

DEVELOPING CHEMICAL SENSORS TO OBSERVE THE HEALTH OF THE GLOBAL OCEAN

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ABSTRACT

Robotic networks of platforms carrying physical, chemical, and biological sensors that can monitor basic metabolic processes are required to observe ocean health. The sensors must operate for the 5 to 10 year period between research vessel visits with no direct human intervention and little or no chance for sensor recalibration. The sensors and the platforms that carry them must operate from the surface to depths of several kilometers. Here I describe work done by marine scientists to develop integrated networks of chemical sensors with these properties. Much of the focus will be on chemical sensors that can operate for years at a time without laboratory recalibration.

KEYWORDS

Chemical sensors, sensor networks, environmental monitoring.

INTRODUCTION

The paper provides a brief review of a global scale sensor network that is designed to assess the health of the world ocean. The oceans cover 71% of the earth's surface and they provide significant services to society [1]. The oceans have absorbed more than 90% of the excess heat in the climate system that results primarily from burning fossil fuel carbon dioxide, while only about 1% of the excess energy appears as atmospheric warming [2]. Nearly half (40 to 50%) of the anthropogenic carbon dioxide emissions to the atmosphere have subsequently entered the ocean through air-sea gas exchange, mitigating a significant part of potential energy increase to the climate system [3]. These services are at some risk. Warming of the ocean is projected to alter ocean circulation [4], reduce the extent of sea ice, and alter nutrient supply to surface waters [2]. The pH of surface waters has dropped about 0.1 in the past 100 years as the ocean has absorbed anthropogenic CO₂ [2]. This has increased proton concentration by 25%, which results in demonstrable impacts on ecosystem processes [5].

Monitoring the state of ocean health and its services has proven to be a challenge. Historically, sampling of the ocean required a research ship to carry scientists and their laboratory equipment to remote sites where a variety of basic chemical and biological analyses were performed. The vast area of the ocean resulted in most areas being sampled only once per decade or less, with sampling occurring mainly in summer.

Observing the health of the ocean requires a completely autonomous system of robotic platforms that are equipped with chemical and biological sensors [6] [7]. The platforms and sensors must be capable of operating for the 5 to 10 year intervals between visits by ships. The chemical and biological observations must be sufficiently

stable to allow the detection of changing processes in the ocean without returning false signals.

An ocean health network requires two primary components: a robotic platform and a suite of physical, chemical, and biological sensors. Here I describe a system that integrates sensors for temperature, salinity, pressure, oxygen, nitrate, pH, chlorophyll, suspended particles, and downwelling irradiance with profiling floats. The system is capable of operating throughout the world ocean, including regions with seasonal ice cover.

PROFILING FLOATS

Profiling floats are free drifting, battery powered platforms that cycle between the surface and depths near two kilometers (2000 dbar pressure) [8]. The electronics and batteries are contained in a cylindrical pressure housing made of aluminum or carbon fiber (Fig. 1). A typical vertical profile cycle begins with the float descending from the surface to 1000 m where it parks for 5 to 10 days. Vertical position in the water is controlled by altering the float density with a buoyancy engine that receives feedback from a pressure transducer (Fig. 1). At the end of the park period, the float then descends to near 2000 m before it rises to the surface. Physical, chemical and biological measurements are collected during the ascent at specified depth intervals. The sensors will make from 60 to 1000 measurements, depending on sensor power demand and scientific requirements. Once at the surface, float position is determined by the Global Positioning System (GPS) and the observed data are then transmitted via the Iridium communication system to shore-based servers. The data are immediately made available through publicly accessible databases on the Internet, following an internationally agreed data policy. The float then returns to its 1000 m parking depth to repeat the cycle 200 to 300 times.

Floats ascend and descend by altering their density [8]. This is done by pumping oil into or out of an external bladder, which changes the overall volume of the platform (Fig. 1). Seawater density is near 1022 kg m⁻³ at the surface and density increases to values near 1028 kg m⁻³ at 2000 m depth due to seawater compressibility, higher salinity, and lower temperatures. Ignoring the compressibility of the float pressure hull, a float can profile between the surface and 2000 m if it can change its density by $1022/1028 = 0.9941$. For a 30 liter float, that is equivalent to a volume change of 180 ml. The 30 L floats used in our research have a total volume change capability of 260 ml, which provides a very small margin of error in buoyancy control. If the float is too heavy by a few 100 g it can't rise and too light it won't sink. Rise rates are typically 6 m min⁻¹ and 5 to 6 hours are needed to profile from 2 km depth to the surface.

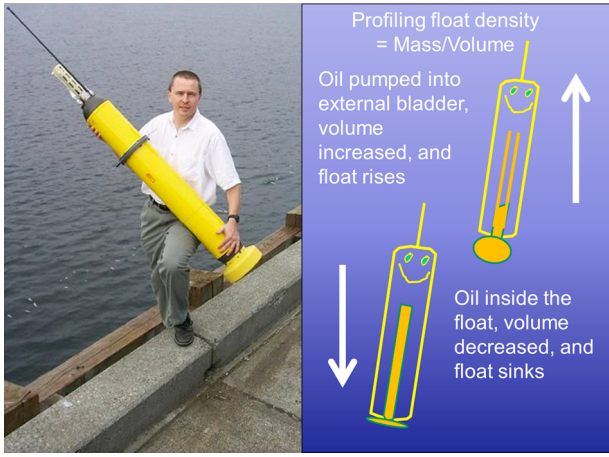


Figure 1: (left) A Teledyne Webb Research APEX (Autonomous Profiling Explorer) float. (right) A schematic of the operation of the float buoyancy engine.

The floats that we use are launched with 3.9 MJoules of energy in the form of lithium primary batteries. About 40% of that energy is available to operate sensors. The remaining energy is used for the buoyancy engine (25%), Iridium communications (15%), the float microcontroller (15%), and battery self-discharge (5%) over a multi-year mission. This energy is used to make about 250 vertical profiles, with about 15 kJoules available for each profile, including 6 kJoules for the sensors. With a 10 day period between vertical cycles, the floats have a lifetime near 7 years before the batteries expire and the float is lost.

Nearly 4000 floats are sustained in the ocean by the Argo program (<http://www.argo.ucsd.edu>), an international collaboration of some 30 nations (Fig. 2). The core mission of Argo is to measure the heat and fresh water content of the upper 2 km of the ocean [9]. All floats carry sensors for temperature, salinity, and pressure to support this core mission. The array is slowly being expanded to include six core chemical and biological sensors for dissolved oxygen, nitrate, pH, chlorophyll, suspended particles, and downwelling irradiance [7]. The extended program, known as Biogeochemical-Argo (<http://biogeochemical-argo.org>), addresses six key scientific topics:

- ocean carbon uptake,
- net ocean primary production,
- ocean carbon export to the deep-sea,
- ocean oxygen balance and impacts on nitrate cycling,
- ocean acidification,
- phytoplankton biomass and bloom timing.

In February, 2017, 297 floats (7.4% of the Argo array) carried one or more of these biogeochemical sensors. The target density for biogeochemical floats carrying all 6 core biogeochemical sensors is 1000 spread over the world ocean.

SENSORS

The physical and chemical sensors on the profiling float must operate as a network in order to achieve the desired performance. In some cases, the sensor has a pressure or temperature coefficient that must be corrected.

In some cases the thermodynamics of the interaction of a chemical with the sensor is temperature, pressure, or salinity dependent and must be compensated. The global observing system then becomes a network of networks. For example, the nitrate sensor requires temperature, salinity, and pressure values in order to compute an accurate nitrate concentration [10][11]. In the following, I provide a basic description of the sensors and their interactions.

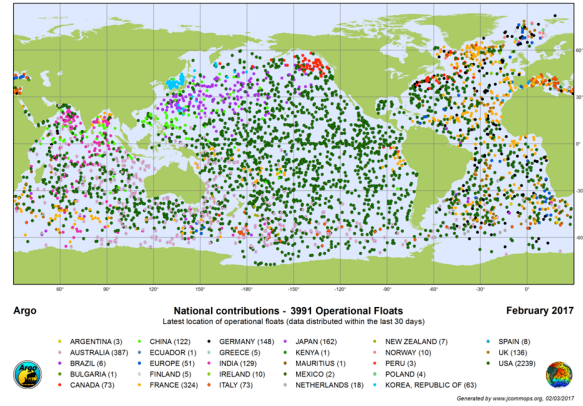


Figure 2: The global distribution of profiling floats in the international Argo program. Dots are colored by nation responsible for float deployment. Figure courtesy of jcommops.org.

Physical Sensors

The core physical properties monitored by profiling floats are temperature, salinity (g kg^{-1}) on the Practical Salinity Scale, and depth. These physical variables are measured with a Conductivity/Temperature/Depth (CTD) sensor [8][12]. These sensors must maintain very high precision, accuracy, and stability in order to meet the core Argo mission (Table 1).

Table 1: Required CTD accuracy and stability. One m depth in seawater is approximately one dbar pressure. Mean ocean salinity is near 35 g kg^{-1} .

Parameter	Accuracy	Stability
Temperature	$0.005 \text{ }^{\circ}\text{C}$	$0.0002 \text{ }^{\circ}\text{C y}^{-1}$
Salinity (PSS)	0.01	0.001 PSS y^{-1}
Conductivity	0.001 S m^{-1}	$0.0001 \text{ S m}^{-1} \text{ y}^{-1}$
Pressure	2.5 dbar	0.8 dbar y^{-1}

Temperature and pressure are measured directly with a fast-response thermistor and a temperature compensated strain gauge. Salinity is derived from conductivity measurements with a three-electrode cell, as well as the temperature and pressure observations. Each of the sensors needed to determine salinity has a different response time. To achieve the desired accuracy specifications for salinity in the current generation of CTDs, seawater is pumped past the temperature sensor and through the conductivity cell at a uniform rate during the vertical profile. This allows a mathematical model that incorporates the various sensor response times and known flow rates to derive salinity with the required accuracy [12].

The current generation of CTD found on profiling floats uses about 2.9 kJoules per profile, or 48% of the 6 kJoules available for sensors. The energy is consumed primarily by the CTD pump. The Argo community is exploring alternative CTD sensors based on inductively coupled salinity sensors, which would not require pumping, and, thus, consume less energy.

Chemical Sensors

The core chemical parameters observed by Biogeochemical-Argo floats are dissolved oxygen, nitrate, and pH [7]. The sensors must be capable of generating climate quality data, which is defined as a “time series of measurements of sufficient length, consistency and continuity to determine climate variability and change” [13]. The performance specifications that result are extremely demanding for a sensor that may operate for nearly a decade without laboratory recalibration (Table 2). Fifteen years ago, there were no chemical sensors that met these requirements. Commercial solutions are now available for oxygen, but require calibration improvements. Our approach to addressing this problem for nitrate and pH has been to find sensor prototypes that are relatively high on the Technology Readiness Level scale, but have not matured due to limitations in technology at the time they were developed. We then apply modern technology solutions to the sensor.

Table 2: Required chemical sensor accuracy and stability.

Parameter	Accuracy	Stability
Oxygen	3 $\mu\text{mol kg}^{-1}$	1 $\mu\text{mol kg}^{-1} \text{y}^{-1}$
Nitrate	1 $\mu\text{mol kg}^{-1}$	0.5 $\mu\text{mol kg}^{-1} \text{y}^{-1}$
pH	0.005	0.003 y^{-1}

Oxygen

The concentration of dissolved oxygen is a fundamental tracer of metabolic processes, including primary production and respiration. It can be completely depleted in some ocean regions, leading to massive shifts in ecosystem structure. The earliest oxygen sensors that were deployed on floats were highly engineered Clark-type amperometric electrodes [14]. While these systems were used to address very significant topics related to ocean metabolism [14][15], they did not have sufficient stability or reliability for use in climate quality research.

Oxygen electrodes have since been replaced by several generations of lifetime-based optodes [16][17]. These sensors utilize molecular oxygens ability to quench the fluorescence of certain luminophores. The most widely used sensors incorporate a platinum porphyrin compound embedded in a gas-permeable foil. Oxygen concentration is determined by measuring the phase shift in the fluoresced red light relative to a modulated blue light excitation signal. The fluorescence is quenched as energy from the blue-light-excited lumiphore is transferred to oxygen when oxygen molecules collide with the lumiphore inside the foil. This shortens the fluorescence lifetime and reduces the phase angle difference between the excitation and fluorescent emission signals [17]. Key to the long-term stability of these sensors is a measurement based on lifetime rather than intensity of the

fluorescence. The lifetime signal is relatively immune to loss of the lumiphore through photobleaching or other processes. The optode consumes only 0.1 kJoule/profile.

Lifetime-based optodes still drift fairly rapidly (several percent per year) in air, a process termed “storage drift” [18]. The error appears primarily as a decrease in sensor gain. Lifetime optodes are much more stable in seawater, with typical drift rates of a few tenths of a percent per year [18]. Fortunately, the sensors make unbiased measurements in air and water. The sensor calibration (gain) error can be assessed each time a profiling float surfaces and the sensor is exposed to air [18]. This requires knowledge of local air pressure, which is obtained from global atmospheric reanalysis models. An accurate oxygen measurement in the ocean then depends on the phase measurement, temperature, salinity, and pressure to give an uncorrected oxygen concentration, and atmospheric pressure to determine a gain corrected oxygen concentration.

Nitrate

Nitrate is a key nutrient that limits phytoplankton growth in much of the ocean. Concentrations may shift over vast areas of the ocean due to anthropogenic processes [19] or changes in ocean mixing [2]. The primary scientific interest is thus in nitrate concentrations within the upper 200 m of the water column, where phytoplankton grow and most anthropogenic influences occur. Until 15 years ago, nitrate could only be determined with acceptable performance in laboratories using complex wet chemical analyses. Ocean monitoring thus required a ship to be present to collect samples for analysis in the lab. However, nitrate does have a moderate UV absorption band due to a π to π^* transition with a wavelength maximum near 200 nm. Optical nitrate sensors have been suggested [20], but were not successful. Low power opto-electronics now make it possible to measure nitrate directly from this absorption signal [21][22].

The nitrate sensor is a spectrophotometer that consists of a stable, low-power UV light source (Hereaus Fiberlight) that is fiber optically coupled to a pressure tolerant optical reflection probe. Light from the source passes through the water, is reflected back to the bifurcated fiber bundle and a portion of the light is directed to a Zeiss MMS 256 element photodiode array detector with custom electronics. Photodiode arrays are preferred because of their inherent UV sensitivity and their suitability for high light level applications.

The UV absorption spectrum of seawater is determined relative to a blank scan of deionized water that is made in the laboratory before the float is shipped. Determination of nitrate would be simple, except that the absorption peak of nitrate is overlapped onto a much stronger spectrum due to dissolved bromide in seawater. To efficiently compute nitrate, the portion of the UV spectrum due to bromide must be removed mathematically before nitrate is computed.

Bromide is conservative in seawater and its concentration can be computed quite accurately from the measured salinity. Unfortunately, bromide absorbs light because it forms a charge transfer complex with water and

the absorption spectrum is quite temperature [10] and pressure [11] dependent. Careful laboratory measurements of the bromide spectrum temperature and pressure dependence are required to enable the estimation of an accurate bromide spectrum from the computed concentration and measured temperature and pressure. It is then possible to quantitatively subtract the bromide influence from the observed spectrum and the nitrate concentration can be computed accurately. The determination of nitrate thus involves in situ observations of the UV spectrum, temperature, pressure, and salinity measurements, and detailed understanding of the bromide spectral properties at varying temperatures and pressure.

The nitrate sensor does suffer from small drifts or offsets due to changes in lamp output or accumulation of organics on the optics [22]. These biases can be removed by measuring the nitrate in the deepest (1 to 2 km) part of each profile, where concentrations are stable in time. The biases occur almost exclusively as constant offsets in computed nitrate. Knowing the error in the deep water allows the entire profile to be corrected.

The nitrate sensor is one of the larger power drains in the float system. It requires 40 joules to make a complete nitrate measurement, beginning with the system in a sleep state, waking it up, operating the lamp for about 500 msec, collecting a dark spectrum with the lamp off for an equivalent period, and then computing the nitrate concentration. The relatively high power consumption limits operations to 70 measurements on a profile, at depth intervals from 100 m at depth to 5 m intervals in the upper 100 m. This consumes about 2.8 kJoules of energy on each profile.

pH

The pH of seawater is a master variable that reflects a variety of processes including photosynthesis, respiration, and air-sea carbon dioxide exchange. A critical application for pH sensors is tracking the decreasing ocean pH (ocean acidification) that accompanies increasing atmospheric CO₂. Globally, this rate of decline is about -0.002 pH y⁻¹ [23]. Ocean scientists have developed unparalleled methods for measuring pH in the laboratory by spectrophotometry using the indicator dye meta-cresol purple with reproducibility over time of 0.001 pH [24]. These methods provide an excellent foundation for sensor calibration, but they have generally not proven to be robust enough for long-term operations in large sensor networks over many years without periodic service. Glass electrodes and potentiometry have also not proved effective.

Ion Sensitive Field Effect Transistors (ISFET) pH sensors have shown promise, but packaging the ISFET die is a challenge [25]. The sensor developed in our laboratory is based on the ISFET die found in the Honeywell Durafet. Improved packages for the die combined with AgCl pseudo-reference sensors that are immersed directly in seawater have proven to be stable and accurate [26][27]. The Durafet incorporates backside contacts that allow the packaging needed for high pressure operation to be relatively simple and reliable for multiple year's exposure to high pressure. These sensors

respond directly to the activity of HCl in seawater. The pH sensitive active layer over the gate gives the sensor a pH response that is indistinguishable from Nernstian over ten decades of pH change [28].

The sensor has an inherent pressure coefficient due to the piezoresistive properties of silicon, as well as a temperature coefficient. Each device must be calibrated in the laboratory at high pressure and low temperature to determine these coefficients, which are individual to each sensor. The desired output is proton concentration, which enables pH on the oceanographic total proton scale to be determined. This requires knowledge of the activity coefficient of HCl in seawater over the pressure, temperature, and salinity range that the sensor is operated.

As for nitrate, sensor performance can be evaluated by comparing sensor pH values to pH estimated near maximum depth from shipboard observations, which have no seasonal signal and change only slowly in space [29]. Changes in sensor pH, relative to the predicted values at depths below 1000 m, are compensated by adjusting the sensor reference potential. Large arrays of these sensors can then be operated with a demonstrated accuracy in pH of 0.007 in the upper ocean [30]. To achieve this performance, the ISFET requires long warmup times of several days. Practically, that means that the ISFET is kept biased for the entire time a float is deployed. As a result, the pH sensor consumes about 0.2 kJoule on each profile, or 4% of the sensor power budget.

Bio-optical Sensors

Core bio-optical measurements on profiling floats are light scattering by particles, chlorophyll fluorescence, and wavelength resolved downwelling irradiance. Optical backscattering sensors are used to assess particle abundance. In the open ocean, these particles are dominantly biogenic, either living plankton or their detritus. Empirical relationships can be used to convert the optical backscattering signal to suspended Particulate Organic Carbon. Chlorophyll fluorescence sensors measure the fluorescence emission of chlorophyll within living cells. They operate with excitation wavelengths near 470 nm and emission wavelengths near 695 nm. Wavelength resolved, downwelling irradiance sensors can be used to determine the amount of light available for photosynthesis at a given depth. The attenuation coefficient of the irradiance also provides an independent estimate of chlorophyll concentration.

The bio-optical sensors require less than 1% of the power on each profile.

Scientific Results

Fig. 3 shows the upper 200 m of a two-year long record of observations made by a profiling float that is operating in the seasonal ice zone near Antarctica. These observations extend down to 1700 m depth. This record illustrates the consistency of the biogeochemical measurements that are made in extremely harsh conditions. Periods when sea ice covers the surface are shown as black bars over the temperature panel. Seawater freezes at -1.8°C. If the float sees temperatures colder

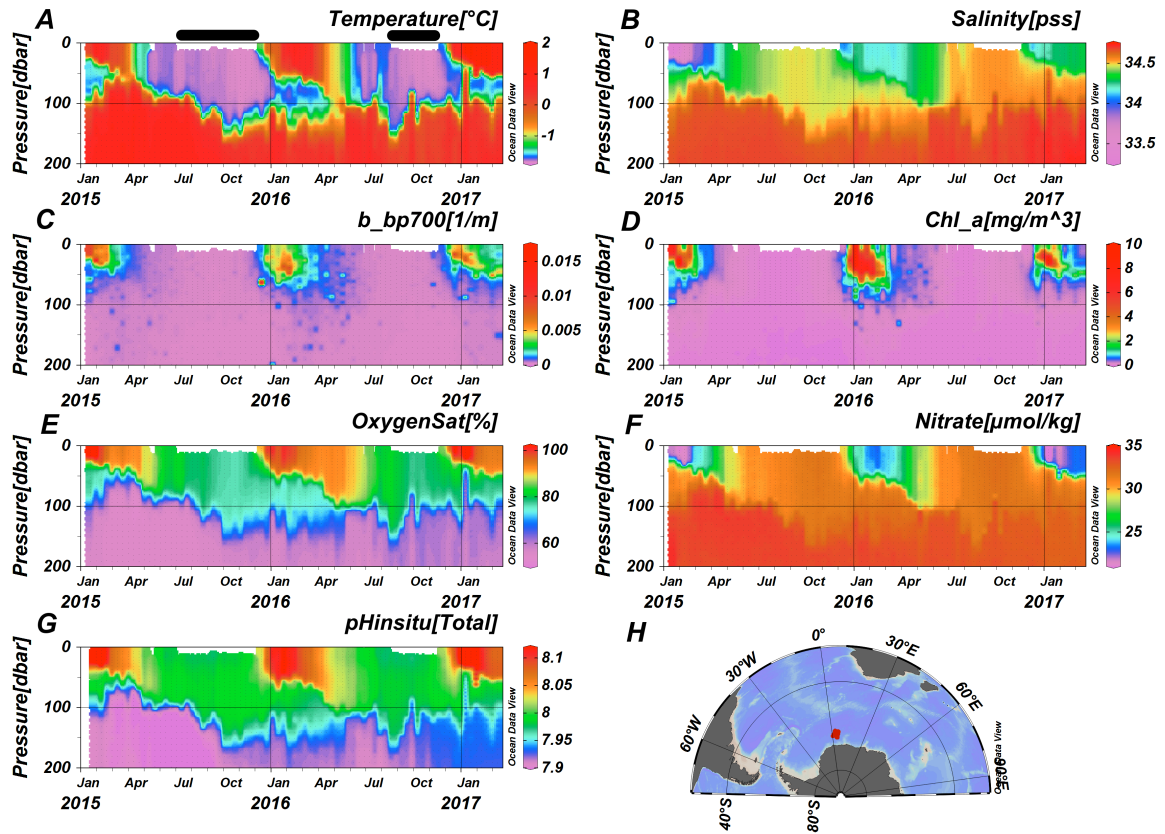


Figure 3: Profiling float 9099 (WMO # 5904468) observations of temperature (A), salinity (PSS, B), optical backscatter by particles at 700 nm (b_{bp} , C), chlorophyll a fluorescence (D), oxygen saturation relative to atmospheric equilibrium (E), nitrate (F), and pH (total proton scale) at in situ temperature and pressure (G) in the upper 200 m of the water column (1 m = 1.01 dbar pressure) versus time. Map (H) shows float profile locations as red dots. Black bars indicate presence of ice.

than -1.78°C above 20 m depth, it will stop its ascent to avoid the possibility of hitting ice. It then returns to 1000 m and continues to profile. Data collected under ice are transmitted to shore when the ice retreats.

As the water warms each year (Fig. 3A), an ice-edge phytoplankton bloom forms in the slightly fresher (lower salinity) water produced by the melting ice (Fig. 3B). The bloom is seen as an increase in backscattering of light (Fig. 3C), and confirmed to be phytoplankton by a corresponding increase in chlorophyll fluorescence (Fig. 3D). As the phytoplankton grow, the net photosynthesis creates an increase in oxygen concentration of some $50 \mu\text{mol kg}^{-1}$, shown here as the percent saturation relative to equilibrium with the atmosphere (Fig. 3E). Accumulation of phytoplankton biomass reduces nitrate concentrations by $14 \mu\text{mol kg}^{-1}$ as the nitrogen is assimilated to meet metabolic requirements. Growth of phytoplankton removes CO_2 from the water, increasing pH by 0.12. This corresponds to the removal of $90 \mu\text{mol kg}^{-1}$ of CO_2 .

The float shown in Fig. 3 has made 78 vertical profiles and has sufficient energy reserves to make 170 more profiles. There is no evidence of significant sensor degradation in the two years it has operated. We are now operating 80 similar floats in the Southern Ocean with data available in real time at <http://socc.com.princeton.edu>. These floats now allow ecosystem metabolism to be assessed throughout the Southern Ocean.

CONCLUSIONS

Significant strides have been made in the development of chemical sensors that can operate through large pressure and temperature gradients in the ocean and return reliable data over many years. These systems are being operated in networks that will provide unprecedented views of ocean health [6][7]. There are, however, significant other needs. Sensors for methane, nitrous oxide, dissolved phosphate, dissolved Si (orthosilicic acid), and dissolved iron are major needs. Improved bio-optical sensors that provided particle size spectra in the range 0.5 to $100+ \mu\text{m}$ are needed.

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