

Chemical and Biological Sensors for Time-Series Research: Current Status and New Directions

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INTRODUCTION

Technological advances have often led to major improvements in our understanding of ocean phenomena. Despite the fact that the oceans cover more than 70% of our planet and have a profound impact on global climate, weather patterns, human health, agriculture, and commerce, our ability to make sustained measurements of ocean processes is limited and much of the oceans remain largely unexplored. The National Science Foundation's Ocean Observatories Initiative, through the Ocean Research Interactive Observatory Networks (ORION) Program, will establish a network of seafloor observatories linked by fiber-optic/power cables, as well as permanent and relocatable moorings in coastal regions and relocatable deep-sea moorings. Along the continental United States the ORION infrastructure will be coupled with the National Ocean Partnership Program's Integrated Ocean Observing System (IOOS). These combined systems will permit unprecedented high-frequency, *in situ* measurements of dynamic physical, chemical, and biological properties that occur over varying temporal and spatial scales. This new approach will require

ABSTRACT

Ocean observatories will require extensive use of sensors and sensing systems to enable time-series observations and interactive experiments on remote permanent and mobile platforms. In this paper we assess the "readiness" of chemical and biological sensors that will be critical to the success of ocean observatories. We conclude that although there have been many technological advances in the development of sensors in recent years, few chemical or biological sensors are capable of long-term deployment (~ 1 year). In particular, sensors in coastal regions and near hydrothermal vents will need to be regularly serviced for biofouling for the foreseeable future, while sensors on deep-water observatories that spend limited time in the euphotic zone may be able to operate for longer periods. A number of exciting new technologies hold great promise for sensors in the years to come. Significant effort and resources, however, are urgently needed for sensor development to ensure that the opportunities for science and discovery made accessible by ocean observatories are fully realized.

extensive sensing systems on permanent and mobile platforms to enable real-time interactive observations and experiments of the earth-ocean-atmosphere systems.

Numerous workshops (Daly, 2000; Seyfried et al., 2000; Glenn and Dickey, 2003; Jahnke, 2003; Rudnik and Perry, 2003; Gallager and Whelan, 2004) and a National Research Council (2003) report have identified compelling science questions that require time-series observations and the sensors needed to address those issues. Examples of high-priority sensors include: oxygen, nitrate, ammonium, urea, silica, phosphate, pH, total inorganic carbon, pCO₂, alkalinity, dissolved and particulate organic carbon and nitrogen, methane, hydrogen sulfide, dissolved halogens, iron species, magnesium, hydrogen, and microbial activity. Mass spectrometers are highly desirable sensors because they can simultaneously detect a wide variety of the species listed above. Acoustic and optical sensors are needed to measure a variety of physical, chemical, and biological phenomena, such as physical microstructure, microbial activity, phytoplankton and zooplankton species identification, abundance, properties, and

physiological rates, and fish biomass and distribution. The reader should refer to these reports for discussions of critical issues and recommendations for sensor development that are beyond the scope of this paper.

Here we assess the current status of "readiness" of different types of chemical and biological sensors that will be crucial to the success of ocean observatories (Tables 1-7). Sensors are categorized by developmental stage and deployment capability to highlight where additional efforts are urgently needed to ensure that essential sensors will be capable of long-term deployment during the initial stages of the observatory initiative. This is especially important given the difficult challenges and long development time (up to 10 years) for new sensors. Some privately held sensors that have been deployed for extended periods have better documentation of performance than those commercially available, so that reliability of available instruments cannot be easily assessed. Continued development of sensing systems also will be vital to realizing the full potential of the observatories. Please note that the sensors listed herein are not an inclusive list and endorsement is not intended over

other available products. Due to page limitations many excellent sensors could not be described. Lastly we highlight some examples of exciting new directions for sensors and sensing systems that may be available for use in years to come.

Oxygen Sensors

The oxygen concentration in marine systems is essentially dependent on three main processes: gas exchange with the atmosphere (solubility equilibrium), mixing of waters away from the surface, and biological changes in oxygen levels (production of oxygen through photosynthesis and consumption of oxygen in oxidative microbial processes). High-quality *in situ* sensors are thus essential to monitoring such processes effectively. Ideally these sensors would have a fast response, be very sensitive to changes in the oxygen concentration, and be stable for long time periods even in highly productive waters. Unfortunately, no such paragon exists!

A relatively recent review of methods of seawater analysis (Graßhoff et al., 1999) states: "Nearly all sensors used for *in situ* registration of dissolved oxygen in seawater are of the amperometric membrane covered electrode type introduced by Clark et al. (1953)." Although this is no longer true as other analytical approaches now exist (Table 1), the Clark-type design is still perhaps the most widely used. In this design, oxygen passes through a gas-permeable membrane into an inner compartment where it is reduced cathodically at a polarized electrode. The sensor current thus depends on the oxygen concentration outside the membrane, and the rate of diffusion through the membrane and the inner electrolyte. A number of problems have been reported with such sensors, particularly dynamic errors occurring when they are used in a profiling mode, i.e., subject to rapid changes of temperature and pressure. This has led to various refinements.

A significant improvement, proposed by Dr. Chris Langdon (Lamont Doherty Earth Observatory, Columbia University) and adopted in instruments from YSI Environmental, was to pulse the polarizing potential

applied to the cathode every few minutes. It is off during the rest of the time, so the oxygen levels inside the membrane can recover. This makes the method more or less flow independent, and reduces most of the effects that are membrane dependant. There are many benefits, such as a longer period between calibrations, less oxygen consumed, flow rate dependency removed, and the repeatability of measurements improves by an order of magnitude. However, the response time suffers as a result. This approach has been used on drifting floats (e.g., those used in the Atlantic Climate Change Experiment), and a second generation of this design has been used recently on moorings (e.g., Emerson et al., 2002; and on the O-SCOPE mooring at Station P in the North Pacific).

Another approach (Atkinson et al., 1995), which has been tested though not developed commercially, does away with the membrane completely and uses the seawater itself as the electrolyte together with a micro-hole to create reproducible diffusion conditions. A related method (Gundersen et al., 1998) uses a miniature

Clark-type sensor to produce an extremely fast response sensor (90% within 50 ms). A further benefit of its small size is rapid temperature equilibration as well. Such sensors are available commercially from Unisense (Aarhus, Denmark) and are being tested in oceanographic applications. Oxygen can also be determined rapidly using linear sweep voltammetry at a gold amalgam electrode (see e.g. Glazer et al., 2004).

In contrast, Sea-Bird Electronics, Inc. (Bellevue, WA) has substantially re-engineered the basic macroscopic Clark electrode system to produce their SBE 43 Dissolved Oxygen Sensor.

The SBE 43 is intended for profiling measurements in the ocean in conjunction with a CTD system, but is also capable of use for limited time periods in a moored environment as a result of its relatively low drift.

One difficulty with all of these profiling systems lies in achieving an effective calibration, as the sensor response depends to a large degree on the temperature (which affects the diffusion of oxygen into the Clark cell) as well as on pressure. Thus the calibration

TABLE 1

Current status of oxygen sensors. Development stages are I: Sensor currently operational and commercially available; II: Sensor successfully deployed in marine environment for > 1 month with consistent results but not commercially available; III: Mature development, transition to long-term deployment in progress; IV: Mature development, potential for transition; V: Early stage of development with successful short-term deployments in seawater; VI: Bench-top prototype in operation. Power (based on available information; watts, W, or amps, A) is consumption during operation. Sensor response time is in seconds (s), minutes (min), or hours. The sensors deployment capability is shown for moorings (M), drifters (D), glider (G), autonomous vehicles (A), profiling (P), towed vehicle (T), ROV or HOV (R), and shipboard (S)

Sensor	Development stage	Power	Response time [†]	Deployment capability	Source/contact
Pulsed Clark-type oxygen sensor	III	4 - 9 mA @ 12 VDC*	~ 60 s	M, D	CLangdon, LDEO langdon@ldeo.columbia.edu
Rapid-Pulse™ Clark-type oxygen sensor	I	ψ	~ 60 s	M, P (200 m)	YSI Environmental www.ysi.com
Micro Clark-type (non-pulsed)	III	2 mA	< 1 s	P	Unisense www.unisense.com
SBE 43 Clark-type (non-pulsed)	I	60 mW	~ 15 s	P, M	Sea-Bird Electronics, Inc. www.seabird.com
FOXY Fiber Optic Oxygen Sensor	I	150 mA	~ 30 s	M	Ocean Optics www.oceanoptics.com
Planar Oxygen Sensor Spots	I	6.6 W	~ 30 s		PreSens www.presens.de
Oxygen Optode	I	80 mA	~ 30 s	P, M	Aanderaa www.aanderaa.com
Gas Tension Device PSI-02 Pro	I	0.8W	hours	M	Pro-Oceanus www.pro-oceanus.com

[†]Depends, in part, on temperature. * Assumes sampling rate of once per hour or every 5 min. [†] Can only be deployed in a YSI sonde system.

equations are daunting (e.g., Owens and Millard, 1985; Atkinson et al., 1996).

An alternate analytical approach to sensing dissolved oxygen depends on the ability of oxygen as a triplet molecule to efficiently quench the fluorescence of certain luminophores, an effect called "dynamic fluorescence quenching." Collision of an oxygen molecule with a fluorophore in its excited state leads to a non-radiative transfer of energy. The degree of fluorescence quenching relates to the frequency of collisions, and thus to the concentration, pressure, and temperature of the oxygen-containing media. There are a variety of approaches to monitoring this effect: either monitoring the intensity of the fluorescence itself, or monitoring the fluorescence lifetime, or monitoring the phase-shift of the emitted light.

The simplest of these approaches is to simply monitor the intensity of the fluorescence itself, relating the degree of quenching to the oxygen concentration. The earliest *optodes* used in marine systems were based on this approach and, indeed, it appears that the FOXY fiberoptic oxygen sensor (available from Ocean Optics, Dunedin, FL) employs a similar intensity-based technique. Wang et al. (1999) reported results from using this sensor to monitor oxygen changes in an estuarine environment. The calibration of such an intensity-based detection scheme, however, can drift due to degradation of the chromophore with time. Consequently, other manufacturers have incorporated either a lifetime-based detection scheme (e.g., the sensor systems manufactured and distributed by PreSens GmbH, Regensburg, Germany), or a phase-shift detection scheme (e.g., the oxygen optode manufactured and distributed by Aanderaa, Bergen, Norway. Note that the Aanderaa system is based on an oxygen-sensitive foil manufactured by PreSens; Aanderaa supplied the electronics and packaging to make it into an oceanographic instrument).

The relatively slow response of these optical probes (see e.g., Glazer et al., 2004) results from the presence of a gas-permeable membrane placed over the sensing foil containing the immobilized chromophore (usually a ruthenium complex). This membrane

is added to make the sensor more rugged, to avoid interferences from fluorescent materials in the water, and to protect the sensor from direct sunlight. As yet, there has been only limited use of such sensors in the oceanographic community. A number of groups are presently evaluating the Aanderaa sensors for various applications: drifters, mooring, profiling floats and first indications show promise. Potential science that can be done with such a sensor attached to a profiling float is indicated in Joos et al. (2003).

As with the Clark-type sensors, effective temperature compensation is an essential part of the sensor calibration and a cornerstone of accurate measurements in an environment where the temperature changes. The sensors are also pressure sensitive, the sensitivity to oxygen being slightly lessened at increased pressures.

Another promising new technology for oxygen measurements is membrane inlet mass spectrometry (see e.g., <http://www.hpl.umces.edu/dga/>), which has been engineered to perform underwater (see e.g., <http://cot.marine.usf.edu/hems/underwater/>). Using this approach, *in situ* oxygen, as well as argon and nitrogen, may be measured. Quantitative assessment of this suite of gases can provide useful benchmarks for data interpretation.

A final approach to measuring the oxygen partial pressure in water in a moored system involves using a so-called gas tension device (Pro-Oceanus Systems, Halifax, Canada). This determines total gas pressure in water by direct measurement of the pressure on the gaseous side of a gas-permeable membrane that is in contact with the water. Using such a device in concert with a second similar device that incorporates a chemical absorbent for oxygen, thus removing oxygen more quickly than it diffuses through the gas-permeable membrane, allows an estimate of the oxygen partial pressure by difference. As yet, there is limited experience with this dual system; however, the original gas tension device is capable of excellent long-term precision and is well-suited for use on a mooring (see e.g., Emerson et al., 2002).

In conclusion, there is no single perfect approach to measuring oxygen concentrations

in seawater at this time. The newest incarnation of the Clark-type sensor (the Sea-Bird SBE 43) seems to be robust and is designed for profiling applications. Its long-term drift (over a period of a year), however, is expected to be significant. The second-generation pulsed oxygen sensors (currently only available as prototypes) include modifications aimed at extending battery life, increasing data storage capacity by data compression algorithms, improving membrane and solution stability, and new anti-fouling schemes. As a result, their operational period has been extended up to six months. The Aanderaa optode has been tested to have a long-term stability (more than 6 months), although its response time is slow (up to a few minutes). It is being incorporated into a number of platforms (moorings, profiling floats, drifters) at this time, and the results of this more widespread use should become known in the coming year or so. As this experience is gained, the efficacy of the various prophylactics against biofouling, an essential part of long-term stability, will become clearer.

Nutrient Sensors

Although a wide variety of elements are essential to life in the oceans, only a relatively small number of essential elements are classified as nutrients. Elements such as nitrogen, phosphorus and silicon are termed nutrients based on their distinctive vertical profiles in the upper ocean. The profiles of nutrient elements exhibit an extraordinary dynamic range. Nutrients characteristically have high concentrations in the deep ocean, while concentrations near the surface are often below detection limits even for state-of-the-art instrumentation. The gradient of nutrient concentrations in the transition zone, between high and low concentrations, generally encompasses the euphotic zone and can be very dynamic in response to both physical and biological processes. Thus, *in situ* nutrient measurements are exceptionally challenging.

Essentially all labile inorganic and organic forms of nitrogen, phosphorus, and silicon can be considered as priority analytes. Important bioavailable forms of nitrogen include ammonia, nitrite, nitrate and urea. Import-

tant forms of phosphorus include both orthophosphate and organic species, while dissolved silicon in seawater is considered to be present strictly as monomeric forms of silicic acid. All of the nutrient sensors described in Table 2 are based on either conventional colorimetric procedures or direct measurements via UV spectroscopy. Potentiometric measurements of nitrate and ammonia (YSI Inc.) are suitable only for freshwater environments. The spectrophotometric sensors shown in Table 2 have a wide range of response times, physical dimensions, power requirements and measurement capabilities.

The UV sensors for nitrate absorbance measurements (MBARI-ISUS and SUV-6)

at the top of Table 2 are notable for their fast response times (seconds). These sensors may be especially suitable for profiling operations. The sensitivity of direct (reagentless) nitrate measurements is likely somewhat poorer than that of some of the Table 2 colorimetric sensors. The limit of detection for one ISUS observation is on the order of 1.5 μM (± 3 SD), while 30 seconds of signal averaging can reduce the detection limit to 0.2 μM (Johnson and Coletti, 2002). The resolution limit of the SUV-6 is also given as 0.2 μM (Finch et al., 1998; Prien and Hydes, 2003).

The NPA and DPA instruments of SYSTEA are capable of measuring four nutrients per instrument (Table 2). The maxi-

mum deployment depths of the two sensors are 10 m and 4500 m. The detection limits for ammonia, phosphate, nitrite and nitrite plus nitrate are given as 50 nM, 10 nM, 11 nM and 16 nM for the NPA system, and 100 nM, 10 nM, 13 nM and 32 nM for the DPA system. No documentation for the stated sensitivities is currently available. It is stated that both of these four-channel systems are capable of measuring silicate in place of one of the other nutrients. Measurements of different nutrients are sequential. The endurance of these instruments in moored operation is stated in different forms: (a) up to one month depending on measurement intervals, (b) 350 total measurements, and (c) four to

TABLE 2

Current status of nutrient sensors. Development stages and deployment designations as in Table 1. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Analytes measured	Development stage	Power (Watts)	Sampling time	Deployment capability	Source/Contact
MBARI-ISUS	nitrate	I	12	s	M,A,P,T, R,B	Satlantic/ WETSAT www.satlantic.com www.wetsat.com
SUV-6	nitrate	V	4	s	P	Ralf Prien OED-SOC** Ralf.prien@soc.soton.ac.uk www.valport.co.uk
NPA	nitrite nitrate/nitrite orthophosphate ammonia	I	10	min	M	SYSTEA, www.systema.it
DPA	nitrite nitrate/nitrite orthophosphate ammonia	I	7	min	M,A,P,T,R	SYSTEA, www.systema.it
TPA	Tot. nitrogen Tot. phosphorus	I	10 - 20	~ 0.5 hour	M	SYSTEA, www.systema.it
NAS-3X	nitrate silicate phosphate ammonium	I	~ 3.4	min	M, P	EnviroTech LLC, www.n-virotech.com
EcoLAB	nitrate silicate phosphate ammonium	I	3.1	min	M,P	EnviroTech LLC, www.n-virotech.com
SubChemPak	nitrate nitrite Fe ^{II} /Fe ^{III} phosphate	I	50 - 150	s s s min	M,A,P,T,R	SubChem Systems, Inc. www.subchem.com
DigiSCAN	nitrate	II		min	M,A,P,T,R	YSI Inc. www.ysi.com
YSI 9600	phosphate	II		min	M,A,P,T,R	YSI Inc. www.ysi.com
SEAS-II	nitrate nitrite Fe ^{II} /Fe ^{III} ammonia Cu	V V VI VI VI	15	s s s min min	M,A,P,T,R	R. Byrne, USF-COT*, byrne@marine.usf.edu

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ten weeks due to reagent expiration. In the absence of special reagent preservation procedures, the less than ten-week limitation imposed by reagent degradation would be common to all wet chemical colorimetric procedures. The TPA system of SYSTEA is capable of total nitrogen and total phosphorous in place of ammonia and nitrite. The detection limits for total N and P is given as 3 ppb and 2 ppb. The TPA system is generally similar to the NPA and TPA systems, and it is stated that approximately one hour is required for a full cycle of four measurements.

The NAS-3X and EcoLAB systems of Envirotech LLC provide nutrient measurements with stated detection limits equal to 50 nM for nitrate and ammonium and 60 nM for phosphate and silicate. The EcoLab system is a four-channel version of the NAS-3X in which four nutrients are measured simultaneously. The endurance for nitrate, ammonium, phosphate and silicate measurements are six months, four months, two months and two months, respectively. The standard depth capability for both instruments is 100 m, with options for 250 m and greater. These sensors are stated to be extremely resistant to biofouling. However, the characteristics of these sensors are not well documented in scientific publications.

The SubChemPak analyzer is a three wavelength, four-channel system comprised of the SubChem Systems, Inc. reagent delivery module and the ChemStar four-channel absorption detector of WET Labs, Inc. Measurements of nitrite, nitrate, phosphate and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ can be obtained to depths of 200 m. Previous descriptions of this sensor (Hanson and Moore, 2001) have emphasized its use for measurements of spatial distributions (profiling and towed deployments). The system's relatively high power consumption would not be problematic in these cases. The 15 cm pathlength of the SubChemPac system is unique among commercially available sensors. This relatively long pathlength should translate to detection limits on the order of ten nanomolar.

The MBARI sensor, originally known as the DigiSCAN, is scheduled for commercial production as the YSI 9600 Nitrate Analyzer. Some aspects of the operation of this system

were described by Weeks and Johnson (1996). The resolution of this sensor for nitrate measurements is stated as approximately 0.16 μM . The system can also be adapted for phosphate measurements. The instrument has been deployed in various environments for periods between one and three months with samples taken once per hour.

The SEAS-II sensor of USF-COT is a single channel system that can be used for both absorbance and fluorescence measurements. Pathlengths on the order of one to two meters promote high sensitivity and high resolution. Iron and nitrite, for example, can be measured with detection limits on the order of 2 nM. The sensor's Ocean Optics diode array detector allows measurements at user-defined wavelengths. Measurements are obtained at a frequency up to approximately 1 Hz. Both sampling frequency and the timing of measurements are user defined. Using only the sensor's internal batteries, electrical endurance is 190 watt-hours. The sensor's depth range is 500 meters. SEAS-I characteristics are described by Steimle et al. (2002) and Callahan et al. (2004).

A number of novel sensors have not been included in Table 2. The osmotically pumped nitrate analyzer (OsmoAnalyzer) described by Jannasch et al. (1994) utilizes conventional colorimetric chemistries and has a detection limit of 100 nM, with a measurement time somewhat less than one hour. This instrument was successfully operated in a saltwater aquarium for approximately one month and performance was assessed during several field studies (e.g., Chapin et al., 2002; McGillicuddy et al., 1998). The nitrite/nitrate analyzer of Daniel et al. (1995 a, b), which is also based on conventional colorimetric analysis, has a 40/hr measurement frequency and a nitrate detection limit of 0.45 μM . The analyzer was connected to an attending vessel via a 300 m power cable, which also linked the sensor's electronics with the shipboard central processing electronics. Floch et al. (1998) used an identical system for silicate measurements with a detection limit of 0.3 μM . In addition, Masserini and Fanning (2000) have described a three-channel shipboard analyzer for fluorimetric analysis of nitrite,

nitrate and ammonia. The system is being prepared for *in situ* deployment and has reported detection limits of 4.6 nM (nitrite), 6.9 nM (nitrate) and 1 nM (ammonia).

The sensors depicted in Table 2 have a wide range of measurement objectives and, accordingly, a wide range of capabilities. Since direct UV observations of nitrate (MBARI-SUS and SUV-6) are exceptionally fast, these sensors are ideal for obtaining very rapid chemical profiles. Both of these sensors are also suitable for long-term measurements, but the sensitivity and specificity of direct UV detection is expected to be somewhat poorer than is the case for measurements obtained using wet chemical procedures. The SubChemPak and SEAS sensors are oriented toward profiling and towed operations, but are also capable of long-term measurements. The long pathlength of these systems allows not only increased sensitivity, but also an enhanced rate of sampling because relatively high absorbances can be obtained before colorimetric reactions have gone to completion. As evidenced by relatively long sampling times, most of the remaining sensors in Table 2 are oriented toward moored operations, but can in principle also be used for observations of spatial distributions. The sensitivities listed for the various sensors in Table 2 are not altogether consistent. For the colorimetric sensors in the table, the best guide to sensitivity will be the molar absorbances of sensed analytes and spectrometric pathlength (Byrne et al., 1999). In general, there is an extreme dearth of peer-reviewed discussion of instrumental characteristics and operation in the field. Some instruments are marketed with essentially no peer-reviewed documentation of instrumental capabilities.

Carbon System Sensors

Primary CO_2 system variables include CO_2 fugacity (f_{CO_2}) or partial pressure (p_{CO_2}), pH ($-\log[\text{H}^+]$), total dissolved inorganic carbon (C_T), and total alkalinity (A_T). Three of these primary variables (f_{CO_2} , pH, C_T) are directly linked via equilibrium thermodynamics, while the relationship between A_T and the remaining primary variables requires an assessment of the alkalin-

TABLE 3

Current status of *in situ* CO₂ system sensors. Development stages and deployment designations as in Table 1. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Analytes measured	Development stage	Power (Watts)	Sampling time	Deployment capability	Source/Contact
SAMI-CO ₂ SAMI-1500	fCO ₂	I	2.4	min	MM,P	Sunburst Sensors www.sunburstensors.com
CARIOCA	fCO ₂	II		min	M	http://www.lodyc.jussieu.fr/ carioca/home.html
MBARI- ΔpCO ₂	ΔpCO ₂ atm/seasurface	II	8-12	min	M	LI-COR Inc. http://www.licor.com/env/
Fiber-optic CO ₂ sensor	pCO ₂	V			M	D. Walt, MTLOC-DC [*] -Tufts dwalt@emerald.tufts.edu
SAMI-pH	pH	V	~ 2.4	min	M	M. Degrandpre, UM mdegrand@selway.umt.edu
SEAS-II	pH	V	15	s	M,P,A,T,R	R. Byrne, USF-COT ^{**} byrne@marine.usf.edu
AMpS	pH	VI	~ 10	s	M,P,A,T,R	R. Bellerby, BCCR-GI-UB† richard.bellerby@gfi.uib.no
Deep-sea pH probe	pH	VI		s	M,P,R	N. Le Bris, IFREMER nadiene.le.bris@ifremer.fr
RATS	C _T	V		min	M	F. Sayles, WHOI, fsayles@whoi.edu

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ity contributions of minor protolytes including borate, phosphate and silicate. Requirements for accuracy and precision of C_T and A_T measurements are generally stringent because of the limited dynamic range of these variables in seawater. In best practice, shipboard measurements of these two variables, via coulometry and acid-base titrimetry, provide precisions on the order of 1 - 2 μM and 2 - 4 μM respectively. The achievable precision for spectrophotometric pH measurements, on the order of 0.0004 pH units, allows ocean pH to be measured with a high resolution. Similar results can be achieved for measurements of f_{CO2}.

Measurements of f_{CO2} typically involve either infra-red measurements of CO₂ in a gas phase that has been equilibrated with the seawater (either by direct contact, or through a membrane that is permeable to unionized CO₂), or measurements of pH in a solution phase of known alkalinity that has been equilibrated with the seawater (again through a membrane that is permeable to unionized CO₂). Direct measurements of seawater pH, as well as pH measurements in equilibrated solutions for the purposes of f_{CO2} measurements, generally involve spectrophotometric observations of indicator absorbance ra-

tios. Such measurements, in good practice, have very stable calibrations that do not require additional calibration in the field. These calibrations depend predominantly on the properties of the indicator dye itself, and to a much smaller extent on the properties of the spectrophotometer that is being used (Robert-Baldo et al., 1985; DeGrandpre and Bachr, 1999). The coulometric and titrimetric procedures used on shipboard for C_T and A_T measurements are not readily amenable to *in situ* analysis. As such, progress on sensors for these variables has generally been slower than for measurements of the remaining primary variables. The sensors listed in Table 3 for measurements of C_T and A_T involve procedures that are distinct from those used in shipboard analyses.

The performance characteristics of the SAMI-CO₂ sensor are especially well documented (DeGrandpre, 1993; Degrandpre et al., 1995, 2000; Degrandpre and Bachr, 1999), and the sensor has been routinely used for scientific investigations (DeGrandpre et al., 2002; Bachr and Degrandpre, 2004). Observations of dissolved indicator absorbance ratios provide f_{CO2} relative precisions on the order of 0.3 to 1%. The system is reported to be capable of

year-long deployments, and has performed well in low temperature environments over a period of five months. The operational principles of the CARIOCA f_{CO2} sensor (Lefevre et al., 1993) are similar to those of the SAMI-CO₂ sensor, and the performance characteristics of the two instruments appear to be generally similar. Although the time constant for sensor equilibration appears to be somewhat longer for the CARIOCA system (20 minutes) than for the SAMI system (5 minutes), hourly sampling should be adequate for oceanic observations on moorings. CARIOCA measurements have been compared with shipboard f_{CO2} measurements in the Sargasso Sea (Bates et al., 2000), and the instrument has been used on drift buoys in the Greenland Sea for a period of six months (Hood and Merlivat, 1999).

The pCO₂ measurement system of Friederich et al. (1995) is designed for precise observations of differences in CO₂ partial pressure at the air/sea interface (ΔpCO₂). The sensor is based on commercially available instrumentation for non-dispersive infrared spectrophotometry. Deployments in excess of two months evidenced excellent instrumental stability. This instrumentation is routinely used for scientific observations (Chavez et al., 1999).

The $p\text{CO}_2$ sensor of Tabacco et al. (1999), presented in Table 3, is a fluorescence-based fiber optic system in a relatively early stage of development. Although the sensor exhibited long-term drift in sea trials, and the overall performance characteristics of the system are not well characterized relative to the SAMI and CARIOCA systems, the methodology appears to be promising and is currently being tested by YSI.

SAMI-pH sensors utilize indicator absorbance ratios to achieve a measurement precision better than ± 0.005 pH units (Martz et al., 2003). SAMI-pH measurements agree with laboratory spectrophotometric pH measurements within approximately 0.003 units. The instrument has a response time on the order of six minutes, and appears to be well suited to long-term moored operations. Like the SAMI-pH sensor, SEAS pH measurements are based on absorbance measurements at three wavelengths. Although SEAS-pH sensor development has emphasized a rapid response time (~ 2 s) for profiling operations, the instrument has also been used for moored measurements in the North Pacific over a period of approximately three weeks. The spectrophotometric response of the system, which utilizes an Ocean Optics CCD array spectrometer, is essentially identical to that of laboratory instruments (e.g. HP 8453), and short-term precision is approximately 0.001 pH units.

The AMpS shipboard spectrophotometric system (Bellerby et al., 2002) achieves an on-line precision better than 0.001 pH units with a measurement frequency of 20 samples per hour. The system is suitable for moored measurements in the surface ocean, and a miniaturized sensor is being prepared for deep-sea operations. The shipboard spectrophotometric system of Tapp et al. (2000) has a precision similar to that of the AMpS system, indicating that pH precisions on the order of 0.001 and better can be routinely achieved using compact CCD array spectrometers. The system of Tapp et al. (2000) is apparently not being modified for autonomous deployments.

Due to stringent requirements for precision and accuracy, potentiometric pH sensors are not generally suitable for autonomous

measurements in the surface ocean. For the purpose of CO_2 system characterizations in surface waters, measurement resolutions on the order of 0.01 and accuracies between 0.1 and 0.2 are unsatisfactory. Nevertheless, potentiometric pH measurements can be quite useful in some circumstances. The very large pH range and sharp pH gradients in hydrothermal systems somewhat reduces the significance of accuracy and precision and heightens the importance of rapid response times. Le Bris et al. (2001) demonstrate the utility of potentiometric pH measurements subsequent to careful consideration of the influences of pressure, and especially temperature, on electrode calibrations (slopes and intercepts). A variety of potentiometric pH sensors, including those of In-Situ Inc. (www.insitu.com), Sea-Bird (www.seabird.com), and YSI (environmental.ysi.com), may also prove useful for examination of pH gradients in benthic systems that are approximately isothermal.

The WHOI/Sayles RATS sensor is currently the only operational *in situ* system for total CO_2 measurements. Measurements are obtained conductimetrically following exchange of CO_2 between acidified seawater and the interior of a CO_2 permeable tube that contains dilute NaOH. Six-week tests over a temperature range between 8° and 24° C, as well as *in situ* tests over a period of two weeks, produced measurement precisions equal to ± 2 μM in each case (Sayles, personal communication). System endurance based on either power consumption or reagent limitation is ~ 700 analyses. This sensor system incorporates spectrophotometric pH measurements to provide a comprehensive description of the marine CO_2 system.

In situ membrane introduction mass spectrophotometers (Short et al., 2001; Wenner et al., 2004) are currently being adapted for measurements of total CO_2 . This new capability requires only the addition of in-line acidification to current technology already available.

A shipboard system for measurements of pH, f_{CO_2} and C_T (Byrne et al., 2002) is currently undergoing sea trials. *In situ* measurements are planned for 2004 - 2005. A system for potentiometric C_T has been described by Choi et al. (2002). While this sensor may be

useful in some applications, the system's 30 μM measurement imprecision presently precludes its use in CO_2 system studies.

There are presently no sensor systems being tested for autonomous *in situ* alkalinity analyses. It has been shown, however, that A_T measurements can be obtained using the same system that is currently being readied for *in situ* measurements of pH, f_{CO_2} and C_T .

Biological Sensors

Conventional sampling technologies (e.g., water bottles, nets, pumps) limit the ability of biological oceanographers to assess the abundance and distribution of organisms over a broad range of temporal and spatial scales. Observations need to be made at space and time scales relevant to organisms' behavior and physiology and life history rate measurements. Optics and acoustics are the primary technologies currently being used to detect and identify organisms in the water column, however, neither can quantify all the critical variables alone and both have strengths and limitations. For example, most optical sensors resolve targets on small spatial scales (μm to m), while acoustics is the only method available that can detect zooplankton and fish over much larger spatial scales (mm to km) and provide a visualization of biophysical interactions in aquatic systems. Both methods share a common background in wave propagation theory, which uses properties of absorption and scattering. Both technologies also have experienced major advances in hardware and software development, particularly in signal and imaging processing, and in model development in the last two decades. The Grand Challenge for these technologies is still remote species identification. Optical scattering and absorption sensors now routinely provide information on particle size and density, phytoplankton phylogenetic groups (i.e., diatoms, prymnesiophytes), and estimates of photosynthesis (reviewed in Dickey and Chang, 2001), but only imaging and microscopy by humans has yielded species identification. Some optical sensors are being deployed on moorings, drifters, and gliders but only a few bioacoustic sen-

sors have been deployed on moorings or Autonomous Underwater Vehicles (AUVs) for short durations (days-months). Numerous optical imaging systems to assess phytoplankton and zooplankton (see reviews in Jaffe et al., 2001; Wiebe and Benfield, 2003) have been developed in the last few decades, but few are capable of long-term deployment as part of observatories. Recent advances focus on the use of sensing systems which integrate a suite of 'smart' sensors (e.g., optics, acoustics, environmental variables). It is envisioned that these systems will be capable of automated internal calibrations *in situ*, and that they will be able to detect changing gradients and then make decisions about altering sampling intervals or send an alert back to shore for further instructions.

Some of the challenges for developing optical sensors for mobile platforms are generic, while others are more or less stringent depending on the platform constraints and intended mission duration (Rudnick and Perry, 2003). For example and in contrast to floats and gliders, powered AUVs can accommodate larger payloads and sensors with higher power demands, such as multi-wavelength spectrometers, imaging systems, and flow cytometers. Only radiometric sensors that are sufficiently small and power conservative have been incorporated into floats and gliders (i.e., downwelling irradiance, beam c , backscattering, and fluorescence sensors). Other engineering challenges become important only for longer deployment. For missions of short duration (i.e., days) issues of biofouling and sensor drift are not as great a concern as they are for missions lasting from months to years.

Optical sensors

Radiometric measurements in the near UV and visible wavebands are widely used as proxy measurements for important biogeochemical variables in the ocean. Phytoplankton absorb visible radiation predominantly in the blue, blue-green, and red portions of the visible spectrum as a function of pigment composition and fluorescence or re-emit a small fraction of absorbed light at 683 nm. Their scattering spectrum is dependent on size (ranging from $\sim 0.7 \mu\text{m}$ to

several hundred microns), refractive index, and absorption spectrum. Non-algal organic particles, such as bacteria and detritus, are relatively weak scatterers and absorbers, with absorption maxima in the UV. Chromophoric dissolved organic matter (CDOM) strongly absorbs in the UV, its peaks associated with humic and fulvic acids, mycosporin-like amino acids (MAAs), nucleic acids, and specific amino acids. Suspended minerals are highly efficient scatterers, although strong absorption features have been observed in iron-rich minerals. The optical sensors used to measure these proxies include active radiometric systems with integrated light sources and passive radiometers deployed in- or above-water. Protocols for many sensors are published as JGOFS procedures and NASA SIMBIOS documents. Because several variables may contribute to the optical signal at any single wavelength, it is often necessary to use a combination of measurements to decrease uncertainty in proxy resolution. Variability in the fundamental relationship between the optical measurement and the concentration of the proxy also argue for a combination of measurements to reduce uncertainty in the conversion factor. A rich literature exists for extraction of proxy information from optical sensors.

Active optical sensors use lamps or LEDs as the light source and measure inherent optical properties (IOPs, i.e., properties not affected by natural illumination conditions) such as absorption (a), scattering (b), and attenuation coefficients ($c = a + b$). Passive radiometers depend upon natural illumination conditions and measure apparent optical properties (AOPs) such as downwelling irradiance (E_d), upwelling radiance (L_u), diffuse attenuation coefficient (K_d), and reflectance. IOPs and AOPs are related via the radiative transfer equation, and IOPs can be estimated from AOPs through solution or inversion of the radiative transfer equation (cf. Gordon et al., 1975). Because IOP sensors have internal light sources, power consumption rates are higher than for passive sensors. However, they can operate at night and below the photic zone, making it possible to detect phenomena such as diel

changes in particle concentration, sinking phytoplankton aggregations, and detached nepheloid layers. AOP instruments depend only on sunlight and therefore consume less power. However, they cannot operate at night or below the photic zone (typically 10 to 150 m, depending on the concentration of optically active material in the water).

The WET Labs ac-9 (so-named because it measures absorption and attenuation at nine wavelengths, and allows total scattering to be derived) was introduced in the last decade and has been widely deployed from ships using profiling and towed systems and on moorings for weeks to months (Table 4). These meters are flow-through systems with path length options of 25 cm for open ocean waters and 10 cm for more turbid waters. Recent modifications have increased the number of wavelengths measured and improved electronic stability. Although not commercially available, Kirkpatrick et al. (2003) developed a liquid-capillary waveguide to measure CDOM; this system has also been used for total particulate absorption measurements on AUVs and gliders. Size and power consumption limit current autonomous application of absorption meters to moorings and short-term deployments on autonomous platforms. The use of copper tubing on the inlets of ac-9s has reduced biofouling on mooring applications (Chavez et al., 2000), but in highly productive regions biofouling remains a serious problem. Drift in calibration during long-term deployments remains problematic, but could be addressed by metered injections of a calibration dye, similar to systems being developed for nutrient standards in conventional colorimetric nutrient analyzers. Small transmissometers such as the C-Rover, provide light-weight options for mobile platforms, but are less rugged than traditional transmissometers, a potential logistical drawback for the rigors of ship-launched deployments of moorings in hostile environments. Sequoia Scientific's LISST (Laser In-Situ Scattering and Transmissometry) measures small-angle, near-forward scattering with a laser diffraction technology. The LISST provides a robust

measurement of particle size distribution; a choice of size ranges and additional parameters are available from several different models. The HOBI Labs C-Beta offers an alternative measurement for the beam attenuation coefficient, using a folded-path

geometry for 30 and 90 cm path lengths. A choice of backscattering sensors exist that use flush-mounted optical windows to measure multiple angles of backscatter and offer a selection of wavelengths. Pulse modulation of the signal minimizes con-

tamination by ambient light, allowing measurement in full sunlight. The size and power consumption vary, from the larger HOBI Labs' HydroScat-6 (six wavelengths) to the smaller WET Labs' ECO VSF series. Turbidity meters, such as offered by

TABLE 4

Current status of optical sensors for commercially available examples. Development stages, power [based on available information; watts (W), amps(A)] and deployment designations as in Table 1. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Development stage	Power	Sampling time	Deployment capability	Source/contact
ac-9 absorption & attenuation meter	I	9 W @12 VDC	s	M,P,T,A	Wet Labs, www.wetlabs.com
C-Rover transmissometer	I	400 mW	s	D,A	Wet Labs, www.wetlabs.com
C-Beta backscattering & attenuation	I	70 mA @ 15 VDC	s	M,T	HOBI Labs, www.hobilabs.com
CYCLOPS-7 chlorophyll fluorometer	I	<300 mW	s	M,P,T,A,S	Turner Designs, www.turnerdesigns.com
ECO Pucks™ fluorometer or scattering meter	I	70 mA 7–15 at VDC	s	all	Wet Labs, www.wetlabs.com
UV AQUAtracka CDOM and hydrocarbon fluorometer	I	495mA at 12V d.c.	s	M,T,S	Chelsea Technologies, www.chelsea.co.uk
LISST Laser In Situ Scattering and Transmissometry	I	160 mA @ 9 V max	s	M,A,T	Sequoia Scientific, Inc., www.sequoiasci.com
HydroScat-6 backscattering & fluorescence	I	3 W	s	M,P,T	HOBI Labs, www.hobilabs.com
ECO VSF backscattering meter	I	85 mA @ 12-15 VDC	s	M,P	Wet Labs, www.wetlabs.com
Turbidity meter	I	6 mA peak @ 7-20 VDC	s	M,P	Seapoint Sensors, www.seapoint.com
FASTtracka fast repetition rate fluorometer	I	0.5 A @ 18-72 VDC	s	M,T,P,S	Chelsea Technologies, www.chelsea.co.uk
bbe FluoroProbe multispectral fluorometer	I		s	M,P,T,A	bbe Moldaenke GmbH, www.bbe-moldaenke.de/
OCR-504 multispectral irradiance meter	I	25 mA at 9 VDC	s	M,D,A,G,P,T,S	Satlantic, www.satlantic.com
HyperOCR hyperspectral irradiance meter	I	2 W at 18- 72 VDC	s	M,T,S	Satlantic, www.satlantic.com
BIS multispectral scalar irradiance meter	I	2mA per channel	s	M,D,A,P,T,S	Biospherical, www.biospherical.com
GLOWtracka bioluminescence	I	40 mA @ 12 VDC	s	M,T,P	Chelsea Technologies, www.chelsea.co.uk

Scapoint Sensors, uses similar technology. All sample more frequently than once per second. The use of wiper blades to reducing fouling on the optical windows and the use of copper foil in the vicinity of the windows and blades have met with some success in reducing biofouling.

Fluorescence is not strictly an IOP or AOP, but different aspects of fluorescence can be measured by both active and passive sensing systems. The principle underlying fluorescence is straightforward: $F = E * a * \phi$, where F is fluorescence, E is irradiance of the excitation light source, a is the absorption coefficient of phytoplankton photosynthetic pigments and ϕ is the fluorescence quantum yield. If E and ϕ are constant, then fluorescence is directly proportional to the absorption coefficient—itsself a function of phytoplankton biomass or CDOM concentration, depending on the wavelengths selected. Chlorophyll fluorescence as a phytoplankton biomass proxy has a long history of measurement in the ocean. Lorenzen (1966) obtained the first continuous profiles of chlorophyll fluorescence by attaching a submerged pump to the end of a garden hose and pumping water to an on-deck fluorometer, sometimes with shocking results. Fortunately the technology evolved, and fluorometers were placed in pressure cases, integrated with the then-evolving CTDs, and lowered through the water column to directly obtain profiles of chlorophyll fluorescence. The first *in situ* fluorometers were large both in size and power consumption; modern fluorometers are at least an order of magnitude smaller in both. Two basic types of fluorometers in use today are pumped flow-through models, where excitation and detection occur inside the instrument and non-pumped models with flush-mounted optical windows, where excitation and detection occur in a volume external to the sensor that is potentially exposed to sunlight. Variability in the ratio of fluorescence to phytoplankton chlorophyll and carbon make interpretation of fluorescence somewhat problematic. Instruments such as the Chelsea FASTtracka fast repetition rate fluorometer (second generation soon to be released) use high intensity

flashes to probe photosynthetic physiology. Fluorometers with strong UV excitation lamps have been used to detect CDOM, oil, tryptophan, and other organics. Small CDOM fluorometers with near UV excitation wavelengths show reasonable agreement with more conventional absorption measurements. Multi-spectral fluorometers, such as the bbe Fluoroprobe that can assess different algal groups based on excitation/emission characteristics and multiple compounds (e.g., oil, CDOM), are becoming more available. Biofouling continues to be a concern for long-term deployments of fluorometers; however, copper tubing and shutters have been successfully used to extend deployment times.

AOP sensors are classified as functions of geometry and spectral characteristics. Three sensor geometries are cosine irradiance, E_d or E_u (proportional to the cosine of the incident upwelling or downwelling light); radiance, L (per steradian for a given solid angle, typically nadir); and scalar irradiance, E_o , (radiance over $\sim 4 \pi$ steradians). PAR (photosynthetically available radiation) sensors are broadband and measure all photons between 400 and 700 nm with units of total quanta $m^{-2} time^{-1}$. Spectral sensors measure energy within specified narrow bandwidth in units of $W m^{-2} nm^{-1}$. Multispectral sensors typically measure several to \sim ten wavelengths, with options including UV, visible, and near IR wavelengths. Hyperspectral sensors cover the full spectrum, although bandwidth varies with specific instrument. The multispectral sensors are typically smaller with lower power consumption than the hyperspectral sensors. Specialized sensors, such as Biospherical's Natural Fluorometer that measures Lu at chlorophyll fluorescence wavelengths, or other monochromatic sensors are also available. Copper shutters have been successfully used to reduce biofouling of optical surfaces.

Bioluminescence can be considered as a special optical case, rather than as a strict IOP or AOP. Bioluminescence is the result of an exothermic internal chemical reaction that releases energy as light, either as an apparently spontaneous event or in response

to mechanical stimulation. A subset of bacteria, dinoflagellates, zooplankton, and fish are bioluminescent; hence, the magnitude and spectra of bioluminescence are invaluable diagnostics of the presence and abundance of specific species. Bioluminescence is measured with very sensitive passive radiometers able to detect the very low light levels associated with night-time bioluminescence. The Chelsea GLOWtracker is primarily designed for dinoflagellate bioluminescence. Systems to detect, or stimulate and detect, bioluminescence from zooplankton remain research instruments.

Optical imaging sensors

A variety of different systems (Table 5) have been developed to image particles and organisms, ranging in size from small phytoplankton and marine snow up to small fish, with the ultimate goal of being able to remotely obtain taxonomic information on species based on pattern recognition algorithms. The Phido-Ø is a two-dimensional imaging fluorometer that provides a high-resolution image of phytoplankton and physical microstructure simultaneously (Franks and Jaffe, 2001). The free-falling camera has a 32×32 cm field of view, with a $312 \mu m$ resolution, and images undisturbed water in front of its path. The FlowCam (Fluid Imaging Technologies) is another system for phytoplankton that utilizes a continuously imaging flow cytometer with a particle resolution of 5 - 1000 μm . A submersible version is being transitioned for use on moorings up to 100 m deep to rapidly assess community structure, and provide particle counts and fluorescence and/or scatter data. The Thin Laser Light Sheet Microscope (TLSSM) is a relatively new prototype technology designed to image the distribution of microbial particles in a 3-dimensional fluid (Fuchs et al., 2002), which could yield insights into functional interactions within the microbial loop.

The Optical Plankton Counter (OPC) doesn't provide an image, but is a particle detector that uses optics to profile the cross-sectional area of each particle in its beam path. The measured area is then related to an equivalent spherical diameter (ESD),

TABLE 5

Current status of optical imaging sensors. Development stages, power [based on available information; watts (W), amps(A)] and deployment designations as in Table 1. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Development stage	Power	Sampling time	Deployment capability	Source/contact
Phido-Phi phytoplankton camera	IV	200 W	2Hz	D,A,P,S	J. Jaffe, SIO, http://jaffeweb.ucsd.edu
LOPC Laser Optical Plankton Counter	III	< 20 W	s	T	www.brooke-ocean.com , www.focaltech.ns.ca
FlowCAM microscope & flow cytometer	III	20 W	s	M,S	www.fluidimaging.com
Thin light sheet laser microscope	VI	100 W		A,P	J. Jaffe, SIO, http://jaffeweb.ucsd.edu
VPR II video camera	IV	2 A @ 48 VDC; 3 A @ 300 VAC*	117 - 750 ml/s	M,P,T	Seascan, Falmouth, MA
SIPPER2 laser line-scan camera	V	~100 W	10L/s	A,T,R	B. Flanery, USF-COT wflanery@marine.usf.edu
SIPPER3 laser line-scan camera	VII	20-60 W	15L/s	M,A,P,T,R	B. Flanery, USF, wflanery@marine.usf.edu
OceanCam deep-ocean camera	I	12-15 volts	s	M,T	Southampton Oceanography Centre
UVP video camera	IV		25 Hz	P,S	www.obs-vlfr.fr/~pvm/indeng.html
ZOOVIS-SC camera with strobed light sheet	V	34 W	s	M	M. Benfield, LSU, m Benfica@lsu.edu

*Small and large models

which is derived by equating the measured area to that of a circle and then extracting its diameter. OPCs are widely used to rapidly estimate zooplankton biomass (Herman, 1992; Woodd-Walker et al., 2000; Zhang et al. 2000), but species cannot be determined. The next generation Laser Optical Plankton Counter (LOPC) is smaller, reduces coincident particle counts, and is reported to be able to resolve higher plankton densities as well as measure shape outlines of particles >1 mm ESD. Particle profiles (100 μ m –35 mm) can be generated at flow rates up to 12 knots (Brooke Ocean Technology Ltd.). The strengths and weaknesses of the OPC and LOPC sensors and their use on different platforms are reviewed in a workshop report (Zhou and Tande, 2002). To date the OPC and LOPC have been used primarily on towed vehicles or in free-fall. The LOPC is currently being transitioned for use on mobile platforms by D. Checkley and R. Davis (SIO).

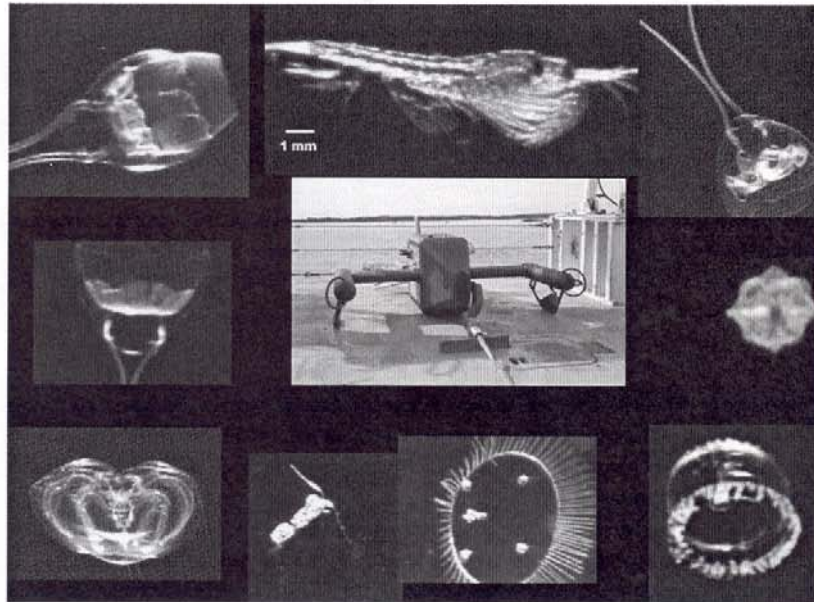
The Video Plankton Recorder (VPR, Davis et al., 1996) is an imaging system for particulates, phytoplankton, and zooplankton that uses forward scattered light. Recent configurations include a high-speed towed unit (VPRII), an autonomous battery-operated system for deployment on a CTD rosette (AutoVPR), a miniature system integrated into the AUV REMUS, and a moored profiling system (AVPPO, see below). The current VPR optics employ a high-resolution digital camera and a synchronized strobe sampling at 60 Hz. Depending on the optical configuration of the VPR, it can image 10 μ m - 2.5 cm organisms, with an image volume of 117 - 750 ml, providing a sampling rate of 210-1350 L/min. The sample volume is upstream of the camera to minimize disturbance and uses specialized image-processing routines to identify planktonic taxa in real-time (Tang et al., 1998; Davis et al., submitted; Fig.1). The automated classification method is sufficiently

accurate for estimating abundance patterns of dominant major taxa, but not for less abundant taxa. The range in overall accuracy is 61–79% for 4–7 taxa, with accuracies for individual taxa ranging between 45–91%. Classification error is small relative to natural variability in abundance of dominant taxa. The VPRII and AutoVPR are rated for 500 m depth and the AVPPO is currently being used for extended deployments on a near-shore profiling mooring from 100 m (see below). In addition, three-dimensional imaging and plankton tracking relative to turbulence is now possible with a 3D-VPR deployed on ROVs (Gallager et al. 2004).

Another approach is the Shadowed Image Particle Profiling and Evaluation Recorder (SIPPER), which uses two high-speed digital laser line-scan cameras that record continuous images of organisms in two dimensions in water flowing through a 96 x 96 mm sampling tube (Samson et al. 2001;

FIGURE 1

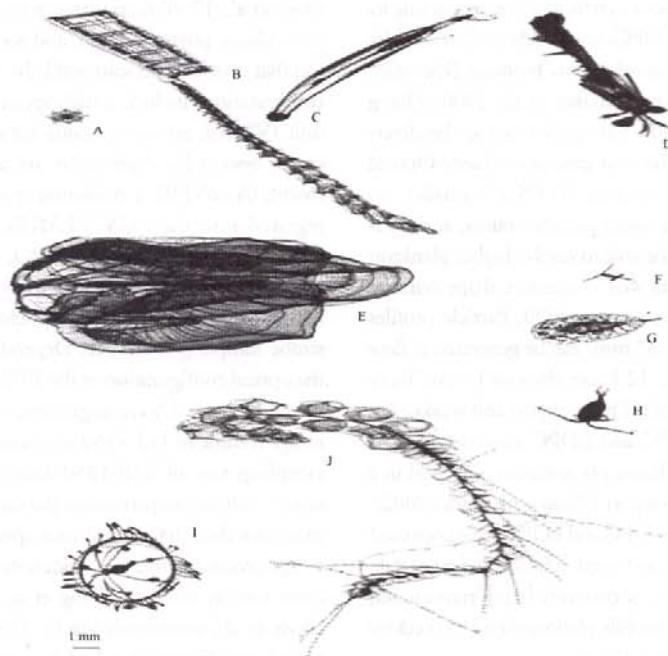
The Video Plankton Recorder (VPR) II on a high-speed towed vehicle is shown on the deck of the R/V *Oceanus*, along with some images collected on a cruise across the Atlantic Ocean.



Remson et al., 2004). Organisms between 15 μm and 10's of cm may be imaged. The benefits of this technology are the larger sampling area and the ability to image large organisms, such as siphonophores, entirely intact (Fig. 2). Highly mobile organisms, however, such as large shrimps, may not be quantitatively assessed owing to avoidance; a problem common to all imaging systems. This system has been towed off ships and used on an AUV. Current modifications include improvements to the image recognition software (currently 70 - 75% accuracy for 46 classifications in highly diverse tropical systems, Luo et al., 2004; Tang et al., in press), changing the configuration so that it can be used on moorings or in profiling mode, and enhancing the hardware so that it can operate to 1000 m (B. Flanery, personal communication). Other camera imaging systems, such as the Underwater Video Profiler (UVP; images 1.3 - 70 L, operates to 1200 m; Gorsky et al., 2000) and the Zooplankton Imaging and Visualization System (ZOOVIS; 50 μm resolution, 12 cm field of view, strobed light sheet for illumination of targets in focus, oper-

FIGURE 2

Shadowed Image Particle Profiling and Evaluation Recorder (SIPPER) images from the West Florida Shelf: (A) spumellarian radiolarian, (B) doliolid, (C) chaetognath, (D) mantis shrimp larvae, (E) lobate ctenophore, (F) cyclopoid copepod *Oithona* sp., (G) poecilostomatoid copepod *Copilia*, (H) calanoid copepod, (I) cnidarian; hydrozoa cf *Obelia*, (J) physonect siphonophore (images courtesy of A. Remson).



ates to 250 m; Benfield et al. 2003) have been used in profiling mode and could be transitioned for use on moorings. Cameras, such as the OceanCam (Southampton Oceanographic Centre), also have been developed for time-lapse photography of deep-sea biology and sedimentary processes. The OceanCam can operate at 6000 m depth for over a year on moorings. Other efforts to improve image recognition include the Zooscan software that recently became commercially available (www.zooscan.com) and is intended for automated analyses of preserved net samples.

Acoustic sensors

Bioacoustics (transmitted sound/active mode) is a cost-effective, efficient, and essential tool that can provide unique insights into the behavior and spatial and temporal variability of biological populations on many scales. Quantitative interpretation of acoustic backscattering, however, remains a chal-

TABLE 6

Current status of acoustic and microbial sensors and sampling systems. Development stages, power [based on available information; watts(W), amps(A)] and deployment designations as in Table 1. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Development stage	Power	Sampling time	Deployment capability	Source/contact
<i>Acoustics</i>					
EK60	I	50-100 W	s	A,T,S	Simrad (split beam) www.simrad.com
EK2000	I	< 250 W	s	A,T,R,S	Simrad (200kHz Multibeam)
TAPS	I	8.4 W	s	M, P, T	www.aard.tracor.com/home/eco/MarEco.html
BIOSPAR	V	35 W	s	M,D	P. Wiebe, WHOI pwiebe@whoi.edu
FishTV multibeam (435 kHz, 1.6 Mhz)	IV	500 W	4Hz	S	J. Jaffe, SIO jules@mpl.ucsd.edu
<i>Acoustic tags</i>	I	7-360 days*	s	Fish	Hydroacoustic Technology Inc. www.htisonar.com
<i>Acoustic tags</i>	I	up to 191 days*	s	Fish, invertebrates, mammals	VEMCO, www.vemco.com
<i>Archival tags</i> temp, salinity, pressure	I	5 years†	s	Fish, birds, mammals	Star-Oddi, www.star-oddi.com
<i>Microbial</i>					
Environmental Sample Processor (ESP)	V	3-4 W	min-hours	M, D, S	C. Scholin, MBARI scholin@mbari.org
Aqua Monitor smart water sampler	I	2-740 mA @9-15 volts		M, A, T	WS EnviroTech www.wsenvirotech.com

*Lifetime of tag depending on sampling interval †Battery life based on sampling interval > 15 min apart ** Small and large models

lence, particularly for zooplankton (Griffiths et al., 2002). Continuing efforts in sensor validation, model development, and analytical methodology are urgently needed. A number of other issues remain including noise effects, separating backscattering due to turbulent microstructure from that of biological origin, a better understanding of how animal density, size, and shape influence target strength variability, and improved knowledge of model parameters, such as sound-speed and density contrasts.

Most acoustic systems are mounted on the hulls of ships, towed, or used in profile mode alongside ships, but a few have transitioned to other platforms. A SIMRAD EK500 echosounder (Table 6) was successfully deployed in the AUV Autosub-2 in the Southern Ocean (Brierley et al., 2002). Fernandes et al. (2003) review the use of mobile platforms for fisheries acoustics and note that advances in power-source technology are needed to extend operational ranges. Limitations due to the size/weight of transducer ceramics, especially at low frequencies, may soon be offset by advances in

broadband and multibeam sonar. The Tracor Acoustic Profiling System (TAPS) is an example of a multi-frequency echosounder, which is being used on moorings in upward, downward, or horizontal mode. It can operate in combination with real-time telemetry for remote control of some parameters for durations up to 6 months depending on battery support (Holliday et al., 2003). The Bioacoustic Sensing Platform and Relay (BIOSPAR, Wiebe et al., 1995) was deployed for short periods (days - weeks) on a mooring and a free drifter using two downward-looking dual-beam transducers. Battery design included photovoltaic solar collectors that could provide power to the system for over a month even without additional sunlight. Several other laboratories are currently developing systems for use on moorings that could be available for observatories in a few years. One such model is the FishTV, a three-dimensional acoustic imaging system, which obtains acoustic and optical images simultaneously for information on target species and behavior (Jaffe et al., 1998; J. Jaffe, personal communication).

Acoustic Doppler Current Profilers (ADCP), typically used to profile water velocity on ships and moorings, also have been used to assess zooplankton backscatter. Until recently, however, ADCPs were not rigorously calibrated and therefore the volume backscattering data could not be converted to abundance or biomass. New methods may enable more quantitative results making these a lower cost alternative for some programs. In addition, ADCPs can provide information on zooplankton vertical migration rates (Heywood, 1996) and swimming behavior within aggregations (e.g., Zhou and Dorland, in press).

A different use of active acoustics (Table 6) employs marine mammals and fishes as mobile platforms using ultrasonic telemetry (e.g., Voegeli et al., 2001). Archival tags attached to the animals gather environmental and spatial information and may monitor physiological parameters, which are transmitted to fixed benthic recorders, buoys, or satellite receivers. Passive acoustic recording packages also are deployed on moorings or as sonobuoys to estimate population abun-

dances from calling patterns of marine mammals and fishes for up to a year (McDonald et al., 1995).

Microplankton sensors and sampling systems

Microbial populations are particularly difficult to assess in marine systems as direct visualization and culturing of organisms does not distinguish the entire spectrum of species present in the environment. Many different groups are working on techniques for automated species-level identification using molecular probes. Genomic sensors hold tremendous promise, but are in an early stage of development. One such autonomous genosensor that is currently being tested uses a microfluidics system and nucleic acid sequenced based amplification technology to detect a range of organisms *in situ*, such as the red tide species, *Karenia brevis*, *Synechococcus*, and human enteroviruses (Smith et al., 2004).

Sampling systems, which can perform a variety of activities such as sample collection, pretreatments, dilution, concentration, filtration, extraction, and bubble concentration are urgently needed for *in situ* applications. The Environmental Sample Processor (ESP) is being developed to detect multiple microorganisms using molecular probe technology, as well as perform sample collection, concentration, different analyses, and sample archival (Scholin et al., 1998). The ESP is in a period of transition from prototype and short-term deployments to development and application of a "second generation" unit that will be wet-tested later this year. The current design is aimed for mooring deployments at depths up to 4,000 m, but could potentially be used on an AUV or a drifter in future years (C. Scholin, personal communication). Another laboratory working on innovative ways to accomplish automated sample treatments has a prototype system that can characterize particle density, size, and chemical composition in a particle suspension, then concentrate or dilute the sample as needed (L. García-Rubio, personal communication). This system has been demonstrated for *in situ* identification and clas-

sification of pathogens (Alupoaei et al., 2004) and other microorganisms, such as *Cryptosporidium* and *Giardia* (Callahan et al., 2003). A number of challenges, however, must be overcome before a sophisticated sampling system will be suitable for remote use in the oceans. One of the few commercially available samplers is the Aqua Monitor (WS EnviroTech). This is a relatively simple plankton collection system (50 discrete/100 – 1000 ml samples) that has been successfully deployed for a year collecting weekly samples and can be used on a variety of platforms.

Sensors and Samplers for Studying Seafloor Hydrothermal Systems and Cold Seeps

Over the past decade, a number of sensors and samplers have been developed to investigate the spatial and temporal variability of fluids venting at high temperature seafloor vent sites and at cold seeps. While many of the issues related to sensor development in these environments are similar to those for other ocean environments (e.g., calibration, biofouling, instrument drift), others are specific to the harsh chemical (e.g., low pH, high sulfide, high metal, volatile-rich) and thermal (temperatures >400°C) conditions. An added complication when transitioning the sensors/samplers from *in situ* to long-term use is the dynamic nature of the environments. This includes biofouling (specifically colonization of instruments by organisms as large as mm to cm in size), perturbation of the environment (particularly at cold seeps) in low temperature areas, corrosion, deposition of minerals, and possible incorporation of the instrument into the growing vent deposit at high temperature locations. The need for *in situ* and long-term measurements within these environments has been recognized (see Seyfried et al., 2001; Gallager and Whelan, 2004) and considerable progress is being made. The current status of sensors and samplers is shown in Table 7.

High temperature vents

For the high temperature environment (in acidic, >300° C fluids), there are several sensors now capable of making *in situ* measurements (e.g., H₂, H₂S, pH, resistivity (as a proxy for Cl)). Of these the resistivity sensors have been successfully deployed for greater than one month within hot vent orifices (Lilley et al., 2000). The other sensors have worked *in situ* and are currently being modified for long-term deployment at high temperatures (Ding et al., 2001, in prep; M. Lilley, personal communication). Modifications are also underway for long-term use of some of these sensors in lower temperature areas (e.g., the H₂/H₂S sensor has worked successfully for 13 days within a *Riftia* colony (W. Seyfried, personal communication).

There are also a number of "incubator" type instruments for use at high temperature vents, that are constructed of titanium and use Ti sheathed thermocouples or Resistive Temperature Detectors (RTD). These instruments are capable of temperature measurements *in situ* within sampling chambers or within actively forming deposits, and allow recovery of materials (minerals and associated microorganisms) from areas of known temperature history (e.g., Reysenbach et al., 2000; Tivey et al., 2003; E. Dunn, personal communication; D. Kelley personal communication).

A few instruments are being developed for use at high temperature vents that are non-invasive, e.g., ALISS (measures ambient light emission) and DORISS (laser Raman spectrometer). Laser induced breakdown spectroscopy (LIBS) is also a possible technique that is being investigated for non-invasively (or semi-invasively) measuring elemental concentrations of some elements within high temperature vent fluids (A. Chave, S.M. Angel, personal communication).

Another technique that has been used successfully to examine long-term variability within moderate to high temperature fluids, involves intermittent or continuous sampling of hot fluids into the cooler ambient temperature environment, with addition of acid during sampling, and storage in cooler regions on the seafloor (Wheat et al., 2000; Kadko et al., 2000). The McLane Remote

TABLE 7

Current status of vent and seep sensors/samplers. Development stages, power [watts(W), amps(A), volts(V)] and deployment designations as in Table 1, except Ia is commercially available but not modified for long-term deployment and IVa is operational *in situ* but not modified for long-term deployment. Sampling time is sensor's processing time per sample in seconds (s), minutes (min), or hours

Sensor	Development stage	Power	Sampling time	Deployment capability/ T°C range	Source/contact
Temperature (RTD)	I		s	R/0-400°C	Onset computer; DeepSea Power and Light
pH (YSZ ceramic, Ir/IrO ₂ , Ti/TiO ₂)	III	10 ⁻¹ W	s	R/10-400°C	W. Seyfried, K. Ding *
Sulfide/H ₂ S	III	10 ⁻¹ W	s	R/10-400°C	W. Seyfried, K. Ding *
H ₂ (Au)(Pt)	III	10 ⁻¹ W		R/10-400°C	W. Seyfried, K. Ding *
H ₂ (Au ₃ OPd ₅ O)	III		s-hours	R/20-400°C	M. Lilley, UWashingon lilley@u.washington.edu
Resistivity (proxy for Cl)	II		s	R/lowT-400+°C	M. Lilley, UWashingon lilley@u.washington.edu
Temperature arrays Ti sheathed thermocouples	II	10 ⁻² W	s	R/0-400+°C	A. Bradley/M.K. Tivey, WHOI mktivey@whoi.edu
Mineral microcosm temperature array	IV	9 v up to 1 year	s-hours	R/0-400+°C	E. Dunn, Arizona State University eedunn@asu.edu
Microbial incubator separate chambers/wafers	II		s-hours	R/0-360°C	D. Kelley, UWashingon kelly@ocean.washington.edu
Vent cap <i>in situ</i> growth chamber	II		s	R/0->150°C	A-L. Reysenbach*
ALISS (Ambient Light Imaging Spectral System)	V		s-min	R	A. Chave/S. White *
DORISS (Deep Ocean Raman In Situ Spectrometer)	IVa	420 W	s-min	R/0-350°C	P. Brewer/S. White *
Gamma detector	II		s	R/0-100°C	D. Kadko UMiami, dkadko@rsmas.miami.edu
InSpectr-MIMS mass spectrometer	Ia	<100 W	s-min	M,T,A,P0-200°C	G. Eaton, Applied Microsystems, Ltd. greg@aml.bc.ca R.T. Short/D. Fries, USF*tshort@marine.usf.edu G. McMurtry*
Mass SURFER – rotating field mass spectrometer	V	8 W contin.	min	All/0-400°C	G. McMurtry, UHawaii garym@soest.hawaii.edu
DeepQuad MIMS – quadropole mass spectrometer	VI	100 W peak; <1 W standby	min	All/0-100+°C	G. McMurtry, UHawaii garym@soest.hawaii.edu
NEREUS – mass spectrometer	V			M,T,A /0-35°C	R. Camilli, WHOI rcamilli@whoi.edu
Gemini – mass spectrometer(CH ₂)	VI	30 W	s	M,T,A /0-35°C	R. Camilli, WHOI rcamilli@whoi.edu
Redox potential (Eh)	III		s	R, A/0 to 20°C	K. Nakamura*
pH (glass electrode)	IVa		15 s	R/0-120°C	N. Le Bris *
Sulfide/Fe/NO ₃ (Alchemist)	IVa		15 s	R/0-30°C	N. Le Bris *
METS underwater methane sensor	I	160 mA	s-min	R,M,P,T/0-20°C	Capsum; www.asd-sensors.com/capsum.htm
Electrochemical analyzer (O ₂ , H ₂ S, FeS, Fe(II), Mn(II), Zn(II), S ₂ O ₃ ²⁻ , S _x ²⁻)	III		s	R,S,P,M/1.5-100°C	G. Luther, UDelaware with Analytical Instrument Systems, Inc. ais@aishome.com luther@udel.edu
Scanner (H ₂ S, Si, NO ₃ , Mn, Fe)	II	24 W	~30 s	R, P/0 to 20°C	K. Johnson, MBARI johnson@mbari.org

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TABLE 7
continued

Sensor	Development stage	Power	Sampling time	Deployment capability/ T°C range	Source/contact
ZAPS (Mn, UV Fluorescence)					G. Klinkhammer, OSUgklinkhammer@coas.oregonstate.edu
MCA-2000 (Si, H ₂ S)					T. Gamo, UTokyo
GAMOS (Mn)					T. Gamo, UTokyo
SUAVE (Mn, Fe, H ₂ S, pH)					G. Massoth*
AIS (H ₂ S)					J. Radford-Knoery*
ISUS (HS ⁻ , Br ⁻ , NO ₃ ⁻ , DOC)	I	12 W	0.5 s	All/ 0 to -20°C to >200°C (but limited HS ⁻ as pH drops)	NO ₃ ⁻ ; Satlantic/ WETSAT, www.satlantic.com, Other: K. Johnson, MBARI, johnson@mbari.org
OSMO Analyzer (Fe; other possible)	II	100 uW contin.	30 min	M or benthic deployment only; 0 to 20°	H. Jannasch/T. Chapin/K. Johnson, MBARI, jaha@mbari.org
OSMOSampler	II			R/0->30°C	H. Jannasch/C.G. Wheat*
McLane Remote Access Sampler	II				McLane Research Laboratories, Inc., www.mclanelabs.com
McLane Water Transfer System	II				McLane Research Laboratories, Inc., www.mclanelabs.com
Medusa -flow rate, transmissometry, T, gas tight sampler	I	<<1 W	s	R/0-500°C	Earth-ocean systems Ltd /or A. Schultz, OSU adam@coas.oregonstate.edu

* Brewer et al. (2004), Chapin et al. (2002), Ding and Seyfried, Jr. (1996a, b), Ding et al. (2001, in prep), Gamo et al. (1994), Jannasch et al. (1994), Johnson and Coletti (2002), Johnson et al. (1986), Klinkhammer (1994), Le Bris et al. (2000, 2001), Massoth and Milburn (1997), McMurtry and Smith (2001), Nakamura et al. (2000), Radford-Knoery et al. (1997), Reysenbach et al. (2000), Short et al. (1999), Luther et al. (1999), Fries et al. (2004), Wheat et al. (2000), White et al. (2002).

Access Sampler is capable of collecting 48 samples at predetermined intervals, while the OsmoSampler can make collections continuously for days to months. OsmoSamplers have been field tested on short term (days) to long term (years) deployments in a variety of environments, including boreholes, low temperature vents, high temperature vents, sediment (pore water profiles - harpoon style), moorings, and in estuarine settings (Jannasch et al. 2003, in press; Wheat et al., 2000, 2003). These samples allow study of the temporal variability of a number of elements, including K, Ca, SO₄²⁻, Mn, Ba, Fe, Cl, Mg, Si.

Low temperature vents and cold seeps

A greater diversity of sensors and long-term samplers is currently available for use in the lower temperature environments at vent sites and cold seeps. These include sensors that can measure pH using an electrode, and ES, HS⁻, Fe, nitrate, nitrite, O₂, Fe, S, Mn, Zn, Si, CH₄, Br⁻, and DOC at temperatures from ambient to 20°C, and

in some cases to 100°C, using a variety of techniques including conventional flow analysis, flow injection analysis, colorimetry, chemiluminescence, voltametric detection, and UV detection (see Table 7 and references therein). Mass spectrometers for use *in situ* also are being developed (Short et al., 1999, 2001; McMurtry and Smith, 2001; Fries et al., 2004). Although their power requirements are relatively high, mass spectrometers provide panoramic measurement capabilities and, perhaps at times, superior yields of "information per Watt" than single analyte sensors. One design, based on development work at the University of South Florida, is commercially available from Applied Microsystems, Ltd. (Table 7).

Long-term samplers that have been used in low temperature environments include continuous OsmoSamplers (that collect ~1 to 50 ml/week), the McLane Remote Access Sampler that collects up to 48-100 to 500 ml samples at pre-timed intervals, the McLane Water Transfer System that collects particulates by filtering

up to 24 samples at pre-timed intervals, and the Medusa system that measures temperature, flow rate, and transmissometry, and collects 6-120 ml Ti gas tight samples at pre-timed intervals (Table 7 and references therein).

Needs

Several key areas require focused attention for low temperature environments, including the development of biological sensors and samplers, such as the Environmental Sample Processor (see above and Table 6), and transition of existing sensors and samplers for longer-term deployments to allow monitoring. A list of desired sensors for measuring various parameters, and the levels of desired range and sensitivity, is given in Table 8 (Gallager and Whelan, 2004). In high temperature environments, continued development of existing sensors, transition of these sensors for long-term deployment, and development of sensors that measure other parameters (e.g., metals, CO₂, CH₄, organic species) are needed. *In situ* sensors are necessary because fluid species change and metals

precipitate when removed from the pressure/temperature conditions within vents. High-frequency sampling is required to investigate both short and long-term variability in local and sub-surface processes. Other issues complicate the transition from short to long-term *in situ* observation, such as the harsh pH and temperature conditions of the fluids and the dynamic nature of the vent (e.g., the vent opening can migrate over time). Solutions to this problem include building sensors that are planned for incorporation into a growing vent structure, or building sensors with time-limited exposure to the hot fluid. For the latter case, a robotic device could be used to locate the vent orifice (e.g., using an infrared sensor), allowing the sensor to be placed within the flow and then removed (Gallager and Whelan, 2004).

Integrated Sensing Systems

Integration of sensors into functional instruments, which address specific scientific questions, is seen as an essential step toward providing a multi-disciplinary and a multi-scale context to the measurements made by observatories. Examples of such systems include the Autonomous Vertically Profiling Plankton Observatory (AVPPO), which is currently deployed at the Martha's Vineyard Coastal Observatory (MVCO, <http://4dgeo.whoi.edu/vpr>), the Gulf of Maine

Ocean Observing System (GoMOOS; www.gomoos.org/), the Coastal Ocean Observation Lab (COOL; <http://marine.rutgers.edu/cool/LEO/LEO15.html>), the Physical Oceanographic Real-Time System (PORTS; <http://ompl.marine.usf.edu/PORTS/index.html>), and the Coastal Ocean Monitoring and Prediction System (COMPS; <http://comps.marine.usf.edu/>). The AVPPO, which is the most biologically focused, has been operational for about three years semi-continuously and was designed for use in coastal regions up to 100 m depth with currents up to ca. 4 kts. The AVPPO is driven by an underwater winch coupled with an electromechanical system for sampling the water column from the air-water interface to the seafloor. It provides a real-time data stream from a variety of biological, bio-optical, hydrographic and physical sensor systems. These data are synthesized and visualized on a web-based display and data archive. The AVPPO profiling package carries the following sensors: a Seascan, a VPR to quantify large phytoplankton, micro and meso-zooplankton, and marine snow; a Wet Labs transmissometer, chlorophyll fluorometer, and CDOM fluorometer; a PAR downwelling light sensor, Sea Bird conductivity and temperature sensors; a Wet Labs ac-9 absorption spectrometer; roll, pitch, yaw sensors; a Satlantic 7 channel OCR200 radiance sensor; a Satlantic 7 channel

OCI200 irradiance sensor; an Aanderaa optode oxygen sensor; an Imagenics 881a sector scanning sonar for observing fish; a WHOI-built bioluminescence sensor (Solid State Bathy Photometer), and a MAV-3 time of flight Doppler Velocimeter (NOBSKA Associates). An uplooking 300 KHz ADCP is mounted on the winch frame and the addition of a Satlantic nitrate sensor is planned. Currently, the observatory is serviced about once every 4 to 6 weeks using a small boat, at which time optical windows and sensors are cleaned and the ac-9 is calibrated. Biofouling within the pumped water lines for the CTD, ac-9, fluorometers, and oxygen optode is eliminated by using copper tubing where logistically possible. Copper shutters will be installed on the optical windows this year.

New Directions

Numerous emerging technologies and analytical techniques show great promise for marine applications. In the following section we highlight a few of these new approaches that would benefit from accelerated development for use by observatories. The Laser Induced Breakdown Spectroscopy (LIBS, www.arl.army.mil/wmrd/LIBS), mentioned above, utilizes a pulsed laser to create a microplasma on the material of interest then a spectrophotometer captures the transient light to identify and quantify elements. It is an inexpensive analytical technique that can be used on solid, liquid or gaseous phases. Its sensitivity to all elements remains to be tested, but it appears to be typically between 0.1 - 200 parts per million and no sample preparation is needed, making it a quick and easily adaptable technology for automated monitoring or robotic applications. Double-pulsed nanosecond LIBS allows detection of elemental composition in water (Angel et al., 2001). The Army Research Lab and Ocean Optics Inc. are currently collaborating on developing sensors for this technology. Potential uses include the simultaneous measurement of trace metals, nutrients, and dissolved gases, and measurement of chemical odor plumes from marine animals.

TABLE 8

Vents and seeps sensor wish list*

Parameter/ Species	Optimal Range	Sensitivity
Temperature (°C)	0-400(°C) 0-3(°C)	±0.5 units ±0.001 units
pH (general)	2-10	±0.1 units
pH (CO ₂)	5-8	±0.001 units
H ₂ S, H ₂ , CH ₄	1-10 nmol/10-100 mmol	2-5%
CO ₂	2-100 mmol	2-5%
Cl ⁻	30-1000 mmol	2-5%
Fe ²⁺ , Fe ³⁺ , Mn	1 nmol - 25 mmol	2-5%
O ₂	0-250 μmol	2-5%
NO ₃ ⁻	0-40 μmol	2-5%
NH ₄ ⁺	10 nmol - 10 mmol	2-5%
NO ₂ ⁻ , N ₂ O	0-4 μmol	2-5%
SO ₄ ²⁻	1nmol - 1 mmol	2-5%
Organics, C ₁ -C ₅	Not presently established	2-10%
Metals, Cu, Zn, As, Pb, Co	Not presently established	2-10%

*from Gallager and Whelan (2004)

Raman spectroscopy is another technique used to identify and characterize the chemistry and structure of materials in a non-contacting, non-destructive manner. A laser light is shone on a sample; light is scattered, a tiny fraction of which is shifted in frequency as atoms in the material vibrate. Analysis of the frequency shifts (spectrum) of light reveals the characteristic vibration frequencies of the atoms and thus the chemical composition and structure of the sample. Particles as small as 1 μm can be identified. Both infrared and Raman vibrational spectroscopy can be combined to provide greater analytical power. Raman spectroscopy may be used to characterize macromolecular structure of organic compounds such as amino acids, lipids and proteins (Angel et al., 1999). Brewer et al. (2004) recently modified and successfully tested a laser Raman Spectrophotometer (DORISS) on gas, liquid, and solid samples in the deep ocean (3,600 m) using an ROV. Other potential uses include the *in situ* identification of sea floor minerals and determining the chemical composition of pore water and vent plumes. Currently both LIBS and Raman techniques, coupled with *in situ* imaging using the VPR, are being developed for plankton and particulate characterization in the ocean (C. Davis, S. Angel, S. Gallager, personal communication). In general, however, these instruments still have significant challenges, requiring miniaturization and lower power consumption for general use in the ocean (Gallager and Whelan, 2004).

Improved spectral deconvolution techniques and model development/interpretation are being used to extract a greater amount of information from multiwavelength ultraviolet/visible transmission spectroscopy (Callahan et al., 2003; Alupoai et al., 2004). These new analytical techniques allow investigators to differentiate among strains of microorganisms (Fig. 3) and determine their concentration, size, mass, chemical composition, and amount of nucleotides and other chromophores within cells. Initial work has focused on enteric bacteria and protozoans, however, such techniques could be readily transitioned to marine communities since the spectrophotometer instrumentation required

is already miniaturized and adapted for use in marine environments (see section on chemical sensing). Multi-frequency and broadband acoustic data are likely amenable to this analytical approach as well.

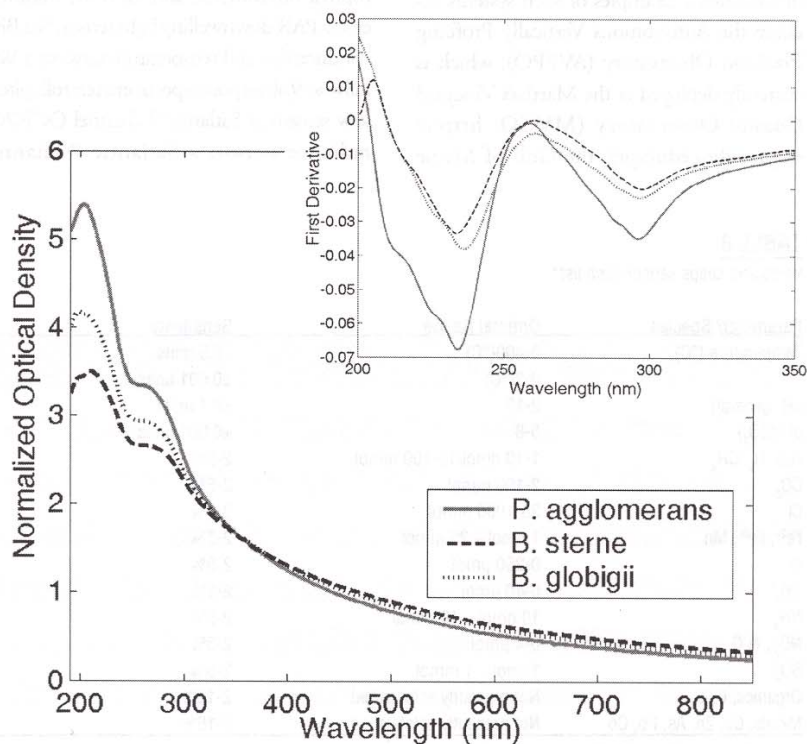
Major Issues and Recommendations

A number of workshop reports describe in depth the major issues for sensor development and community recommendations (e.g., Daly, 2000; Seyfried et al., 2000; Gallager and Whelan, 2004). Here, we list some of the issues and briefly summarize the recommendations from those workshops. Common themes included the need to accelerate sensor development given the long time-frames (up to 10 years) to bring sensors to operational status, and the current funding process. We must identify and encourage

methods to transition prototype sensors to mass production (possibly through science-technology partnerships and through Small Business Initiative Research programs). The long-term reliability of sensors (stability, accuracy, precision, and internal self-calibration) is essential. Rigorous field validation (confidence in data interpretation) is still needed for most sensors currently in use. The Alliance for Coastal Technologies (ACT) plans to verify performance specifications of essential sensors, starting with some commercially available dissolved oxygen sensors during summer 2004. In addition, standardization is needed for interfacing sensors and sensing systems, for power and communication (modularity, Plug-N-Play issues), and to ensure that future additions of rapidly evolving technologies are compatible. Coherence in sampling volume of multiple sensors and optimized sampling rates are a concern, and

FIGURE 3

Typical normalized optical density spectra measured from suspensions of *Pantoea agglomerans* (a surrogate for *Y. pestis*), *Bacillus anthracis Sterne* (which is the same organism as anthrax with the lethal factors genetically removed), and *Bacillus globigii*, a commonly found organism in the same genus as anthrax. All samples analyzed 6 hours after each culture was started. The inset plot is the first derivative of the optical density spectra. (Plot courtesy of L. Garcia -Rubio, USF).



additional efforts are needed in miniaturization of electronics and power packages. Platforms (i.e., profiling moorings, AUVs, gliders, etc.) either require major development (e.g., profiling moorings) or must continue to be improved. Biofouling and corrosion also remain a serious problem in near-surface, benthic, and vent environments. A summary of biofouling issues and current prevention technologies are described in an ACT Workshop Report (2003).

The selection process for sensor development must depend on the science questions, just as the level of accuracy and precision depends on the underlying physical, chemical, and biological phenomenon and associated time and space scales. Recommendations to address the issues listed above include: (1) set up a coordinating committee to advise agencies, sensor developers, and user groups on all issues (inter-sensor comparisons, interface and power hardware and software standards, establish international calibration protocols, performance testing and review), (2) use NASA's rigorous sensor development program as a model for prioritizing development of core and community sensors, (3) establish a failure reporting system like the National Transportation Safety Board, and (4) establish a dedicated instrumentation facility to maintain and calibrate sensors and to support sensor use. The latter would be an important resource for training users, so that a greater number of investigators would have access to sensors and sensor data, encouraging a broader use of sensors. In addition, a workforce must be trained (support personnel, data managers, and repair) following the example of Rutgers' new Masters in Operational Oceanography Program. It also was recommended that "smart" sensors, sensing systems, or smart nodes should be developed that can detect natural scales of variability and respond in some pre-programmed way to collect data more intensively during or near the phenomenon of interest. Sensing systems that share common resources (light, detectors, pumps) are needed to collect multivariate environmental data to better interpret phenomena. Another recommendation was to establish more test-bed facilities, especially

for high-temperature sensors, and establish an information exchange network for developers and users, which would highlight new funding initiatives and ship-time/deployment opportunities for sensor testing.

Summary

Despite recent advances, few chemical or biological sensors are ready for long-term (~ 1 year) deployment on observatories, even many of those classified as currently operational and commercially available (Development Stage I). Response times of sensors, dynamic range (from eutrophic bay to the open ocean; from the surface to the ocean bottom), sensitivity and detection levels, stability (drift), internal calibrations, storage of reagents, size, power requirements, and biofouling limit the accuracy of results and/or duration of deployment. Many promising sensors have stated capabilities that are poorly documented, making it difficult to evaluate them. The availability of biological sensors, in particular, is lacking, especially for long deployments. Concerted effort and resources need to be devoted to the continued development of sensors, sensing systems, and sampling systems in order to achieve the full potential of ocean observatories.

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