in two volumes on chemical sensor systems for aquatic sciences.[28,29] In addition, in situ electrochemical sensors have been reviewed,[30] as were chemical and biological sensors for time-series research.[31] The two volumes contain chapters that describe a variety of continuous flow analyzers, electrochemical sensors, and optical sensors for in situ measurements of dissolved chemical species. Most of this work remains focused on the research required to develop prototype sensor systems, and relatively few chemical sensors are available that are sufficiently robust for routine and widespread use in networks. Here we focus on chemical monitoring systems that have matured to the point where there are data records from instruments deployed in the field for at least 1−2 months.

Why are autonomous chemical sensors not in broader use? The scarcity is related to the analytical challenge in making autonomous chemical measurements in natural waters with complex background matrices against which low analyte concentrations must be detected.[1] In the laboratory, these analytical challenges can be overcome through the use of very sophisticated instrumentation. These complex measurements often involve several analytical steps and are the so-called hyphenated methods: for example, gas chromatography−mass spectrometry, organic extraction−graphite furnace atomic absorption spectrophotometry, and isotope dilution−high-resolution inductively coupled plasma mass spectrometry.[3] While a number of laboratories have developed portable instrumentation based on sophisticated methods such as ICP-MS,[32] they still require frequent operator attention and, in many cases, they require a portable laboratory on site to provide power and clean working spaces. In situ chemical sensors or analyzers that can be deployed in network arrays for long time periods require much simpler and more robust methods of chemical analysis.

A variety of approaches have been used to monitor chemicals in situ. Most familiar are sensor systems in which the sample interacts directly with the sensor without additional chemical manipulations. These include electrochemical sensors such as membrane-covered Clark oxygen cells[33] and pH electrodes. A variety of more sophisticated sensors based on electrochemical analyses are now possible,[30] which enable studies of chemical speciation in unique environments.[34] Direct optical chemical sensors are also becoming more common. Fluorescence quenching sensors based on immobilized platinum and ruthenium complexes are available for measurement of oxygen.[35,36] Spectrophotometers can be used in situ for the direct determination of nitrate and sulfide using their distinctive ultraviolet absorption spectra.[8,37] All of these instruments must either be extremely stable or be capable of self-calibration[38] in order to produce quality data over long periods of time.

Simple sensor systems that are capable of operating without drift for long periods of time and that are sufficiently selective and sensitive are not yet available for most chemical species of interest in the aquatic environment. As a result, in situ chemical monitoring often requires more complex instrumentation, which is used to perform multistep chemical analyses in the same manner as the familiar continuous flow analyzers that are used on board ships. These instruments generally require more complex apparatus with pumps, valves, fluidic manifolds, separate detectors, and reagent reservoirs and highly trained operators. These analyzers are often based on the principles of flow injection analysis.[39] Reviews[40,41] describe a variety of these in situ analysis systems.

One of the major challenges to operation of chemical sensor systems is biofouling of sensor or analyzer surfaces. In highly productive coastal and estuarine waters, sensor surfaces may be overgrown by organisms within a few weeks (Figure 3). The biofouling organisms may create microenvironments that alter chemical concentrations, block optical paths and create barriers to the flow of chemicals to sensing surfaces. A variety of methods have been adapted to mitigate the effects of biofouling.[42,43] However, none has proven universally successful and each system requires empirical assessments to find effective methods.

In the following sections, we describe the chemical sensors that have been deployed in situ, in lakes, rivers, or the ocean,

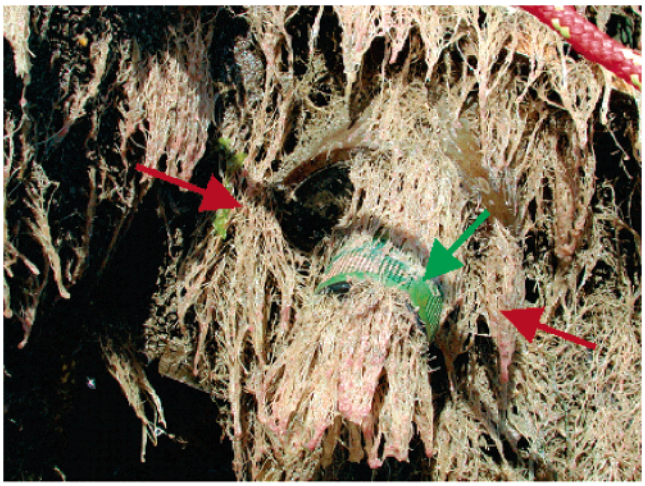

Figure 3. An ISUS optical nitrate sensor encrusted with hydroids. Red arrows identify the outside diameter of the instrument (12.5 cm), and the green arrow points to a copper antifouling shield that protects the optics. Used with permission. Copyright 2006, MBARI.

and which have data records that extend over periods of at least a few months. Given the long time frames required to bring chemical analysis systems to this level of maturity, these sensors are likely the main candidates for deployments in the next generation of chemical sensor networks. We then describe examples of the networks that are now operating and which use these sensors or analyzers.

2.1. Dissolved Gases Other Than CO_2

A variety of sensors exist for dissolved oxygen, total gas pressure, and methane that have demonstrated endurances in excess of a month while deployed in situ. Sensors for dissolved gases, particularly oxygen, are probably the most widely used chemical sensors in aquatic environments.

2.1.1. Dissolved Oxygen

Oxygen sensors are of particular interest because of the role of oxygen in metabolism. The dissolved oxygen concentration is an indicator of primary production of fixed organic material and respiration of organic carbon.[44] The depletion of oxygen below critical levels is lethal to animals.[6,45] Oxygen sensors based on a membrane covered, amperometric electrode (the Clark electrode[33]) are probably the most common chemical sensor system used in the aquatic sciences. They are routinely used on conductivity−temperature−depth−O_2 ($CTDO_2$)/rosette sampler packages that are lowered from ships to collect water and measure the vertical distribution of temperature, salinity, and oxygen. Handheld oxygen sensors are often used for spot monitoring of inland waters.

Biofouling in productive environments can require that Clark oxygen sensors be cleaned or replaced at weekly intervals when they are continuously deployed.[46] Monthly recalibration is required even in very low productivity regions of the upper ocean.[47] As a result, there are not large numbers of long-term records from Clark oxygen electrodes in the aquatic environment, although they are becoming more common as solutions to the biofouling problem are developed. The effects of biofouling on Clark electrodes tend to be least severe in lakes, and they have been used in long-term studies of primary production under ice in northern lakes.[18] In estuaries and the ocean, the applications include studies of gas exchange[11] and respiration and primary production[47, 48] during long-term deployments.

Deployment of oxygen electrodes on vertically profiling platforms, such as floats[24] and gliders,[49] greatly alleviates the fouling problems in marine environments. These platforms spend a substantial fraction of time at depths below the euphotic zone in waters where biofouling is not severe. For example, consider results obtained with the first profiling float equipped with a modified Seabird Electonics SBE43, which is a membrane-covered Clark oxygen electrode. This float was deployed as part of the Argo array (University of Washington float 0894) near the Hawaii Ocean Time series (HOT) station[50] at 22.75° N, 158° W in August of 2002. Float 0894 drifted at a depth of 1000 m and profiled to the surface at 10-day intervals for nearly 3 years, reporting more than 100 oxygen profiles. Before every fourth profile, the float descended to a depth of 2000 m and then rose to the sea surface. As can be seen in Figure 4, float 0894 remained

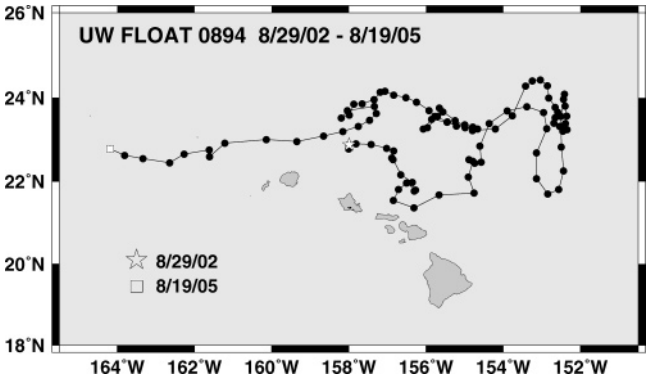

Figure 4. Trajectory of UW float 0894 near the Hawaiian Islands, deployed in August of 2002. The dots show the location of the profiles at 10-day intervals. This float was parked at a depth of 1000 m and collected data from 2000 m on every fourth profile.

in the vicinity of the Hawaiian Islands for most of its 3-year drift, only breaking away to the west during its final 10 profiles. This allows meaningful comparisons to be made with monthly shipboard measurements at the HOT station.

The data observed on a profile of float 0894 from 2000 m to the surface (Figure 5) shows the typical distribution of

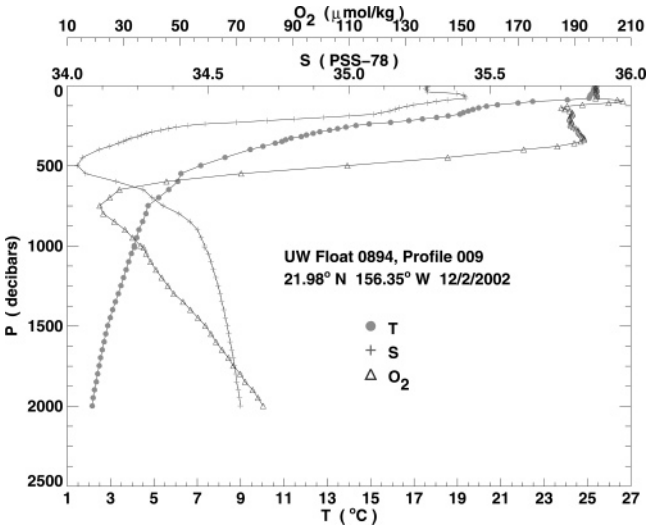

Figure 5. Temperature, salinity, and dissolved O_2 profiles from UW float 0894, profile 009. The dots denote the pressures where data were collected.

temperature, salinity, and dissolved O_2 in the North Pacific. All three variables take on their maximum values near the sea surface. Temperature decreases monotonically from the surface to 2000 m. Salinity and dissolved O_2 show a decrease in the upper ocean with a mid-depth minimum near 500 m for salinity and 800 m for dissolved O_2. The subsurface O_2 minimum is due to a balance between O_2 inputs from the atmosphere and biological production at the sea surface and its loss by respiration in the ocean interior. High oxygen concentrations in the deepest water are produced by the high solubility of oxygen in cold water masses that sink from the surface in polar oceans and spread into the deep basins. Measurements are made at 71 different pressure levels (Note that the pressure at the bottom of a 1 m column of seawater is almost exactly 1 decibar near the sea surface. Deeper in the water column, density increases, and at 5000 m, the pressure increases 1.02 decibar for each meter of depth.[51] For our purposes, we treat the depth given in meters and pressure in decibars as essentially interchangeable numerically.), and the vertical distributions of each property are well resolved.

There is a seasonal cycle in dissolved O_2 concentration measured at the sea surface near the HOT site (Figure 6A). This cycle is primarily controlled by the seasonal cycle of sea surface temperature and the temperature-dependent solubility of O_2 in seawater. The O_2 solubility at the sea surface is highest during the winter, when the sea surface temperature is a minimum. The O_2 concentration steadily increases early in the year as atmospheric O_2 equilibrates with surface water. As the temperature rises in the spring, the water becomes supersaturated with O_2, and by late spring or early summer, dissolved O_2 is removed from the surface waters by outgassing to the atmosphere. This seasonal cycle is seen in both the HOT shipboard O_2 station data, which is collected at the same site each month, and the surface data from profiling float 0894 (Figure 6A).

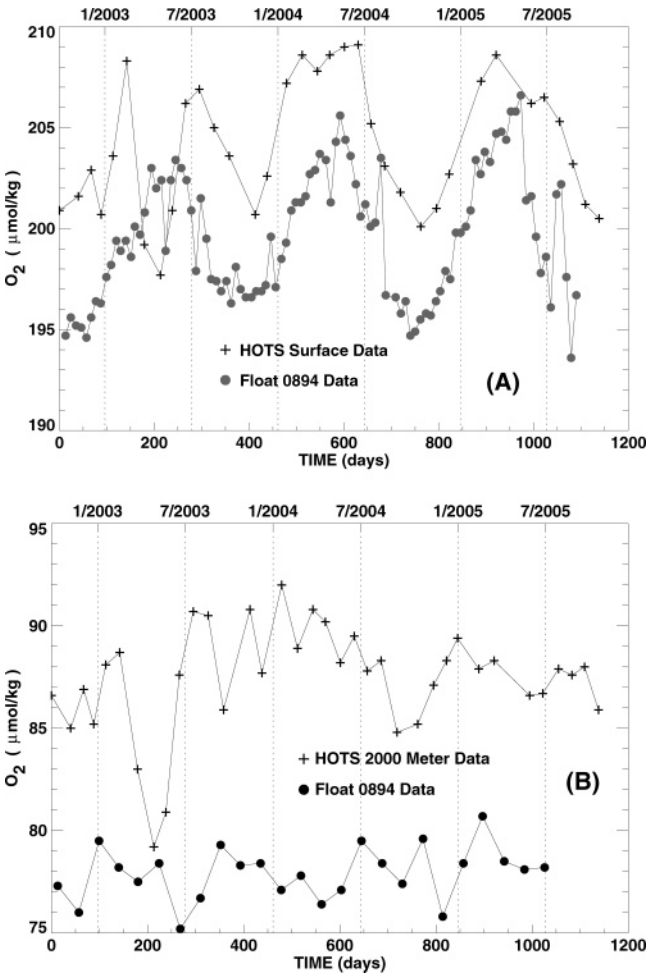

Figure 6. (A) Time series of shipboard surface O_2 data collected at the HOT site, near 22° N, 158° W, and O_2 data from a depth of 5 m collected by float 0894. (B) Time series of shipboard 2000 m O_2 data collected at the HOT site, near 22° N, 158° W, and O_2 data from a depth of 2000 m collected by float 0894. The shipboard values were determined using the Winkler titration method.

While the temporal variability in the shipboard and float O_2 observations is similar, the actual measured values of dissolved O_2 in the two datasets differ consistently by about 5 μmol/kg (a 2.5% offset), with the shipboard values usually higher. Since the shipboard values are determined manually from a highly accurate Winkler titration,[52] they are presumed to be correct. The offset is roughly consistent with the manufacturer's specifications for the SBE oxygen sensor of initial accuracy of 2% of the saturation value. A similar finding emerges for the deep water: there is no systematic divergence over ~3 years time at 2000 m between the shipboard measurements and those collected from float 0894 (Figure 6B). This again suggests a calibration offset on the float sensor, but again the lack of systematic sensor drift over 3 years is highly encouraging. This is an important finding and bodes well for the use of such sensors on profiling floats, where the sensor is unattended for periods of 5 years or more.

The problems created by biofouling have led to considerable effort to develop even more robust oxygen sensors based on alternative technologies. Oxygen quenching of fluorescent compounds containing metal ions such as ruthenium or platinum is one extremely promising technology.[53] Fluorescence sensors do not consume oxygen, and they are less sensitive to fouling that alters the diffusion rate of oxygen through the membrane. At least three commercial products using this principle are now available for in situ measurements. Fluorescence-based sensors respond to oxygen fugacity, as opposed to oxygen concentration in electrode systems. This can make the calculation of oxygen concentration somewhat more complicated in these systems. Fluorescence-based systems may also suffer long-term drift due to photobleaching of the dye and leaching of the dye from the matrix used to immobilize it.[53] Robust, long-term deployments have required systems that use fluorescence lifetime measurement methods. Lifetime measurements are nearly immune to loss of the fluorophore due to photobleaching or other processes when compared to direct detection of fluorescence intensity. Lifetime-based fluorescence quenching oxygen sensors have been deployed for time periods in excess of 1 year with no significant drift.[36, 54] For example, measurements of dissolved oxygen in the North Atlantic Ocean were made over a time period of 600 days on a profiling float of the type described above (Figure 7).[36] Measured oxygen concentrations at a depth of 1800 m, where little change was expected, averaged 295.0 ± 0.7 (1 standard deviation) μM over the entire period. Further, some of the change appears to be related to changes in water mass properties, identified by independent observations of density (Figure 7). These results suggest that oxygen measurements with a precision near 0.1% may be attainable over time periods greater than 1 year. Such capability would enable

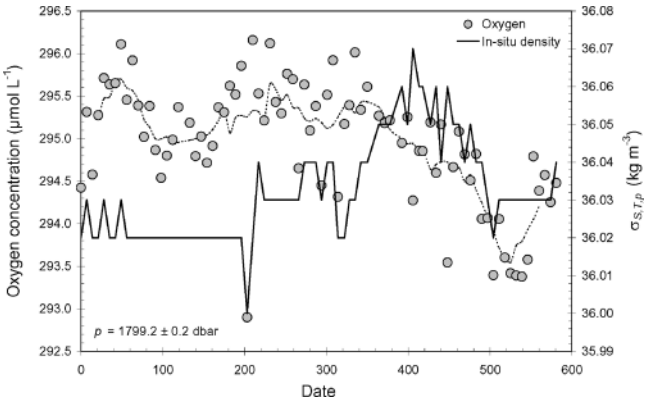

Figure 7. Oxygen concentration measured over 580 days at 1800 m depth on an Argo profiling float in the Labrador Sea. Density values calculated from temperature, salinity, and pressure are also shown. The average oxygen concentration was 295.0 ± 0.7 (1 SD) μmol/L for the 580 day period. The shift in density and oxygen at ~360 days suggests that some of the concentration variability occurred as the float entered a new water mass with different properties. Reprinted with permission from ref 36. Copyright 2006 by the American Society of Limnology and Oceanography, Inc.

completely new methods of observing primary production and respiration in the ocean, lakes, and rivers.

In addition, it is now possible to utilize novel waveforms in voltammetric sensors to measure oxygen without using membranes to protect the electrodes from fouling.[55] Unprotected electrodes may have a variety of advantages, particularly a faster response rate.[56] Better response rates will be key to utilization of oxygen sensors for applications such as the long-term measurements of oxygen flux into sediments by the eddy-correlation method.[57]

2.1.2. Methane and Total Gas Tension

The gas tension device (GTD) uses a rigid, gas permeable membrane and a stable, high-precision pressure sensor to determine the total pressure exerted by dissolved gases.[58] The signal detected by the GTD is dominated by N_2 and O_2 in natural waters. If oxygen measurements are available, then its contribution can be subtracted from the total gas tension to yield the N_2 partial pressure.

GTD instruments are available commercially and have been successfully used on long-term ocean mooring deployments to deconvolve the various processes that may change gas concentrations.[47] For example, oxygen saturation may increase due to biological oxygen production or due to seasonal warming that reduces the oxygen solubility with no actual change in concentration. Seasonal warming will also increase the percent saturation of dinitrogen gas. Parallel increases in oxygen and dinitrogen gas saturation are, therefore, indicative of warming, rather than biological production. Oxygen and GTD sensors has been used on open ocean moorings at the HOT station near Hawaii to compute primary production rates after correcting the observed changes in oxygen for the effects of seasonal warming that were estimated from changes in the degree of N_2 saturation.[47] These instruments have very good, long-term stability, albeit a slow response time that is required for gas to diffuse across the rigid membrane. Efforts are underway to adapt GTDs for oxygen sensing by scrubbing oxygen inside the instrument.

Methane is of considerable interest in aquatic sciences because of its heat-trapping properties in the atmosphere and the role that methane hydrates may play in regulating production of methane in the ocean.[59] Methane sensors are commercially available that utilize a rigid, gas permeable membrane to separate gases from water and a semiconductor methane sensor to measure concentration in the gas phase. The systems have been used for a variety of studies, including long-term measurements of methane in groundwater entering the coastal ocean.[60] The rigid membranes required for high-pressure applications also limit the response rate of these sensors to tens of minutes.

2.2. Inorganic Carbon System

Understanding the long-term variation in the mass of anthropogenic carbon dioxide stored within the ocean, the fluxes of CO_2 across the air−sea interface, and the rates of biological processes that move carbon to the deep sea are leading challenges in biogeochemistry. Complete characterization of the dissolved, inorganic carbon system requires measurement of two independent carbon dioxide parameters and a thorough understanding of the thermodynamic equilibria for acid/base chemistry in the solution under study. The parameters measured in the laboratory include the partial pressure of carbon dioxide in solution (pCO_2), pH, total inorganic carbon (TCO_2), and titration alkalinity (TA).

2.2.1. CO_2 Partial Pressure (pCO_2)

The partial pressure of CO_2 gas dissolved in water is currently the only inorganic carbon parameter that is regularly measured in situ for long time periods. A variety of optical sensors have demonstrated high-quality pCO_2 measurements with endurances of many months on moorings and drifting buoys.[15,61,62] In order to be broadly useful, these methods must have an accuracy of 1 ppm pCO_2. Several methods for pCO_2 measurement are based on equilibrating seawater carbon dioxide across a gas-permeable membrane with a solution containing an acid/base indicator dye.[63,64] The pCO_2 is then determined from the absorption spectra of the acid and base forms of the indicator dye. The response rate may be limited to 30 min or more if transport is entirely by diffusion.[64] To overcome slow response rates, a pump may be used to periodically flush the optical path and refresh the indicator solution.[63]

Combining information from sensors for several chemicals can be especially useful for interpreting the biogeochemical processes in aquatic systems.[18,61] Figure 8 shows a 3.5 month time series of measurements of pCO_2 and dissolved oxygen at two depths in a small lake that was initially ice covered.[18] The combination of multiple sensors at several depths showed a surprising series of events during the spring ice melt. The vertical gradient in chemical properties disappeared before ice melted in late April (Figure 8). This indicates convective overturn of the water column. These convective processes could not be easily observed with more traditional temperature measurements, as the water column was nearly isothermal. The initial overturning was followed by a period of vertical mixing events that supplied large amounts of nutrients to the sunlit waters under the ice, resulting in high primary production rates. These processes have not been observed in programs based on manual sampling.

Direct measurements of the carbon dioxide mole fraction difference between the atmosphere and seawater, from which $\Delta pCO_2 = pCO_2[\text{seawater}] - pCO_2[\text{air}]$ is calculated, have been made using dual-beam infrared (IR) gas analyzers on moorings.[65] In this system, carbon dioxide dissolved in seawater is equilibrated with an isolated gas volume using

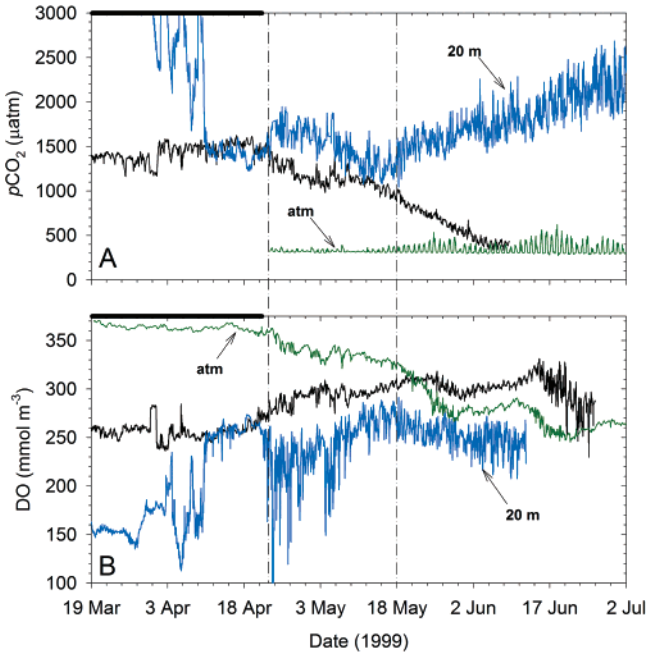

Figure 8. A 3.5 month time series of pCO_2 (A) and dissolved oxygen concentration (B) in Placid Lake, Montana, during the transition from the lake covered with ice, through melting, and into the spring bloom. Measurements were made with instruments at 2 m (solid black lines) and 20 m (blue lines). Atmospheric equilibrium values are shown as green lines marked atm. The two vertical dash-dotted lines bracket three distinct physical periods: (1) under-ice near isothermal conditions (19 March−23 April), (2) post-ice-out deep mixing (23 April−18 May), and (3) stable stratification (18 May−2 July). The heavy lines on the top of each part of the figure represent ice cover. Reprinted with permission from ref 18. Copyright 2004 by the American Society of Limnology and Oceanography, Inc.

wave energy to provide mixing in the equilibrator. The IR analyzer then measures the absorbance difference between one optical cell filled with gas equilibrated with surface seawater and one cell filled with ambient air. The equilibrator cell is periodically filled with ambient air to calibrate the offset between the two beams. Measurements of ΔpCO_2 using this method have been made continuously for year-long time intervals on several of the TAO/TRITON moorings in the equatorial Pacific.[14] A similar system, combined with a Clark oxygen sensor, has been used for shorter periods to examine the processes that control net ecosystem metabolism in a large number of northern lakes.[66] Instruments based on measurements in the gas phase are generally limited to deployments within a few meters of the sea surface.

2.2.2. pH and Other Inorganic Carbon Properties

To fully characterize the state of inorganic carbon dissolved in seawater, which would allow calculation of carbonate and bicarbonate concentrations, one additional CO_2 system parameter must be measured. Seawater pH measurements with glass potentiometric electrodes are most familiar. While significant improvements have been made in the endurance and stability of pH electrodes, there remain significant issues with drift and stability during pressure and temperature variations. There are few long-term studies with potentiometric pH sensors that have yielded useful data in natural waters. Measurements of pH using optical measurements with pH sensitive dyes have generally replaced electrode measurements for high-precision, shipboard studies.[67] In situ pH measurements using spectrophotometric procedures are now being made on an experimental basis.[68] Measurements of TCO_2 and TA with in situ analyzers are still in development.[69]

2.3. Nutrients

Measurements of dissolved plant nutrients (e.g., nitrate, ammonium, phosphate, orthosilic acid/dissolved silicate ion) are an essential component of most biogeochemical studies. The availability of these nutrients in the sunlit surface waters is one of the proximal controls of primary production in most aquatic environments.

2.3.1. Nutrient Analyzers

A variety of adaptations of the standard colorimetric methods[70] for nitrate (reduction on cadmium to nitrite and determination as an azo dye), phosphate, and silicate (as reduced molybdate dyes) have been developed for in situ analyses. These systems operate as continuous flow systems[71−73] similar to an unsegmented continuous flow analyzer or as batch analyzers that use a syringe pump and multiport valve to combine sample and reagents.[17] Several of these instruments are available commercially. The basic hardware in these systems consists of a pump, valves, a fluidic manifold, and a colorimetric detector. These components can be assembled in a variety of ways, and with relatively minor modifications, it is possible to use one set of hardware for a variety of analyses. Systems that use osmotically powered sample and reagent pumps,[71] requiring no external power source, have been adapted for year-long measurements of iron in hydrothermal vent systems at depths in excess of 2000 m.[74] Most systems are designed to be recalibrated in situ at periodic intervals by substituting a blank and standard for the sample.[17,40,41] This can be done with stream selection valves or with individually selectable pumps for each solution.

To date, most of the published, long-term measurement, in situ analyzer systems have focused on nitrate. Colorimetric nitrate analysis systems have been deployed in the open ocean for up to 4 month periods. These systems have been used to demonstrate the impacts of eddies[12] and planetary (Rossby) waves[16] on the upward transport of nutrients from deep water into the euphotic zone, and the subsequent impact on the phytoplankton community. For example, the impact on nutrient concentrations from a sea-surface height depression that is created by a planetary wave is shown in Figure 9.[16] Sea-surface height can be recorded with a precision of a few millimeters, relative to a well-defined orbital path, by satellite altimeters such as the TOPEX/Poseidon instrument. Shifts in surface height must be accompanied by temperature or salinity driven changes in density that compensate the pressure gradient created by the height change. In this case, low surface height in March/April (Figure 9A) is compensated by colder, higher density water (Figure 9B) that upwells from depth and carries high nitrate concentrations (Figure 9C) with it. The upwelled pulse of nutrient-rich water then fuels a phytoplankton bloom that is recorded as an increase in chlorophyll concentration (Figure 9D). In the coastal zone, moored nitrate analyzers have been used to study vertical nutrient transport by internal waves[75] and the impact of lateral nutrient flux through estuaries[72,76] and through the North Sea.[77] Colorimetric nutrient analyzers have been primarily deployed from piers or moorings. Size, power, complexity,

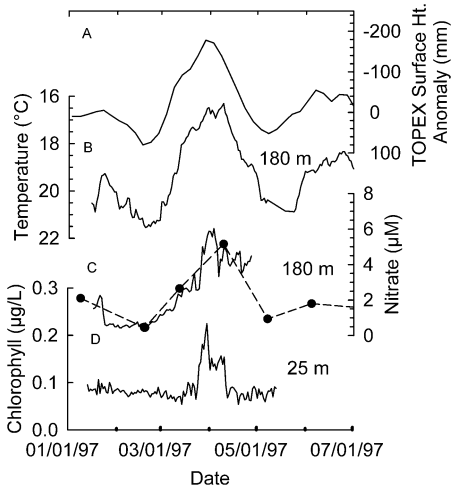

Figure 9. Measurements of (A) the anomaly in sea surface height relative to the long-term mean measured by the Topex/Poseidon satellite altimeter (note inverted scale), (B) temperature at 180 m (note inverted scale), (C) daily average nitrate concentration at 180 m, and (D) daily average chlorophyll concentration at 25 m on the HALE/ALOHA mooring at the Hawaii Ocean Timeseries station north of Oahu. Nitrate was measured with an osmotically powered chemical analyzer.[71] Nitrate concentrations measured in samples collected near the mooring during HOT program monthly visits by ship are shown as black circles. Chlorophyll was determined from the attenuation of sunlight at 490 nm. Adapted with permission from ref 16. Copyright 2004 American Geophysical Union.

and cost would all impact the feasibility of long-term deployments on other types of platforms, such as profiling floats.

2.3.2. Ion Selective Electrodes

Ion selective electrodes have not been used widely on autonomous observing systems because of the difficulty in keeping systems in calibration and because they often lack sufficient specificity in marine systems with high-salt backgrounds.[78] Monitoring systems that utilize ion selective electrodes for long time periods generally include a capability for autonomous recalibration of the system every few hours.[78] However, new sensor membranes are being developed with improved performance. For example, a new nitrate electrode system using *N*,*N*,*N*-triallylleucine betaine chloride immobilized in a polymer membrane has been developed that exhibits long-term (months) stability.[79] Diurnal nitrate variations were found over a 2 month period with this electrode during low-flow conditions in the River Taw, in the southwest United Kingdom.[80] These diurnal concentration changes were subsequently verified with an intensive 90-hour discrete sampling program. In the Danube River, continuous hourly measurements of nitrate concentrations over an 11 month period with ion selective electrodes recorded weekly concentration variations below the Vienna, Austria, wastewater treatment plant that were 50% of the mean values.[81] Ammonium concentrations show daily variations that were 100% of the mean concentration value, with "spot events" or spills that were 300% higher than the mean NH_4 concentration values.

2.3.3. UV Optical Nitrate Sensors

Recent developments in optoelectronics now make it possible to measure nitrate in seawater directly using its UV absorption spectrum.[8,37] Such measurements require no chemical manipulations and will greatly extend the feasibility of routinely monitoring nitrate. The optical systems require approximately 5−10 W for continuous operations, but operation on a reduced duty cycle of about 3 s per complete measurement cycle makes year-long deployments feasible.[7] A significant issue with all long-term deployments is the ability of the sensor system to remain in calibration over long-term deployments. Nutrient analyzers solve this problem by carrying blank and standard solutions on board and periodically substituting these solutions for the sample. UV optical sensors can solve this problem by measuring the absorption spectrum with high resolution. The spectrum contributed by fouling is nearly linear and can be deconvolved from the absorption signals due to nitrate and other UV-absorbing compounds.

Long-term deployments of optical nitrate sensors have been used to calculate daily changes in primary production.[7] Hourly measurements of nitrate on moorings show a diel cycle in nitrate concentration that is created by daytime uptake of nitrate during photosynthesis and restoration at night by physical processes (Figure 10). These changes in

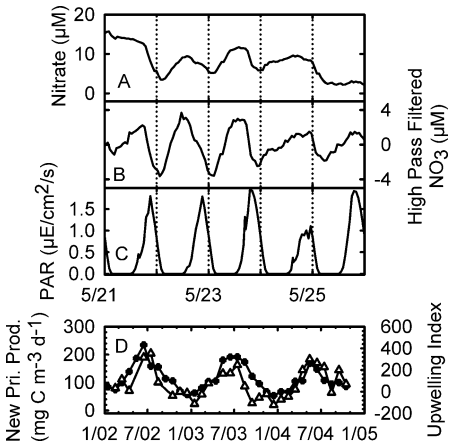

Figure 10. (A) Nitrate concentration measured on the M1 mooring 20 km offshore in Monterey Bay, CA, using an optical nitrate sensor during 5 days in 2004. (B) Nitrate concentrations after high-pass filtering the data to remove frequencies lower than 0.7 cycles/day. (C) Photosynthetically active radiation measured on the mooring with a spectral radiometer. The decrease in high-pass filtered nitrate concentration during daylight is presumed to be due to biological uptake at a fixed nitrogen to carbon ratio of 16 mol of N/106 mol of C, typical of phytoplankton. (D) Monthly average values of primary production, which were calculated from daily uptake of nitrate concentrations measured by autonomous sensors on the M1 mooring as shown in (B) and a N/C ratio of 16 mol of N/106 mol of C, are shown for 3 years from 1/2002 to 12/2004 (open triangles). The upwelling index (m^3 of water upwelled per 100 m of coastline per s), calculated from wind speed and direction and coastline orientation, is also shown for Monterey Bay (solid circles). Adapted from ref 7, Copyright 2006, with permission from Elsevier.

nitrate can be used to estimate the rate of carbon uptake and incorporation into living particles because the ratio of nitrogen to carbon in phytoplankton is nearly constant. The daily estimates of primary production from nearly 3 years of autonomous nitrate measurements show a consistent seasonal variability that is regulated by the rate of upwelling (Figure 10D).

2.4. Empirical Sensors

There are empirical relationships between sensed properties and chemical concentration that can be used to determine the distribution of chemicals in space and time. For example,

it has been shown that there is a relatively constant proportionality between light scattering detected with a transmissometer and the concentration of particulate organic carbon (POC) in seawater.[82] The proportionality occurs in open ocean waters because there are few sources of particles other than in situ production by phytoplankton. This correlation has been used to make long-term observations of POC with transmissometers on profiling floats in the North Pacific[83] and Southern Ocean.[84] These measurements have been used to monitor production of phytoplankton biomass following soil-aerosol deposition events in the North Pacific that release phytoplankton from iron-limitation.[83]

3. Chemical Sensor Networks

Considerable work is underway to develop environmental sensor networks.[85,86] In this section we present examples of chemical sensor networks that have been operated in the aquatic environment for periods of at least 1 month with sensors at multiple locations. There are many challenges in building a network beyond that of developing and operating the sensor for extended periods. These challenges include providing a platform on which to deploy the sensor,[24,87] providing power and communications,[88] and controlling biofouling.[42] Operating a complete network involves much greater complexity than chemical analysis alone. However, here we focus only on chemical sensing.

Most of the systems with chemical sensors that are now in place are focused around oxygen sensors, which are deployed in lakes,[85,87] estuaries,[86,89] or coastal waters[90] to address water quality issues that result when oxygen is depleted in eutrophic environments. In the following, we focus on a set of examples that illustrate the challenges in chemical sensor deployments in difficult environments. These examples emphasize sustained observations in difficult environments. Much of this work is based on newly developed capabilities.

3.1. MBARI/NOAA pCO_2 Array

In section 2.2.1, we described the technology that can be used for measurements of the sea−air pCO_2 difference. Measurements of ΔpCO_2 in surface seawater represent the longest record of autonomous, chemical measurements in the marine environment. Measurements on moorings in Monterey Bay began in 1997 and extend through the present.[15] These long-term measurements allow the effects of infrequent events on carbon dioxide transfer from the air to the sea, such as the El Niño/La Niña climate oscillations, to be assessed in coastal[15] and open ocean environments.[14] The pCO_2 of recently upwelled water is generally very high because respiration of organic carbon in sinking particles releases carbon dioxide into the deeper waters. As a result, pCO_2 is high in the equatorial upwelling zone and in recently upwelled water of the eastern boundary currents along the U.S. west coast. However, during El Niño events, reversals in wind direction along the equator send warm water as a Kelvin wave from the western to the eastern Pacific and then poleward along the continents.[14] This warm water deepens the thermocline and, although upwelling favorable winds continue along the California coast, the upwelled water does not have elevated carbon dioxide concentrations. Chemical sensor measurements on moorings off the California coast show that these effects reach the Monterey Bay region and appear as an annual period with no large increases in surface

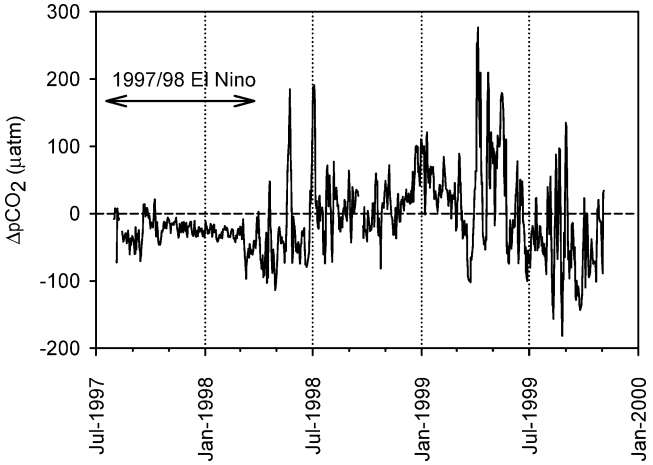

Figure 11. Measurements of the sea−air difference in CO_2 partial pressure made on a mooring in Monterey Bay using autonomous sensor technology. The impact of 1997 El Niño/La Niña, which occurred during the period spanned by the horizontal arrow, on the carbon dioxide system is manifested by low variability due to weakened upwelling. Reprinted from ref 15, Copyright 2002, with permission from Elsevier.

pCO_2 during El Niño years (Figure 11).[15] Such processes can alter the air−sea transfer of carbon dioxide by large amounts. In collaboration with NOAA scientists, this network has been extended to include moorings throughout the Pacific Ocean that are operating in real time (Figure 12).

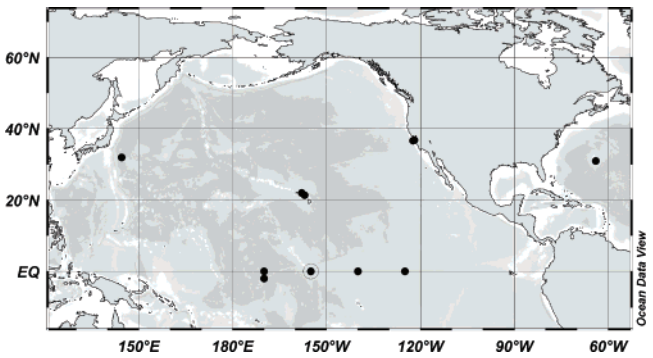

Figure 12. Locations (solid circles) where measurements of pCO_2 are made on remote moorings by the MBARI/NOAA sensor network. Data from these moorings can be accessed on the Internet at http://www.pmel.noaa.gov/co2/moorings/.

3.2. Trans-Pacific Sections of Dissolved O_2 Measured on Argo Profiling Floats

The largest sensor network now operating autonomously in the ocean is the Argo array of profiling floats.[24] As discussed above, Argo is primarily an experiment designed to map the fields of oceanic temperature and salinity over the globe in order to determine the ocean's role in the global balance of heat and freshwater. The float array enables decadal-scale changes in these fields, which are driven by climate change, to be directly observed. In recent years, some floats have been equipped with dissolved O_2 sensors. The goal of this work is to examine sensor performance over times of a few years and to begin to plan future efforts, where the issue of carbon cycling and its relation to climate is likely to be more prominent.

As discussed in section 2.1.1, profiling floats have been deployed using both optical sensors (the Aanderaa Optode)[36] and electrochemical, Clark-cell[91] sensors. Deployments on floats have demonstrated advantages and disadvantages to

each of these sensor types. Optode sensors on floats have proven to be extremely stable over times of a year or more (Figure 7).[27,36] Electrochemical O_2 sensors on floats, manufactured by SeaBird Electronics (SBE), have exhibited more variation. Very little drift has been seen with some sensors over times of several years (Figure 6B), but the mean drift for a large number of sensors is greater than that observed with the Optode sensors, as we discuss below. The Clark cell, however, uses considerably less power in a float configuration than the Optode, an important issue since floats must function unattended over times as long as 5 years. At this point in time, the Argo community is actively exploring the optimal sensor configuration.

In late 2005, a line of 22 University of Washington Argo floats equipped with SBE dissolved O_2 sensors was deployed across the South Pacific Ocean, as shown in Figure 13A.

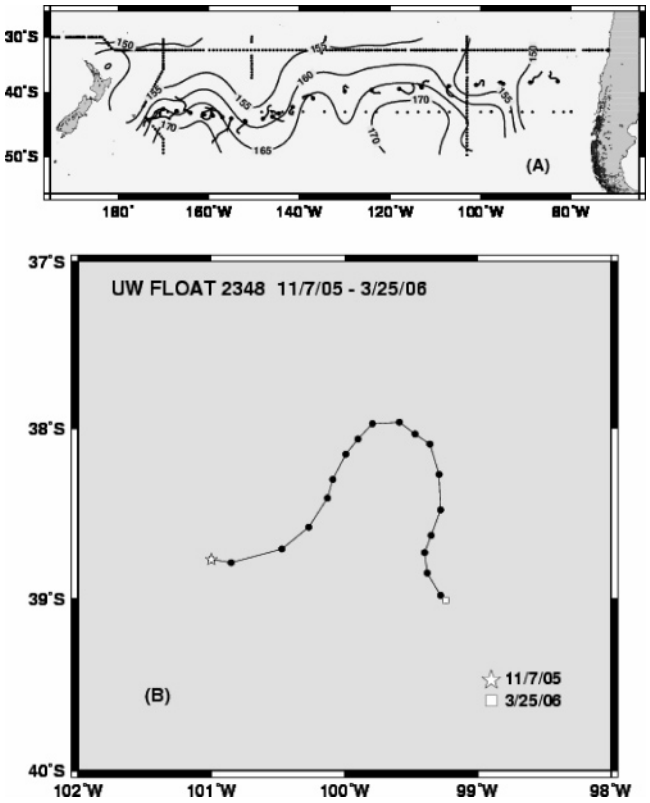

Figure 13. (A) Dissolved O_2 (mmol/kg) at a depth of 2000 m in the South Pacific (labeled contours), determined by objectively analyzing historical data for the region using a Gaussian 300 km correlation function. The historical station data used in the calculation (positions noted by the smaller black dots) were determined using the Winkler titration method. Deployment locations of 22 profiling floats with dissolved O_2 sensors are shown by the larger black dots. The trajectories of the floats from November 2005 through March 2006 are shown as the black lines emanating from the larger dots. (B) The trajectory of UW float 2348 from the South Pacific, deployed in November of 2005. The figure shows the location of the float through March of 2006. The dots denote profile locations. The float was parked at a depth of 2000 m.

This was the first attempt at deploying such a large number of floats with O_2 sensors at one time for the purpose of examining the variability of dissolved O_2 over basin scales. All of the floats were parked at a depth of 2000 m and profiled to the surface at 7 day intervals. A trajectory of one of the floats (Figure 13B) shows typical motions at 2000 m in this portion of the world ocean: the most prominent features are transient motions (eddy variability) that are usually several times larger than the weaker mean circulation. These currents dispersed the float array weakly over the course of several months.

The O_2 sensor drift for each of the 22 South Pacific floats was estimated from the measured oxygen at 2000 m for each profile, minus the initial 2000 m O_2 value (in order to remove the initial offset) (Figure 14). The results indicate that the

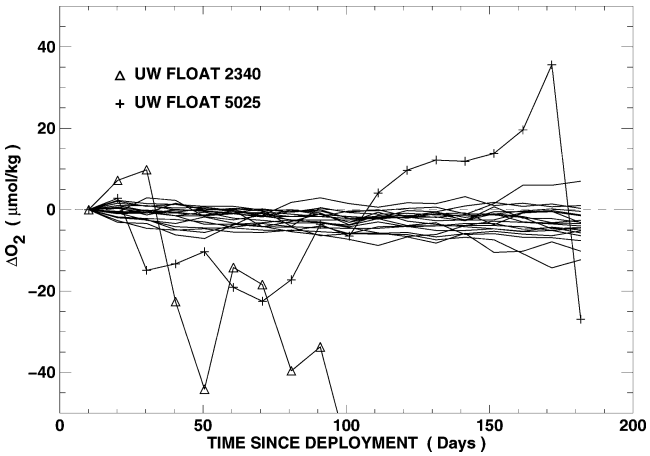

Figure 14. Change in dissolved O_2 relative to the value measured at 2000 m on profile 001, for each of the 22 floats deployed in the South Pacific (see Figure 13). Note that 20 of the 22 instruments showed a weak drift over time toward lower values, while two of the instruments showed a much larger drift. The large drift is presumed to be due to faulty sensors, and data from these two instruments have not been used.

drift over the first 18 profiles for 20 of the 22 floats ranged from ~0 to 10 μmol/kg toward lower values, a relative change of 0−6% (somewhat above the manufacturer's specification). The two exceptions were floats 2340 and 5025 (Figure 14); the erratic drift in the oxygen measurements reported by these two floats' results suggests major O_2 sensor problems. For 20 of the 22 floats deployed (>90%), the SBE O_2 sensors performed reasonably well. These results illustrate one of the strengths of a sensor network. Unreliable sensors can often be identified if they exhibit behavior that is inconsistent with other members of the array.

Data from the first 150 days after deployment are shown for one sensor deployed on float 2348 (Figure 15), whose

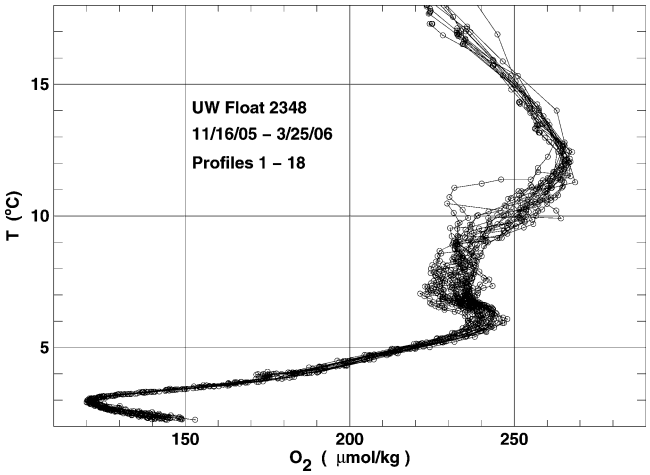

Figure 15. Diagram showing the temperature-dissolved O_2 relation for the first 18 profiles of float 2348 (see Figure 13 for the locations of these profiles). Note the lack of scatter in the data below about 7 °C, indicating the lack of sensor drift.

trajectory is shown in Figure 13B. The O_2 data from profile to profile are quite consistent, forming a tight temperature−O_2 relation. At temperatures in excess of about 7 °C, there is some profile-to-profile variability, indicative of seasonal variations over the 150 day observation period. At temperatures below about 5 °C, where there is little seasonal change in oxygen concentration, there is very little profile-to-profile change in the temperature−O_2 relation (no more than about 2 μmol/kg).

The South Pacific at these latitudes has previously been only sparsely explored. A comparison between the historical database and the float-derived O_2 estimates is not possible for the upper ocean. The seasonal cycle in the upper ocean is too strong, and the variability in the historical O_2 database is too large for meaningful comparisons to be made. Since dissolved oxygen has no seasonal cycle at the parking depth of the floats, however, it is possible to compare the float measurements of O_2 at 2000 m with the historical data (Figure 13A). The first measured O_2 value at 2000 m from each of the floats has been compared in Figure 16 to the

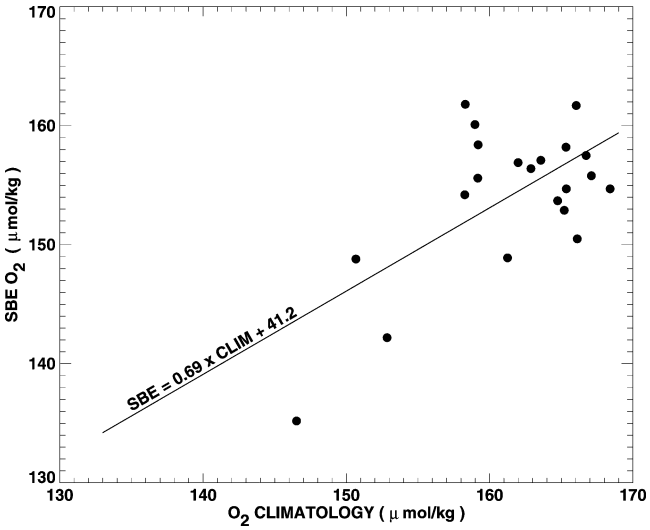

Figure 16. The float-derived O_2 concentration at 2000 m from the first profile for each of the 22 floats deployed at the locations shown in Figure 13 is plotted against the 2000 m dissolved O_2 climatology at the position of the first float profile determined using the contours shown in Figure 13. The line shows the least-squares fit between the float O_2 and the climatology.

value derived from the 2000 m O_2 climatology, based on shipboard measurements, at the float position (Figure 13A). The float-derived O_2 values at 2000 m are generally lower than the climatology, as was also the case with the HOT comparisons (Figure 6).

There are several possible explanations for these offsets. First, the O_2 climatology shown in Figure 13A could be incorrect, due to either faulty historical data, mapping errors, or real changes in the deep O_2 distribution in the South Pacific in recent decades. Each of these potential causes seems unlikely, since the historical data used here are known to be of excellent quality and other, more recent shipboard measurements in this region show values consistent with climatology. The contouring scheme shown in Figure 13 results from objective analysis of the historical data using a 300 km Gaussian correlation function. It is possible that the discrepancies in Figure 16 reflect a problem with the initial calibration of the O_2 sensors at the factory. This would seem to be unlikely, since each sensor is calibrated in a temperature-controlled bath, where sensor-derived values are compared to samples pulled from the bath and then analyzed by the Winkler method. Alternatively, it is possible that the float O_2 sensors could age after leaving the SBE factory. One of the features of the SBE oxygen sensor is that they are always polarized with an internal battery. Since the chemical reaction employed in the Clark cell is operative in air as well as seawater, continuous sensor degradation is possible, although the sensors are in most cases deployed within a few months of being manufactured. Presently, each of these scenarios is being investigated in order to assess the cause of the initial O_2 offsets seen both at Hawaii and in the South Pacific float data.

There is seasonal variability in dissolved O_2 along the upper portions of the section (Figure 17) that is substantially

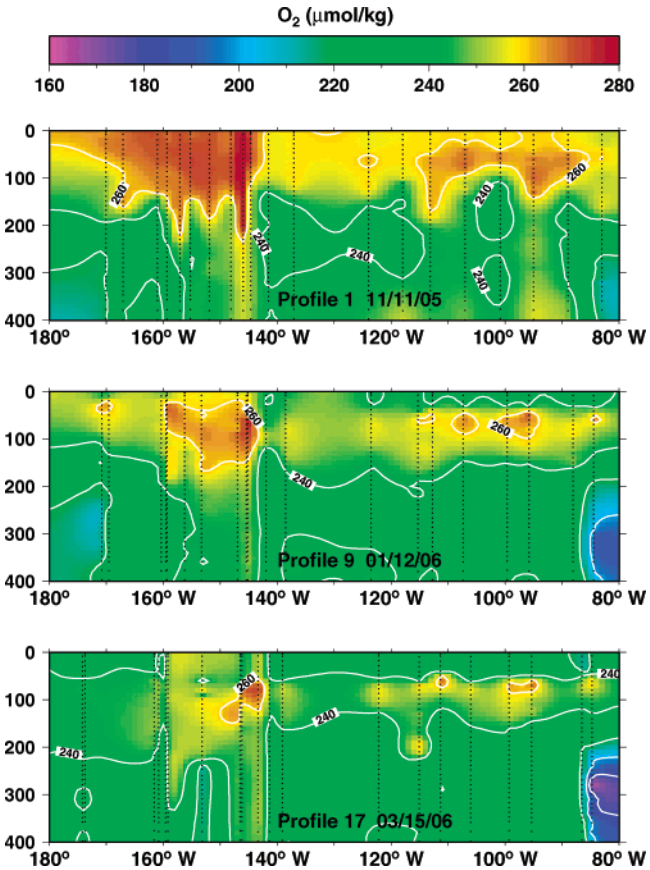

Figure 17. Sections of dissolved O_2 in the upper 400 m across the South Pacific, determined from 20 profiling floats deployed in November of 2005. Data from two of the floats (2340 and 5025) have not been used in this calculation due to the extreme drift exhibited by these two sensors. The positions of the floats are shown in Figure 13. The positions of the float profiles along the sections are noted by the dotted lines.

larger than the apparent sensor drift of ~5 μmol kg^{-1} year^{-1}. Throughout the period of November 2005 through March 2006, the western South Pacific had relatively high dissolved O_2 in the upper 200 m of the water column and lower values in the eastern South Pacific. Below 200 m, there is evidence of low-O_2 water in the eastern portion of the section. This signal intensifies through the austral summer as low-oxygen water is transported poleward along the continental margin. The first profiles (in early November 2005) were from late spring, and the dissolved O_2 in the upper 150 m reached very high values, in excess of 260 μmol/kg in the upper ocean. By mid-January 2006 (1 month into austral summer),

as the water warmed, O_2 was less soluble in near surface waters. The surface O_2 values decreased by 20−30 μmol/kg. Two months later, in mid-March 2006 (near the end of austral summer), the surface O_2 had decreased by an additional 20 μmol/kg over much of the South Pacific. It is anticipated that these instruments should continue to operate for 3−4 more years and, as long as they do not disperse far from their initial positions, it will be possible to monitor the variability in dissolved O_2 across the South Pacific using data from these profiling floats. This will provide unprecedented views of oxygen cycling on the scale of an ocean basin. It will also be possible to assess the performance limits that will characterize relatively large chemical sensor arrays.

3.3. The RiverNet System: Monitoring Nitrate Flux in Rivers

Human induced changes in the nitrogen cycle on land[19,92,93] are recorded in the nitrogen flux of rivers, which integrate the landscape processes in their drainage basins. The global creation of fixed nitrogen (Nr) from human activities (mostly from food and energy production) was ~15 Tg N year^{-1} in 1890 and ~140 Tg N year^{-1} in 1990.[94] Increased rates of anthropogenic Nr production have caused a 4−5-fold increase in the fixed nitrogen flux in the Mississippi River basin and a 8−13-fold increase in the heavily populated regions of the Northeast United States and Northern Europe. Assuming that the per capita Nr production rate stays the same in each region of the world and that the world population goes to 8.9 billion in 2050, ~190 Tg N year^{-1} of Nr will be created from human activities globally in 2050. However, if the Nr creation rates of North America (100 kg N capita^{-1} year^{-1}) are used for the global population of 2050, the Nr created globally in 2050 jumps to 960 Tg N yr^{-1}, which is 7 times greater than the observed 1990 rate and 64 times greater than the pre-Haber-Bosch world of 1890. These projections emphasize the need to better understand Nr flux from watersheds.

Most river monitoring programs rely on monthly or weekly samples,[95] which undersample many water quality variations. For example, intensive 2 h sampling over a 102 day period in the River Main, Northern Ireland, showed that the concentrations of soluble and particulate P and nitrate N were significantly related to short-term variations in flow.[96] Using log-load, log-flow relationships, the load errors for weekly sampling of the River Main, relative to the high-frequency samples, ranged from −20% to +45% for fixed N and P loads.[96] These results suggest that monitoring at weekly or monthly intervals, which creates a bias toward low-flow conditions, can produce large errors when estimating river nutrient loads. However, more intensive river sampling programs cannot be easily sustained and in situ monitoring systems that make measurements in the water and transmit data daily or in real time are required.[86]

The RiverNet program was created in 1999 to continuously monitor water quality and nitrate flux in the Neuse River basin of North Carolina on the Atlantic Coastal plain. Nitrate concentrations and discharge measurements have been made for 5 years at eight different stations (http://rivernet.ncsu.edu). During the 2001−2004 period, nitrate concentration measurements were made hourly with WS Envirotech NAS 2E nitrate analyzers.[17] The NAS 2E requires chemicals and standards that are prepared and maintained with sterile techniques to avoid loss of nitrate in standards. The NAS 2E can make ~720 unattended measurements with one chemical payload, so it must be serviced every three weeks for hourly interval measurements. Stage measurements were made every 15 min by a USGS gauge station or a YSI 9620 Sonde, and converted to discharge with standard rating curve techniques. Nitrate concentrations were interpolated to 15 min intervals and combined with the discharge measurements to estimate flux. In 2004, Satlantic ISUS UV nitrate analyzers similar to those described by Johnson and Coletti[8] were deployed in the basin and used to make measurements synchronously with the stage measurements at 15 min intervals. The UV nitrate analyzers are sensitive to sediment accumulations on the optics during high-flow turbidity events. This problem was addressed by cleaning the optics with an automated, high-pressure water pump before UV measurements were made.

Five-year records of nitrate concentration and river flow are shown at a station below a large wastewater treatment plant in the upper Basin (Figure 18A) and in the lower basin just above the tidal influence of the Neuse River estuary (Figure 18B). Large variations in nitrate concentrations were observed throughout the 5 year records at each station in the Basin at all frequencies that were sampled. These concentration variations are found during high- and low-flow conditions and may bias flux estimates. To illustrate the potential bias of undersampling the high-frequency nitrate concentration variations, daily grab sample results were compared to NAS-2E measurements at hourly intervals and ISUS nitrate concentration measurements at 15 min intervals over a 4 day period at a station in the upper river basin (Figure 19). A 0.45 mg/L concentration spike is seen in the highest frequency data. The daily sample interval resolved only a 0.1 mg/L concentration change over this same period, while the hourly sample interval resolved a 0.25 mg/L concentration peak or only ~55% of the peak height.

Long-term monthly and weekly monitoring records of nutrient concentrations in the upper portion of the Neuse River Estuary (NRE) suggest that phosphorus concentrations have decreased since the 1988 basin-wide ban on phosphate in detergents but that nitrate concentrations have not significantly changed over the same period of time or may have been slowly rising since 1996.[97] Nitrate flux and discharge at the RiverNet station immediately above the NRE for the 2001−2006 period show large interannual and monthly flux variability (Figure 18C). The year 2003 was a period of high discharge and high nitrate flux, while 2001−2002 was a period of drought. Monthly nitrate flux averages have annual decreasing trends where fluxes are high in the winter and spring and then decrease during the summer and fall. The longer term 5 year trend in the Neuse River shows a slight increase in N flux, similar to the trends observed in the estuary. However, the long-term flux trends bear little similarity to the concentration trends, which suggests that nutrient concentrations alone are not reliable indicators of nutrient flux, which controls estuarine water quality. This river N flux data emphasizes that long-term high-resolution records are required to capture the large inter annual variations in these river systems and that average concentrations do not necessarily correlate to nutrient flux and changes in water quality.

Improved monitoring technologies with higher temporal resolution are required to eliminate errors in our N flux estimates from watersheds, particularly in watersheds affected by waste treatment point sources. The sampling frequency required to reliably estimate river N load will be related to

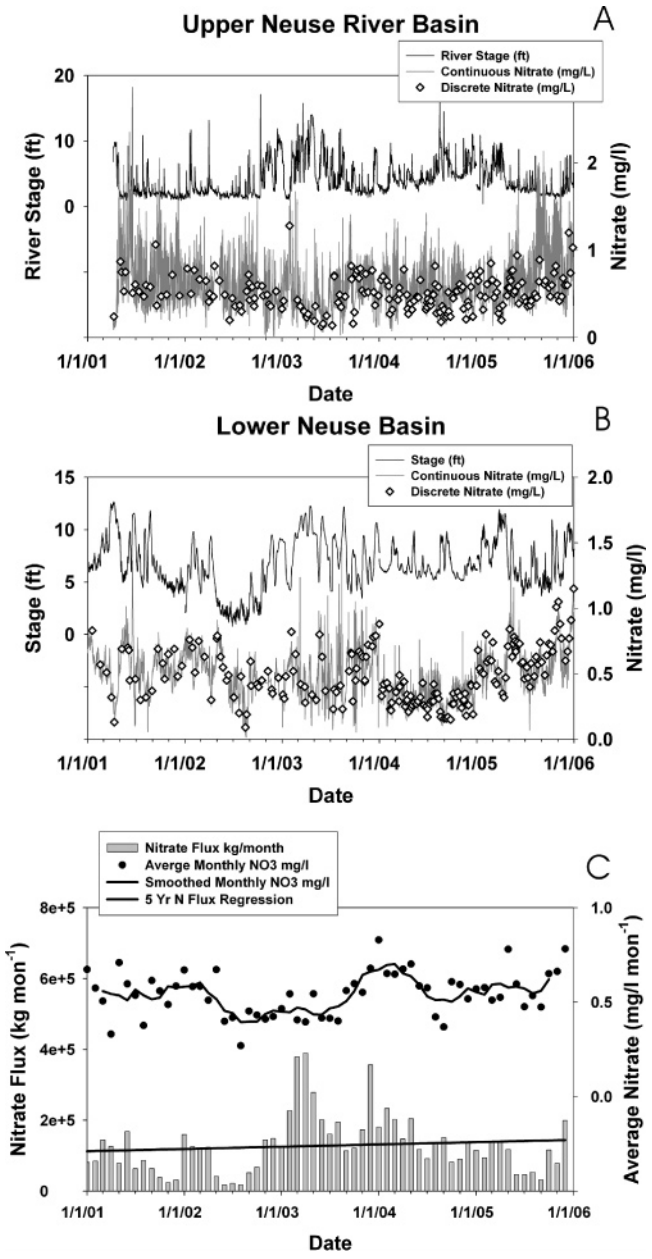

Figure 18. A 5 year time series of nitrate concentrations measured with in situ sensors (gray line), nitrate measured in discrete samples (diamonds), and river stage (black line) in the upper Neuse River Basin just below a wastewater treatment plant (A) and in the lower Neuse River Basin just above the Neuse River Estuary (B). (C) Five year monthly average nitrate concentrations (solid circles) and nitrate flux (gray bars) in the lower Neuse River Basin immediately above the Neuse River Estuary. The 5 year flux regression trend (solid black line) increases, but there is large monthly N flux variability.

discharge variations and the relationship between N concentrations and flow. However, there is much that remains to be learned about N flux in watersheds. It may be that the nitrogen concentration variations or "noise" seen in high-temporal-resolution concentration records is actually a signal that can help identify the importance of different N sources on a watershed scale. Managing surface water quality will be crucial in the future, as population growth increases sewage discharges into surface waters and as groundwater resources are overcommitted or contaminated. Accurate surface water quality monitoring will be essential to make

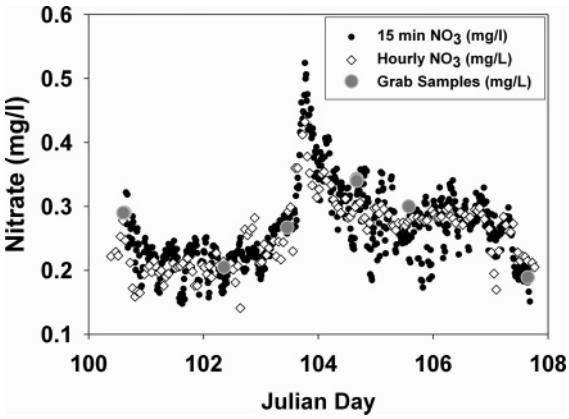

Figure 19. Comparison of grab samples (gray circles), hourly measurements in situ with a NAS-2E analyzer (open diamonds), and 15 min nitrate measurements with an ISUS optical nitrate sensor (black circles) during a nitrate concentration spike in the upper Neuse River basin.

policy decisions to meet our population's water resources needs in the future.

3.4. Land/Ocean Biogeochemical Observatory

The large nutrient loads carried by rivers are focused into the coastal ocean through estuaries.[6,19] These regions are difficult to monitor with sufficient temporal resolution because the interactions of river flow, tidal oscillations, and stratified water columns can produce rapid changes in concentration. An example of an operational estuarine observatory that is capable of providing the chemical measurements that address the coupling of nutrient inputs and ecosystem response at the appropriate spatial and temporal scale is the Land/Ocean Biogeochemical Observatory (LOBO) located in Elkhorn Slough, CA. The watershed is dominated by row crops, and the climate allows two to three harvests per year, which leads to high fertilizer application rates. The observatory network consists of moorings deployed throughout the 11 km waterway that extends inland from the Monterey Bay coastline (Figure 20). Each mooring is equipped with physical and chemical sensors and a telemetry system for data transmission via a wireless

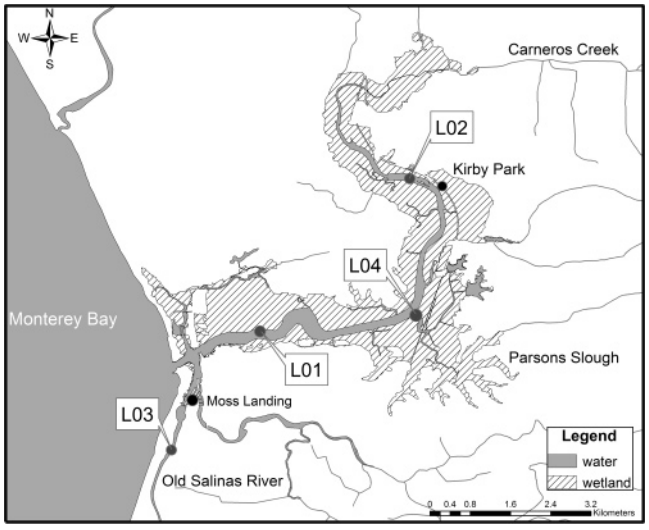

Figure 20. Map of Elkhorn Slough, CA, showing the location of the moorings that house the sensors for the Land/Ocean Biogeochemical Observatory. Data from each mooring is accessible at http://www.mbari.org/lobo.

network. Nitrate and oxygen are measured with optical sensors.[8,36] Data from each instrument is collected hourly by a microprocessor-based mooring controller and transmitted by wireless radio to a computer at the Monterey Bay Aquarium Research Institute in Moss Landing, CA. Once the data is received, it is made available through the Internet at http://www.mbari.org/lobo.

The 2.5-year-long data set from the LOBO L01 mooring located approximately 1 km inland from Monterey Bay (Figure 20) reveals the relationship between nitrate, salinity, and rainfall in the lower estuary (Figure 21). Nearly all of

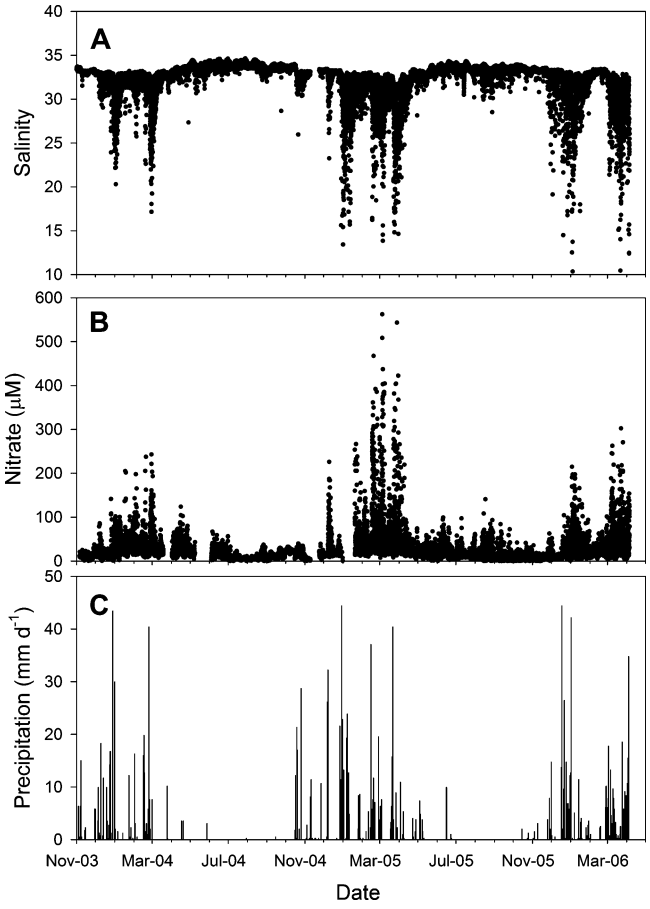

Figure 21. Salinity (A) and nitrate (B) at the L01 mooring of the Land/Ocean Biogeochemical sensor network measured from November 2003 to April 2006. Also shown is daily precipitation (C) at a nearby weather station. Nitrate was measured with an optical nitrate sensor.[8]

the rainfall comes during winter, and each of the three winters that have been monitored autonomously with the LOBO network are characterized by periods of high nitrate concentrations and low salinities. The maximum nitrate concentrations (>400 μM) occur during or after rainfall events and can be more than an order of magnitude higher than those in typical surface marine waters (0−20 μM). During long periods with little or no rainfall (typically May through November) the nitrate concentrations are much lower than the winter values. The high nitrate concentrations and low salinities are produced by runoff from the watershed that flows through cultivated fields and strips fertilizers from the soil.

Surprisingly, brief periods of low salinity and high nitrate can also persist during summer (Figures 21 and 22). A mechanistic understanding of nitrate inputs was identified

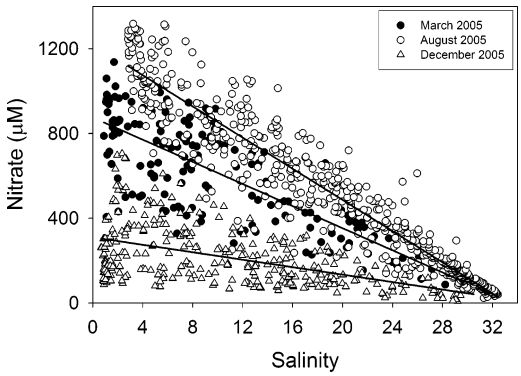

Figure 22. Nitrate−salinity relationship at mooring L03 for the periods March 2005 (filled circles), August 2005 (open circles), and December 2005 (open triangles).

by examining data from across the chemical sensor network at short time scales. Data from the sensor network records high-nitrate, low-salinity water moving from the mouth of Elkhorn Slough toward the inland regions during the rising tide (Figure 23). High nitrate pulses first appear shortly after

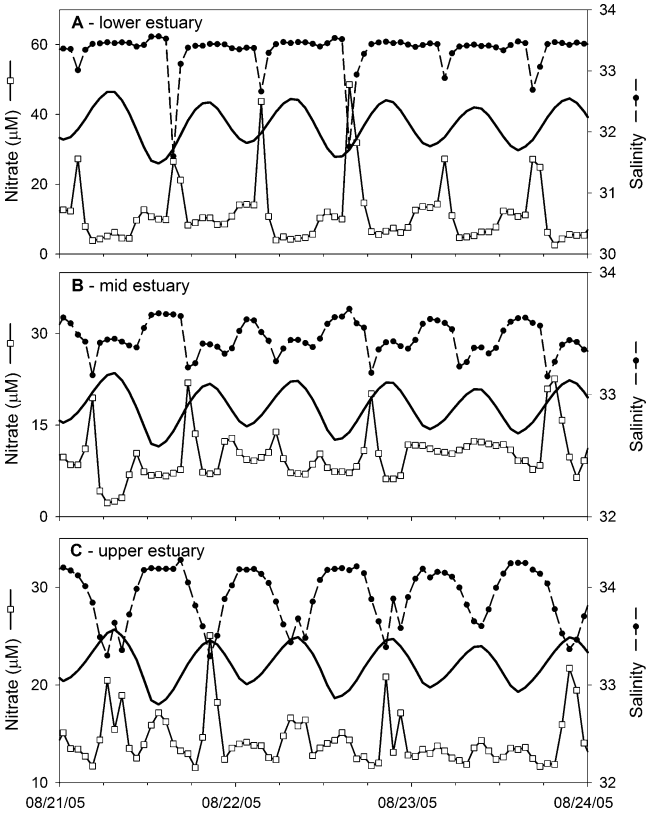

Figure 23. Nitrate and salinity, over a 4 day period, at three locations in Elkhorn Slough, CA: (A) L01, 1.0 km inland (from the Highway 1 bridge); (B) L04, 4.0 km inland; and (C) L02, 6.9 km inland. The solid line indicates the relative tide height.

low tide at the L01 mooring near the mouth of the Slough. These pulses appear at the L04 mooring in mid-Slough later on the tide (Figure 23). They reach the L02 mooring at the head of the Slough at high tide. The two freshwater point source regions of Elkhorn Slough are Carneros Creek at the head of the waterway and the Old Salinas River near the Mouth (Figure 20). The data shown in Figure 23 demonstrates that the high nitrate pulses originate at the Old Salinas River in the lower estuary and propagate landward, a result that is contrary to intuition. The salinity at the L03 mooring,

close to the Old Salinas River, fluctuates between nearly fresh and nearly marine water over the daily tidal cycle during all seasons of the year. This results from the tidally driven flow of salty water from Monterey Bay upstream to L03 at high tide and from freshwater from the Old Salinas River that flows past the mooring toward the ocean during low tide. During the dry season, the freshwater source is irrigation runoff from the intense agriculture in the Salinas Valley. In wet periods, the freshwater comes from precipitation that flows over and through the fields. This produces a high-nitrate, low-salinity source of water at L03 (Figure 22) that enters the mouth of Elkhorn Slough during low tides. This high-nitrate, low-salinity water is then carried inland by the rising tide. The nitrate loading in the source changes on a seasonal basis as the balance between irrigation water and precipitation changes.

The nutrients carried into Elkhorn Slough are linked to elevated rates of primary production, and this must influence the daily changes in oxygen concentration.[46] However, the diel variation in O_2 concentration may also be influenced by variability in physical processes. Long-term observations with a sensor network are key to the deconvolution of the important frequencies that drive spatial and temporal variability of O_2. For example, O_2 concentrations in the main channel exhibit repeatable patterns in diel variability that fluctuate at the spring-neap tidal period of 14 days (Figure 24). These patterns are repeated at each station in the network and must be produced by an interaction between primary production, respiration, and the tidally driven residence time of water in the estuary.

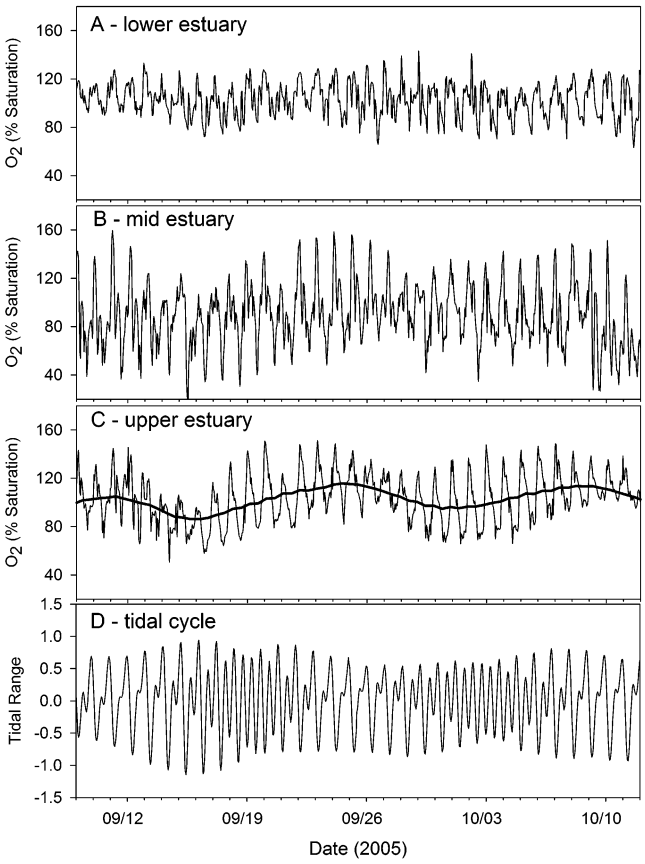

Figure 24. Oxygen at three locations in Elkhorn Slough, CA: (A) L01, 1 km inland (from Monterey Bay); (B) L04, 3 km inland; and (C) L02, 8 km inland. Also shown is the relative change in water depth (m) driven by the tidal cycle (D).

4. Conclusions and Future Prospects

In this review, we have summarized the work that is being done to develop chemical sensor networks that can be used for sustained and autonomous observations within natural aquatic systems. There is now a set of chemical sensors that are clearly capable of operating in situ for long periods of time. These sensors have demonstrated remarkable performance under very strenuous conditions. They validate the feasibility of making accurate chemical measurements in difficult environments for long time periods with no human intervention. While the data returned by these sensors, in some cases, do not match the highest precisions and accuracies available with laboratory measurements, the continuous data records that they return can provide a much broader perspective on environmental processes. The situation is, in some regards, similar to measurement of ocean chlorophyll concentrations using satellite-borne ocean color sensors. The satellite measurements at any one surface location are not nearly as precise or accurate as laboratory based measurements of chlorophyll.[98] However, the global picture returned by satellites is much richer and reveals processes that could not be detected by shipboard sample collection. In this same sense, the data that have been returned with autonomous chemical sensor systems have provided an unprecedented view of biogeochemical cycling that could not be obtained with conventional sampling. It is clearly possible to consider the operation of global-scale chemical sensor networks.

The technologies that enable long-term, autonomous observations will be expanded to additional chemicals. A particularly vital need exists for pH or other carbon system sensors that can complement the existing pCO_2 sensors and which can be used for profiling to ocean depths. In situ sensors also demonstrate the role that chemical speciation plays in determining the bioavailability of ecologically important chemicals.[34] Measurements of chemical speciation have not yet been made in situ for long time periods, but there is a critical need to develop this capability. Long-term, in situ measurements of trace elements such as iron are also critical for our understanding of the role that they play in structuring aquatic ecosystems. Efforts to develop in situ analyzers that are capable of detecting trace elements at subnanomolar concentrations, which are typical of the marine environment,[3] are just beginning.[99]

Existing sensors can also be adapted to additional platforms. For example, it appears to be straightforward to modify the optical nitrate sensors presently employed in moored applications for use on profiling floats.[8] In combination with oxygen sensors, this would allow observations of the processes that drive primary production (nutrient availability) and the ecosystem response (oxygen production and consumption). However, it is also clear that most chemical species will still have to be analyzed in samples that are returned to the laboratory. The rate of progress in developing new sensors capable of long-term operation is not rapid enough to anticipate the time when a much broader suite of chemicals can be sensed autonomously. One of the significant roles of a long-term chemical sensor network will be to provide the contextual information on variations in major biogeochemical processes within which more focused environmental studies can be made using more complex instrumentation.

5. Acknowledgments

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