

Long-Term Nitrate Measurements in the Ocean Using the in situ Ultraviolet Spectrophotometer: Sensor Integration into the APEX Profiling Float

KENNETH S. JOHNSON, LUKE J. COLETTI, HANS W. JANNASCH, AND CAROLE M. SAKAMOTO

Monterey Bay Aquarium Research Institute, Moss Landing, California

DANA D. SWIFT AND STEPHEN C. RISER

School of Oceanography, University of Washington, Seattle, Washington

(Manuscript received 10 October 2012, in final form 4 March 2013)

ABSTRACT

Reagent-free optical nitrate sensors [in situ ultraviolet spectrophotometer (ISUS)] can be used to detect nitrate throughout most of the ocean. Although the sensor is a relatively high-power device when operated continuously (7.5 W typical), the instrument can be operated in a low-power mode, where individual nitrate measurements require only a few seconds of instrument time and the system consumes only 45 J of energy per nitrate measurement. Operation in this mode has enabled the integration of ISUS sensors with Teledyne Webb Research's Autonomous Profiling Explorer (APEX) profiling floats with a capability to operate to 2000 m. The energy consumed with each nitrate measurement is low enough to allow 60 nitrate observations on each vertical profile to 1000 m. Vertical resolution varies from 5 m near the surface to 50 m near 1000 m, and every 100 m below that. Primary lithium batteries allow more than 300 vertical profiles from a depth of 1000 m to be made, which corresponds to an endurance near four years at a 5-day cycle time. This study details the experience in integrating ISUS sensors into Teledyne Webb Research's APEX profiling floats and the results that have been obtained throughout the ocean for periods up to three years.

1. Introduction

Nitrate is an essential plant nutrient and its concentration exerts a primary control on phytoplankton biomass and growth rates in much of the ocean (Falkowski et al. 1998). Annual and seasonal changes in nitrate concentration can be used to track net community production, which is primary production minus respiration at all trophic levels (Wong et al. 1998, 2002; MacCready and Quay 2001). Historically, the concentration of nitrate has been determined only by reagent-based chemical analysis in samples returned to shipboard or shore-based laboratories. During the past two decades, automated chemical analyzers, based on laboratory procedures, have been developed that allow in situ measurements of nitrate to be made on ocean moorings (Jannasch et al. 1994; Sakamoto et al. 2004; Körtzinger et al. 2008). These instruments are relatively complex

and sustained (multiyear) operations have not been widely reported.

More recently, optical nitrate detectors have been developed that require no chemical reagents. Nitrate absorbs light in the ultraviolet with a peak absorption maximum for the π to π^* transition near 200 nm. The molar absorptivity ($\epsilon = 9900 \text{ L mol}^{-1} \text{ cm}^{-1}$; Mack and Bolton 1999) is moderately strong. The determination of nitrate in seawater using this UV absorption peak was suggested 50 years ago (Armstrong and Boalch 1961). However, the deep UV absorption spectrum of seawater is dominated by the combined signal from nitrate and bromide, with a much smaller contribution from dissolved organic matter (Ogura and Hanya 1966). The resolution of the nitrate peak requires measurements at multiple wavelengths. This requirement and technological limitations in UV light sources have not made direct, UV detection practical for in situ applications until the past 15 years. Instruments with various designs are now available (Finch et al. 1998; Johnson and Coletti 2002; Zielinski et al. 2007).

In situ ultraviolet spectrophotometer (ISUS; Johnson and Coletti 2002) optical nitrate detectors have been

Corresponding author address: Kenneth Johnson, MBARI, 7700 Sandholdt Road, Moss Landing, CA 95039.
E-mail: johnson@mbari.org

used on moorings (Johnson et al. 2006; Stabeno et al. 2010), towed vehicles (Johnson and Coletti 2002), and autonomous underwater vehicles (Johnson and Needoba 2008), as well as on CTD–Rosette systems (Pawlowicz et al. 2007; Christensen and Melling 2009). In this paper, the integration of the ISUS optical nitrate sensor into Teledyne Webb Research Autonomous Profiling Explorer (APEX) profiling floats is described. These systems have enabled long-term (years) observations of nitrate vertical profiles in the open ocean. These systems have already begun to contribute to our understanding of nutrient cycling in open ocean waters (Johnson et al. 2010). Nitrate sensors on profiling floats complement the capability provided by oxygen sensors (Körtzinger et al. 2004, 2005; Riser and Johnson 2008; Martz et al. 2008) as a tracer of biological activity because nitrate is not subject to gas exchange across the air–sea interface.

2. Design goals

The design goals for this work were to develop an instrument that was robust enough to be deployed in large numbers by nonspecialists, that could make at least 50 nitrate measurements on a vertical profile from 2000 m to the surface, and that had sufficient power to operate for approximately four years at a 5-day profile interval (~ 300 vertical profiles). To achieve the goal of high reliability and ease of deployment, it was decided that the ISUS components should be integrated into the pressure housing of the profiling float with only the optical probe penetrating the hull. During the course of this work, two designs were used. In version 1 of the instrument, a profiling float hull of the standard length (102 cm) was used. There is not sufficient void volume in this standard APEX hull design to allow a fully integrated ISUS unit to be placed inside the pressure housing. However, because the ISUS uses fiber optics to couple the components, it was possible to place the various components of the instrument in smaller void spaces. Quartz optical fibers were then used to integrate the optical units into a functioning instrument. This approach allowed five prototype instruments to be built and deployed relatively rapidly. Drawbacks to the approach included a relatively complex assembly that was probably not supportable if large numbers of instruments were to be deployed. Second, the additional weight of the ISUS required that a carbon fiber pressure hull be used to achieve vertical stability, rather than the standard aluminum pressure hull. These hulls proved difficult to manufacture reliably and in a timely manner. Third, the design required the optical sensor to penetrate the lower end cap of the pressure hull, while other sensors are located on the upper end cap. The large

offset creates mismatches in sensor data that can be difficult to correct in regions of high vertical gradients. Finally, the optical probe extending from the lower end cap cannot be easily protected from fouling by organic aggregates that may settle on the optics.

Because of these limitations, a revised version 2 of the APEX–ISUS instrument was developed. The pressure housing of the standard APEX design was extended by 20 cm. This provided several important advantages. First, there was sufficient room to hang a fully assembled ISUS under the upper end cap next to the CTD controller board. This allowed the ISUS optical probe to be placed in the pumped stream of the CTD, which provides fouling protection and eliminates large sensor lags due to spatial offsets. Additionally, the extra length provided sufficient vertical stability so that the pressure hull could be constructed from aluminum, which could be readily manufactured using standard materials and procedures. Finally, the additional buoyancy and space allows the number of battery packs to be increased from three to four, which provides enough energy to reach the design goal of ~ 300 vertical profiles. There is, however, one significant disadvantage. The displacement volume of the high pressure pump remains unchanged and, because the float volume is increased, there is a corresponding decrease in the maximum fractional volume change of the float that is possible. As a result, there is a decrease in the maximum depth that can be reached. In this configuration, the extended hull can only reach depths of about 1700 m in much of the ocean, rather than 2000 m with the standard hull.

In the following, the focus is primarily on the design of APEX–ISUS version 2, which is the model that is being used for current work. Results are now being returned by multiple version 2 units deployed in the ocean and some of those data are presented here. In addition, five units of the version 1 APEX–ISUS were deployed and those have operated as expected. These systems have the longest record of observations to date, and is used to assess long-term system performance.

3. Methods

The version 2 APEX–ISUS was constructed from components that were manufactured for a standard Teledyne–Webb Research APEX profiling float (Fig. 1). The extended pressure hull was designed at the University of Washington and manufactured by Teledyne–Webb Research suppliers. The hull is rated to the full 2000-m-depth capability of the APEX float. To verify the pressure rating, one hull was tested to failure at a pressure equivalent to 2600-m depth. The extended hull allows the complete ISUS sensor to be assembled on

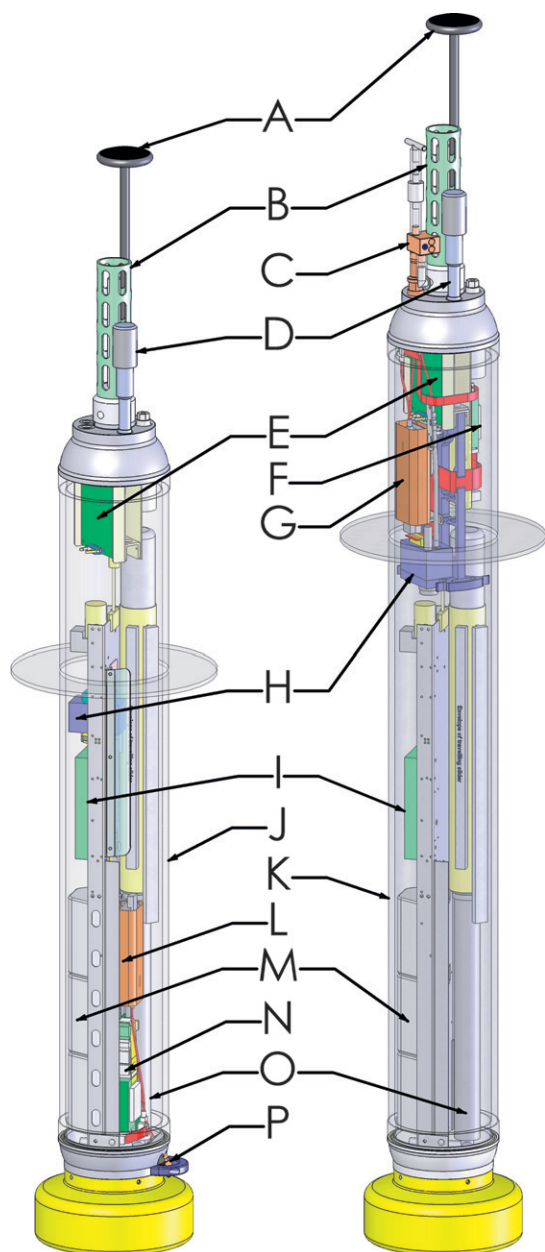


FIG. 1. Versions 1 (left) and 2 (right) of the APEX + ISUS profiling float contain essentially the same components. Nitrate concentrations are measured by the absorption of UV light that is produced by a deuterium light source (L, G) and guided through fibers to a reflection probe (P) and inside the flow cell, (C) and returned to the UV spectrometer (H). ISUS is controlled by a microcontroller (N, F). A combined global positioning system and Iridium satellite telephone antenna (A), CTD (B), oxygen optode (D), and CTD controller (E) are also mounted on the top end cap. All sensors as well as the hydraulic piston pump (O) are driven by the float controller (I). Power for all instruments is supplied by packs of primary lithium batteries (M). Design of version 2 re-located the optical probe into the pumped flow stream of CTD and simplified assembly by mounting all ISUS components on the top end cap (see Fig. 2). Longer length also allowed the use of a simpler aluminum housing (K), vs a lighter carbon-fiber housing required in the original design (J).

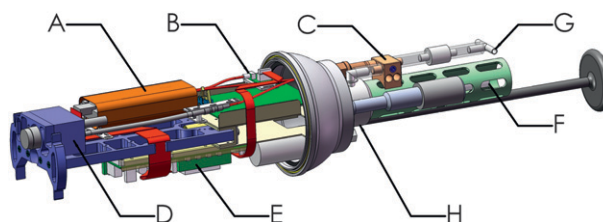


FIG. 2. Upper end cap arrangement in version 2 of the APEX + ISUS profiling float. The UV light produced by the deuterium light source (A) is bifurcated into two fibers for output monitoring by a reference detector (B) and the reflection probe located inside a flow cell (C). Light from the probe is returned via a third fiber to the UV spectrometer (D). ISUS controller (E) collects, processes, and stores the spectra using pressure and temperature data supplied by the CTD via the float controller. A subset of processed data is fed back to the float controller for telemetering to shore. During the ascending profile, the sample is pulled into the CTD (F) and vented out a small T fitting (G) by a magnetically driven pump (H).

a bracket hung under the upper end cap (Fig. 2). The ISUS can be assembled and calibrated without transporting the entire float in this configuration. When the upper end cap of the float is removed to open the float for testing, ballasting, or battery installation, the entire ISUS unit comes out as well.

The ISUS optical probe is mounted in a Society of Automotive Engineers (SAE) 6 O-ring port on the upper end cap of the float. A flow cell fitted over the optics is plumbed into the pumped stream that exits the conductivity cell on the Sea-Bird 41 continuous profiler (41CP) CTD unit. The optical probe is manufactured by Equitech International and has a pressure rating of 2000 dbar. Quartz optical fibers connect the UV light source (Heraeus FiberLight) and spectrometer [Zeiss Monolithisches Miniatur Spektrometer (MMS) UV] to the optical probe.

The ISUS is powered by a 15.6-V supply from the lithium battery packs in the float. Power to the ISUS is switched by a hardware control line from the APF 9 float controller to a mechanical relay on the ISUS controller board. Between profiles, the ISUS is in shutdown mode and draws no power. At the beginning of a vertical profile, the float controller enables power to the ISUS controller board, which employs an Onset Computer TT8 microcontroller. The ISUS controller requires 10–15 s to initialize. It then enters a low-power sleep mode that draws about 1.5 mA current. If the power supply drops below 7.5 V, then the ISUS controller will reenter shutdown mode.

Digital communications between the float controller (designated by Teledyne–Webb as model APF-9) and the Monterey Bay Aquarium Research Institute (MBARI)-designed ISUS controller are accomplished using an RS-232

interface with the APF 9 controller acting as master and the ISUS controller as slave. Nitrate sampling is commanded by the float controller at a set of predetermined depths. When a sampling depth is reached, the APF 9 sends a string of characters over the RS-232 interface. This wakes the ISUS controller from sleep mode and it enters command mode, where it will respond to commands from the APF 9. The APF 9 then sends the current temperature and salinity values to the ISUS and commands it to make a nitrate measurement. The ISUS immediately makes a single UV spectral scan with the lamp on (light scan) and lamp off (dark scan), with no warm up time for the lamp. The light and dark scans are used, along with reference spectral intensities from similar scans of deionized water made in the laboratory, to compute the absorbance spectrum from 200 to 400 nm. The absorbance spectrum is used with the temperature and salinity values passed by the APF controller to compute nitrate as described previously using the temperature compensated, salinity subtracted (TCSS) algorithm (Sakamoto et al. 2009). In this algorithm, the observed salinity and temperature are used to predict the UV spectrum due to bromide and this predicted bromide spectrum is subtracted from the spectrum observed in situ to produce a corrected spectrum. The corrected spectrum then contains only components due to nitrate and an approximately linear baseline due to organic matter and instrumental drift. Nitrate is computed from a multiple regression of this spectrum on the molar absorptivities of nitrate and a baseline linear in wavelength. The ISUS controller returns the computed nitrate value and a subset of the light scan spectral intensities, typically wavelengths from 217 to 250 nm, back to the APF 9 controller. It also returns the mean dark current measured over the first 100 pixels of the detector array and a seawater dark current computed as described in Johnson and Coletti (2002). When all commands are completed and the data are returned to the APF 9, the ISUS controller is then commanded to return to sleep mode until the next sample is acquired. At the end of the vertical profile, the ISUS is returned to shutdown mode.

Each nitrate sample requires about 45 J of power; 60 samples are acquired from 1000 m to the surface. The cumulative power needed for 60 samples amounts to about 20% of the total power budget of the float on each profile. Our typical depth table has samples spaced at 50-m intervals from 1000 to 400 m. Samples are then at 20-m intervals to 360 m, at 10-m intervals to 100 m, and then at 5-m intervals to 5-m depth. No surface sample is collected to avoid contaminating the CTD cell with surface slicks. Below 1000 m, samples are collected at 100-m-depth intervals. Once the float reaches the surface, the nitrate concentrations and the spectral intensities are

transmitted to shore using the Iridium communications system. Sending the spectral data to shore allows nitrate concentrations to be recomputed using improved algorithms as necessary.

4. Results

Twenty-seven APEX-ISUS systems have been deployed in environments from the oligotrophic subtropical ocean to high latitudes in the Southern Ocean and the Arctic (<http://www.mbari.org/chemsensor/floatviz.htm>). A total of more than 2600 vertical profiles have been completed at 5 days between profiles for a combined amount of more than 35 float years of data. These systems have generally operated as expected. One float was lost on deployment. The first float deployed (5145) had a combination of software and hardware problems that caused the nitrate sensor to stop operating after 2.5 yr. This has since been rectified. The ISUS units on several floats stopped communicating with the float controller after periods of 1–2 yr. In some cases the communications stop at a relatively constant depth on each profile. These floats have an IE55 connector on the end cap for direct communications to the ISUS during calibration and one of the pins is an optically isolated reset line for the ISUS controller. The pressure dependence of some communications suggests that the reset line is being shorted to ground, stopping the ISUS, because of variable resistance in the connector that has some pressure dependence, as the cap over the connector is squeezed by pressure. The reset line has now been removed from the connector. All other APEX/ISUS systems built at MBARI and the UW have operated as expected.

Here the focus is on results from three of the version 1 systems that have operated for multiple years and the first version 2 float. Float 5145 was deployed at the Hawaii Ocean Time-Series (HOT) station [A Long-Term Oligotrophic Habitat Assessment (ALOHA)] in the oligotrophic waters of the North Pacific subtropical gyre (Fig. 3a). Surface concentrations of nitrate are always below the instrumental detection limits near Hawaii (Karl 1999). Float 5143 was deployed in the subarctic North Pacific at Ocean Station Papa (OSP; Fig. 3b). Surface nitrate concentrations are almost never depleted in this region (Wong et al. 1998). Float 5146 was deployed in the Southern Ocean. Float 6401, the first version 2 float, is also considered. Float 6401 was deployed at HOT station ALOHA (Fig. 3a).

a. HOT float 5145

Float 5145 was deployed at Hawaii to take advantage of the time series data that are made available at this location by the National Science Foundation (NSF)-supported

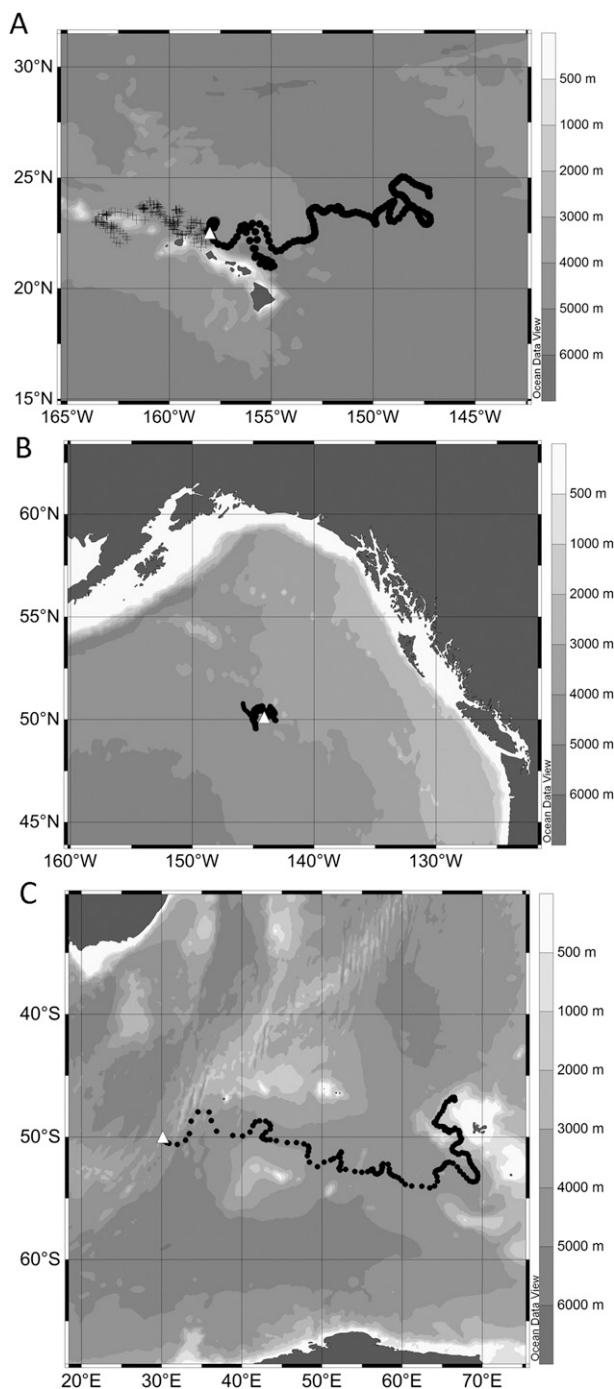


FIG. 3. (a) Profile locations for floats 5145 (solid dots) and 6401 (plus signs). (b) Float 5143 and (c) float 5146. Open triangles in each panel show the deployment locations.

HOT program. As a result of the HOT observations, it is well known that nitrate never exceeds $0.01 \mu\text{mol L}^{-1}$ in the upper 50 m (Karl 1999) and concentrations at 1000 m are also well defined. These two endmember concentrations at the top and bottom of the profile provide

important constraints on sensor performance. Float 5145 collected nitrate data on 195 vertical profiles from 23 December 2007 until 25 August 2010. The results collected on the first 125 profiles have been described (Johnson et al. 2010). After the 195th profile, the compact flash memory card on the ISUS controller was filled and this caused the ISUS software to fail, although the float continued to profile and collect CTD- O_2 data for 240 total profiles, until the float was recovered in October 2011. This software problem did not occur on subsequent floats, as they were deployed with larger-capacity compact flash memory cards. A later revision to the software prevents this problem from occurring even when the flash memory is filled.

Figure 4 shows a comparison of nitrate concentrations measured on the first float profile and concentrations measured at station ALOHA just prior to deployment. There is excellent agreement on the first profile, with the samples analyzed on shore using conventional automated analyzer techniques by the HOT personnel. However, there appears to be some drift in the reported nitrate concentration over time. Figure 5a shows the absorbance value of the UV spectrum at a wavelength of 240 nm that was measured at 1000-m depth on each profile versus time. Nitrate and bromide do not have significant light absorption at 240 nm, and changes in this value must reflect either fouling of the optics, changes in internal light throughput in the instrument, or changes in lamp output. The absorbance at 240 nm underwent three rather rapid shifts toward higher light absorption, followed by periods of constant or decreasing light absorption. Float 5145 was recovered in October 2011 to determine the cause of these offsets. At the time of recovery, it was found that light throughput through the optical sensor was extremely low. Lamp output was relatively unchanged and low light throughput was determined to be due to low transmission in the optical probe. Cleaning the optics with a series of increasingly strong solvents and acids did not improve light throughput. This suggests that either water had penetrated into the optics or mechanical shifts in the mirror had occurred, which led to gradual degradation of the optics, and the changes were not due to fouling of the optics. This degradation must have continued during the year that the float profiled with the ISUS was not operating, which led to the lack of light transmission that was observed. Unfortunately, the sensor reflection probe was mechanically damaged when it was removed for further inspection and the details of the problem could not be diagnosed.

A shift in light absorption will not impact the computation of nitrate if the shift appears as a linear function of wavelength. In this case, the shift will then be convolved with the instrument baseline and it does not

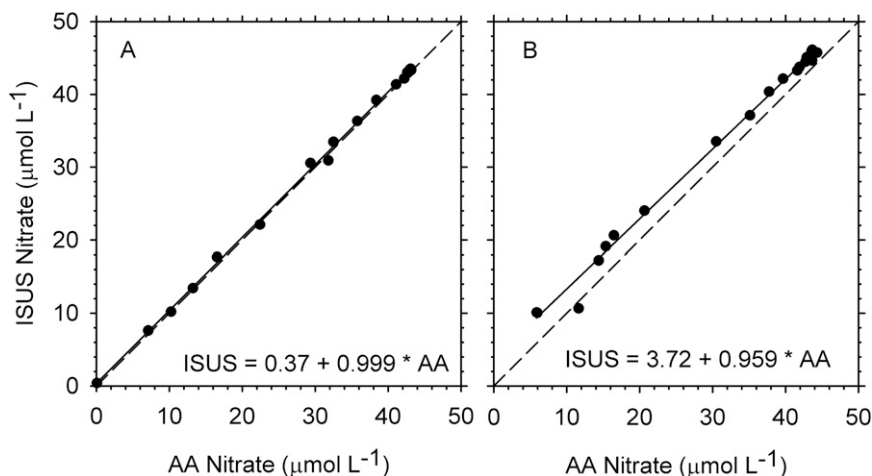


FIG. 4. ISUS nitrate vs nitrate determined in the laboratory by standard automated analytical methods (AA nitrate) for first profile of (a) floats 5145 and (b) 5143. Solid lines are the least squares fits with the equation shown in each plot and dashed lines are the 1:1 relationship.

impact the calculation of nitrate concentration (Johnson and Coletti 2002; Sakamoto et al. 2009). However, coincident with the shifts in light absorption at 240 nm (Fig. 5a), the computed nitrate concentrations at the surface and at 1000-m depth also showed shifts toward lower values, with negative concentrations in the upper 100 m (Figs. 5b,c). Each shift in the absorbance baseline lowered the calculated nitrate concentration by about

$1 \mu\text{mol L}^{-1}$, followed by a period of drift back toward higher concentrations. This means that the spectral shifts have some component that is nonlinear in wavelength. The concentration changes occur as a constant shift to the nitrate reported over the entire profile, as evidenced by the parallel changes in concentration at the surface and at 1000 m (Fig. 5b). The constancy of the shift in nitrate implies that a small, but constant, spectral

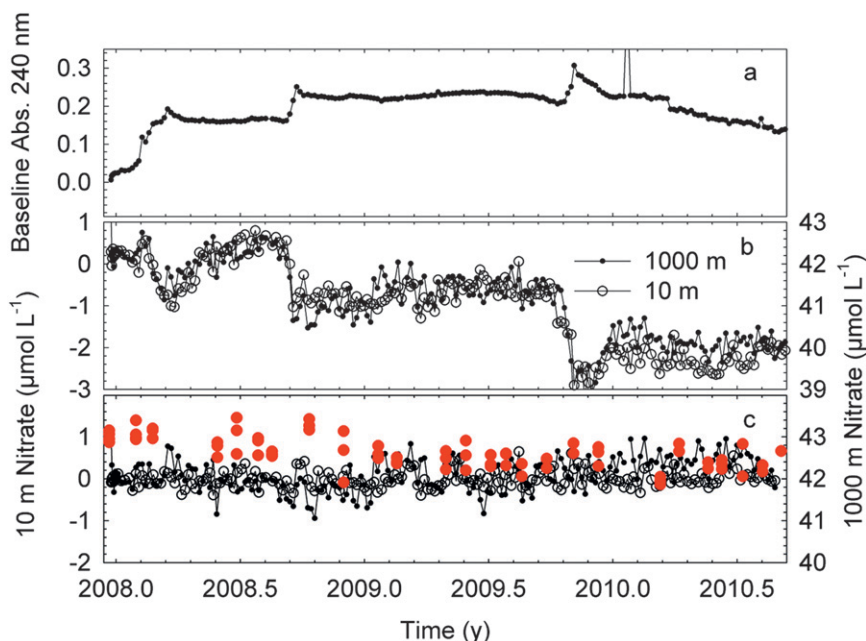


FIG. 5. (a) Baseline absorbance at 240 nm, (b) uncorrected nitrate at 10 and 1000 m, and (c) corrected nitrate at 10 and 1000 m for profiling float 5145, deployed at HOT. Red dots in (c) show nitrate at 1000 m from the HOT database (<http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html>).

component that has a nonlinear dependence in wavelength has been added to each spectrum measured on a profile.

Given that surface concentrations of nitrate near HOT are always near zero (the mean value is around $0.002 \mu\text{mol L}^{-1}$; Johnson et al. 2010) and well below the detection limit of the ISUS sensor, a corrected dataset was produced by computing an offset for each profile as the difference between an assumed surface concentration of zero and the mean nitrate value reported by the float from 5 to 30 m. This offset was then added to the nitrate observed at each depth on the profile, resulting in a mean, corrected nitrate of zero from 5 to 30 m. The corrected nitrate concentrations at 1000 m are shown in Fig. 5c along with the nitrate measurements made at HOT station ALOHA. These corrected ISUS nitrate measurements over 2.5 years are within about $1 \mu\text{M}$ of the HOT data for the entire period.

The vertical nitrate structure observed with the ISUS sensor on the float is quite consistent with the structure that was observed in samples collected with a CTD/rosette sampler near HOT over the same time period (Fig. 6). The response rate of the ISUS nitrate sensor is defined by the time it takes for water to flush the illuminated volume of the sensor, which is about 1 cm^3 . The measurement frequency is controlled by the amount of time it takes to integrate enough light on the detector array to make a measurement. This is typically near 2 Hz, if detector data are stored in memory, but nitrate concentrations are not computed. If nitrate concentrations are computed, then the highest measurement frequency is reduced to near 1 Hz because of the computational overhead in determining nitrate. However, the power demand of the ISUS is high enough that for long-term applications on a profiling float, the measurement duty cycle must be reduced significantly. As noted above, 60 nitrate measurements are made with a single spectral scan for each measurement on a vertical profile.

Despite the fact that the optics of the version 1 ISUS-APEX system are immediately adjacent to the plastic bladder shield at the base of the float, the sensor seems to flush at an adequate rate. However, there is a problem because of the mismatch in location of the float CTD sensors and the nitrate sensor optics. This can be seen by the occasional single-point spikes in nitrate in the upper 100 m, where detectable nitrate concentrations seldom occur (Fig. 7). These spikes almost invariably occur at the base of the strong, seasonal mixed layer, where temperature gradients are at their strongest. Temperature and salinity are significant components of the algorithm used to compute the nitrate concentration (Sakamoto et al. 2009). It is easy to demonstrate that a 1.5-m offset in

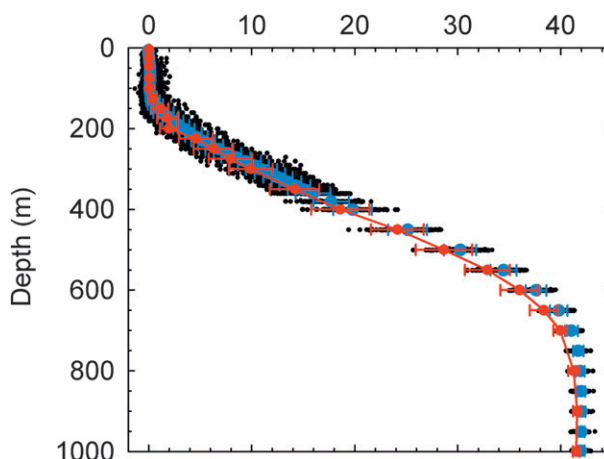


FIG. 6. Corrected nitrate concentrations determined by profiling float 5145 over 2.5 yr near HOT and nitrate determined by the HOT program over the same time. Nitrate was corrected as $(\text{Nitrate}_{\text{raw}} - 0.37)/0.999$ (Fig. 4a) and by correcting for temporal drift, as shown in Fig. 5. Black dots are individual float nitrate values. Blue symbols show mean float nitrate at each depth with the 90% CI for the mean. Red dots and error bars are the mean HOT values and 90% CI for the same period, respectively.

these properties can cause spikes of the magnitude that are seen. It is not a simple matter to lag correct the temperature and salinity values for the spatial offset in sensor locations because of the variable rise rate of the float in strong density gradients. As shown below, the version 2 ISUS-APEX system largely eliminates this problem through collocation of all sensors in the CTD pumped sample stream.

b. OSP float 5143

Float 5143 was deployed at OSP to take advantage of the long history of nitrate measurements that have been made at that station (Wong et al. 1998). It completed 211 profiles from 31 August 2008 to 10 August 2011, when the batteries were exhausted. The float remained within 150 km of its deployment location during the entire period (Fig. 3b). Figure 4b shows the comparison of nitrate concentrations reported on the first float profile versus samples that were collected when the float was deployed and then analyzed in a shipboard laboratory. The float nitrate concentrations appear to be too high over the whole profile. In the subsequent presentation of results from float 5143, the data have been corrected using the regression equation shown in Fig. 4b.

Figure 8 shows temperature and corrected nitrate concentrations measured at 10- and 1000-m depth during this time period. Measurements of nitrate at these depths at OSP, which were made by the Canadian Department of Fisheries and Oceans Line P program, are also shown in Fig. 8. There is a clear seasonal cycle of nitrate in surface

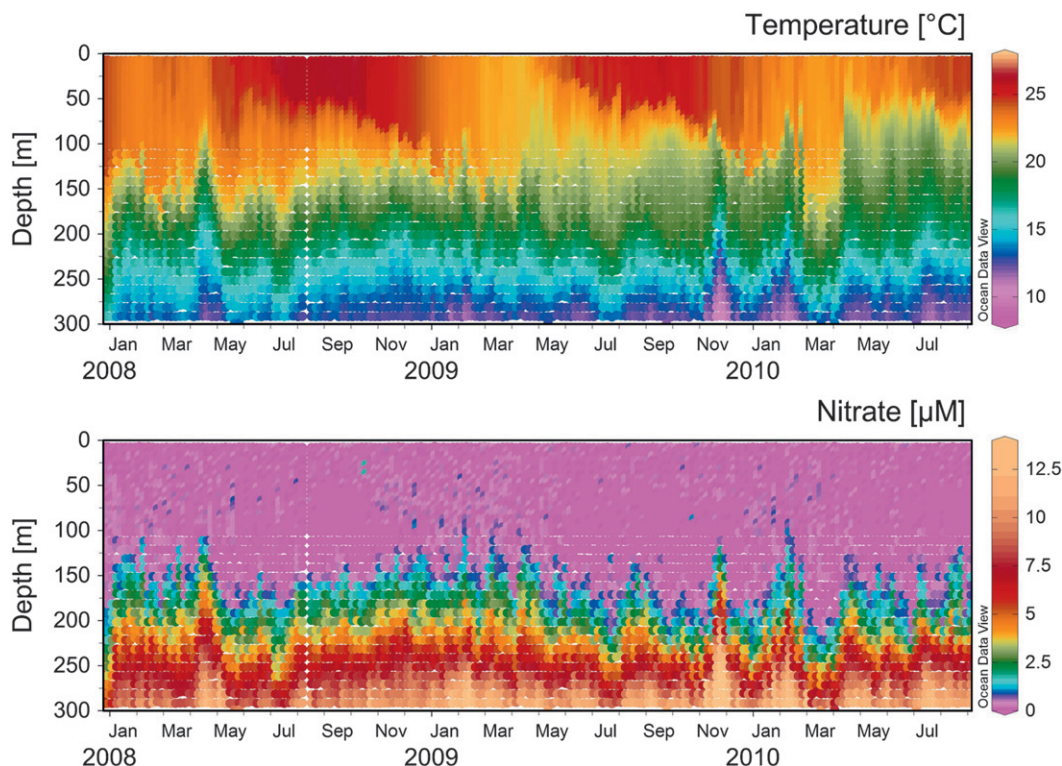


FIG. 7. Sections of (top) temperature and (bottom) corrected nitrate in the upper 300 m measured by profiling float 5145 near HOT.

waters near OSP, with the lowest values in late summer resulting from phytoplankton consumption of nitrate. The profiling float measurements are in excellent agreement with the Line P data near the surface and prior observations made by Wong et al. (1998, 2002). The mean difference between the float and OSP data at 10 m is -0.5 ± 0.8 [one standard deviation (1 SD)] $\mu\text{mol L}^{-1}$. The nitrate measured by the float at 1000 m has a mean of $43.7 \pm 0.4 \mu\text{mol L}^{-1}$ (1 SD) for data collected over a span of 3 yr. The 1000-m float measurements are about $2 \mu\text{mol L}^{-1}$ lower than the Line P data, which have a mean of $46.0 \pm 0.6 \mu\text{mol L}^{-1}$ (1 SD) in the same period. This bias is most likely in the Line P data, as other nearby datasets give nitrate concentrations more similar to the float data. Gridded data from the *World Ocean Atlas 2009* (Garcia et al. 2010) yield a value of $44.5 \mu\text{mol L}^{-1}$ for 1000 m at OSP, while the electronic World Ocean Circulation Experiment (e-WOCE) data at OSP is $44.6 \mu\text{mol L}^{-1}$ (Schlitzer 2000). There is a decrease of $1 \mu\text{mol L}^{-1}$ over the first year of float data at 1000 m and then a return to the initial value (Fig. 8). There is no corresponding change in dissolved oxygen during this period. The $1 \mu\text{mol L}^{-1}$ variation is most likely due to changes in instrumental performance. This change is much smaller than the biologically and physically driven changes observed at the surface. As a result, the profiling

float provides a very useful perspective on biologically driven nitrate uptake in the upper ocean.

c. HOT float 6401

Float 6401 was deployed at HOT to test the performance of the version 2 design in the well-studied environment near Hawaii, as noted above. Beyond easier assembly and longer endurance, placing the ISUS optics in the pumped stream of the CTD should reduce spiking due to a mismatch in the location of the CTD and nitrate sensors in the version 1 instruments. In addition to the mechanical changes described above, the version 2 floats also incorporate several changes in the ISUS software.

One of the most useful software changes is to compute and return to shore the seawater dark current (Johnson and Coletti 2002). The seawater dark current is the light intensity measured near 200 nm, where the ambient bromide ion concentrations in seawater should completely block light transmission. The dark current in these floats is normally determined after the spectral scan with the lamp on by closing the shutter. Several version 2 floats have developed a fault where the shutter does not close fast enough and light contaminates the dark current scan. This produces unrealistic nitrate concentrations. Because the seawater dark current and

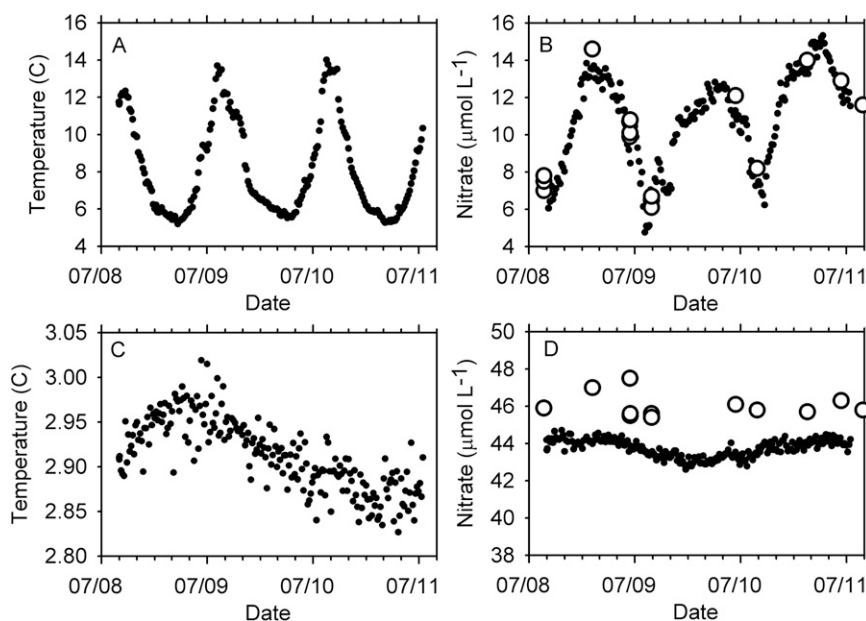


FIG. 8. (left) Temperature and (right) corrected nitrate at (a),(b) 10 and (c),(d) 1000 m measured over 3 yr by profiling float 5143 near OSP in the North Pacific. Nitrate was corrected as $\text{Nitrate}_{\text{Corrected}} = (\text{Nitrate}_{\text{raw}} - 3.72)/0.959$ (Fig. 4b). No drift correction was applied. Open circles in (b) and (d) are nitrate measurements made at OSP by the Institute of Ocean Sciences (and downloaded from <http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/line-p/index-eng.htm>). Line P data were collected and made freely available by the Institute of Ocean Sciences (Canadian Department of Fisheries and Oceans) as part of the Line P monitoring surveys of the Gulf of Alaska.

the raw spectral intensities are transmitted to shore, these data can be reprocessed by using the seawater dark current, rather than the directly measured dark current. Presently deployed versions of the hardware all have the shutter removed and the lamp is turned off during the dark current collection period to avoid this problem.

The nitrate concentrations in the upper 30 m of the water column, which were computed from UV spectra returned by float 6401 from early November 2009 to March 2012, are shown in Fig. 9. Data from float 5145 are shown for comparison. The average rate of change in the data is comparable in the two systems, -0.8 for 6401 and $-1.1 \mu\text{mol L}^{-1} \text{yr}^{-1}$ for 5145, while surface nitrate concentration should be effectively zero for the entire period. However, nitrate concentrations from 6401 show less scatter and fewer spikes than the data returned by float 5145 and the overall trend in the 6401 data is smoother. Analysis of float 5145 after recovery suggested that the sensor drift was the result of degradation of the optics in the reflection probe that is immersed in the ocean, rather than fouling. This conclusion is supported by the 6401 data, which do not show a marked change in sensor drift despite a configuration where the optics are protected by the CTD antifouling

rings that should greatly inhibit growth on the optics. This implies that improving the long-term stability of the optics could be of significant benefit to minimizing drift in nitrate concentration.

d. Float 5146: Correcting for sensor offset

As noted for floats 5145 and 6401, the ISUS sensor often shows small amounts of drift over multiyear deployments on profiling floats. However, the sensor has one important property that can be used to mitigate some of the problem caused by sensor drift. Sensor drift occurs essentially as a constant offset over the entire profile. This is illustrated by Fig. 5b, which shows that offsets in nitrate concentration at the surface and at 1000 m on each profile are nearly identical. If nitrate concentration at one particular depth can be considered constant, then observations at all depths can be corrected for drift by subtracting the constant amount needed to adjust observations at the reference depth to the reference nitrate concentrations (Fig. 5c). An extreme example of this effect is shown by the nitrate measurements collected by float 5146.

Float 5146 was a first-generation float that operated for more than three years in the Indian Ocean sector of the Southern Ocean (Fig. 3c). After 2.4 years of

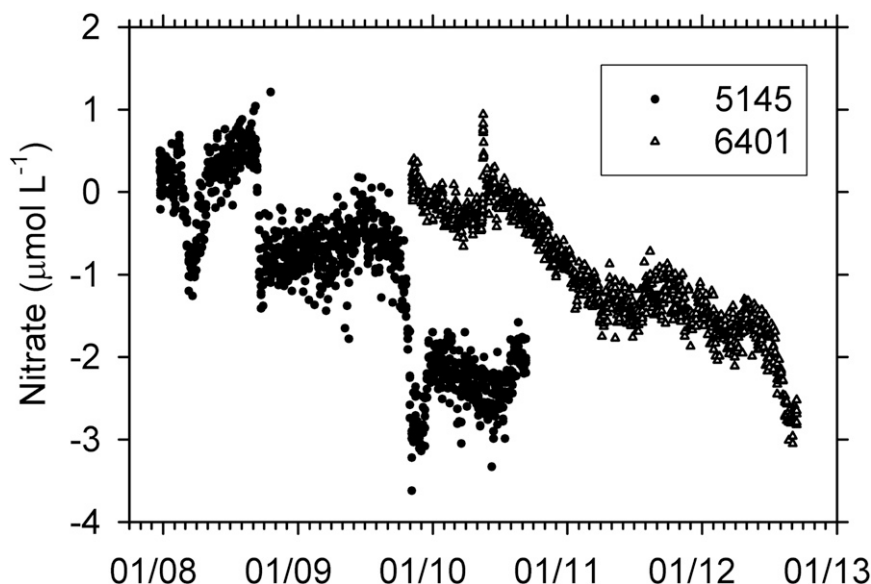


FIG. 9. Uncorrected nitrate concentrations measured in the upper 30 m by profiling floats 5145 (black circles) and 6401 (open triangles) near the HOT time series station.

operation, with little apparent drift in nitrate concentrations, the float grounded on the Kerguelen Plateau. The optical probe on this float was mounted near the bottom of the float and this apparently resulted in significant contact with the sediment. An offset in nitrate concentrations greater than $20 \mu\text{M}$ occurred at both the surface and at 650 m, the deepest depth reached by the float for much of this period. As shown in Fig. 10, these large concentration offsets appear to be nearly the same at the surface and at depth. For example, the difference between nitrate at 650 m and at the surface remained near $10 \mu\text{M}$, although the absolute nitrate concentrations at each depth were offset by $20 \mu\text{M}$.

A corrected nitrate record for float 5146 was produced by using the linear relationship between nitrate and density observed from 500 to 800 m before the float grounded. This equation was used to predict nitrate concentration at 650-m depth from the observed density. The difference between the nitrate observed at 650 m on each profile and the predicted value, based on density observed at 650 m, was then subtracted from the nitrate values observed on each profile. The corrected nitrate concentrations are contoured in Fig. 11. The corrected dataset yields a consistent picture of seasonal change in nitrate concentration around the Kerguelen Plateau, similar to other reports (MacCready and Quay 2001). Over the 3-yr deployment, the largest summer nitrate depletions occurred when the warmest, most stable surface mixed layer formed. Large surface warming and nitrate depletion occurred near the Kerguelen Plateau, similar to conditions at the beginning of the

deployment (Fig. 11). The relationship of the corrected nitrate concentrations to temperature values in the upper 500 m is comparable to that found for observations in the e-WOCE atlas (Schlitzer 2000) to within several micromoles per liter. This suggests that offsets as large as $20 \mu\text{mol L}^{-1}$ are correctable to within about 10%. Although it would not generally be recommended to use data that required corrections this large, it does appear that the data are largely recoverable.

Corrections for the drifts and offsets in nitrate seen with our other sensors, which are on the order of $1\text{--}2 \mu\text{mol L}^{-1}$, should result in data accurate to near $\pm(0.2\text{--}0.4) \mu\text{mol L}^{-1}$. This property of constant offsets was also seen in Fig. 5 for float 5145. Changes in nitrate concentration at the surface were paralleled by changes of the same magnitude at 1000-m depth. Johnson et al. (2010) used the fact that nitrate concentrations at the surface are always zero near Hawaii to produce a corrected nitrate record for the deployment with errors $<0.2 \mu\text{mol L}^{-1}$.

e. Nitrate sensor gain correction

As noted in the previous section, instrumental artifacts primarily occur as an offset in nitrate concentration. The slopes of the lines comparing ISUS data to shipboard nitrate analyses in Fig. 4 are both less than one. The difference from a slope of one is not significant for float 5145 at HOT, but for 5143 the probability is <0.05 that the slope equals one, which suggests that sensor gain corrections should also be considered. Similar comparisons to those shown in Fig. 4 are now available for 11 float

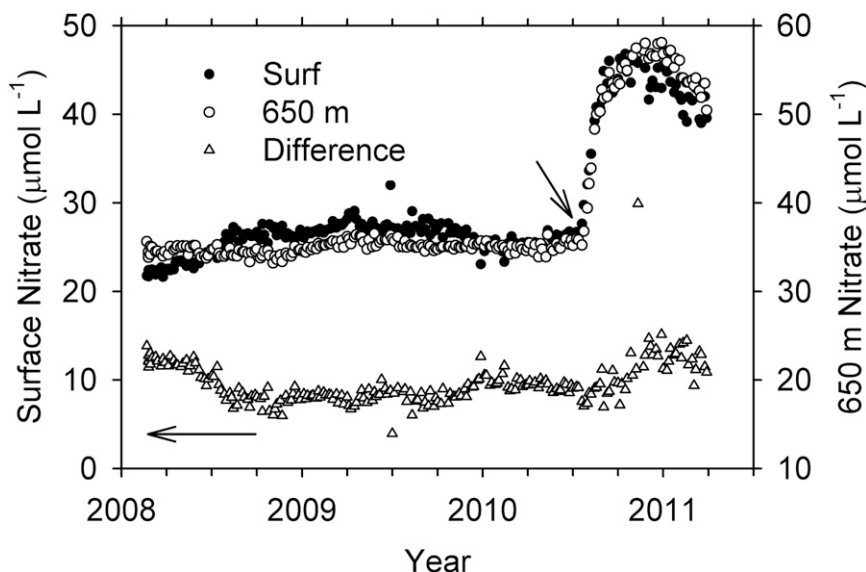


FIG. 10. Uncorrected nitrate measured over 3 yr by profiling float 5146 at 10 and 650 m in the Indian Ocean sector of the Southern Ocean. Triangles show the difference in nitrate concentrations ($650\text{ m} - 10\text{ m}$), which are plotted on the left-hand axis. Slanted arrow shows the time that the float began to touch bottom near the Kerguelen Plateau.

deployments. The mean of all the slopes is 0.986 ± 0.014 [95% confidence interval (CI)], which just overlaps with a slope of one.

There is no generally accepted standard reference material for nitrate in seawater. It is conceivable that the difference from a slope of one is due to variability in the standardization of the sensor, which has been carried out by personnel at MBARI, and the nitrate analyses by HOT, Bermuda Atlantic Time-Series Study (BATS), and OSP time series personnel, as well as by Climate Variability and Predictability (CLIVAR) Repeat Hydrography cruises. Until further experience is acquired, the nitrate sensor data should be corrected only with an offset that may be variable in time, as shown in Figs. 5 and 10, and a gain correction that is constant in time, but which may differ slightly from one. This gain correction may be determined from nitrate measured on an initial hydrocast or by comparison to a well-established climatology for nitrate.

f. Analytical figures of merit

The analytical figures of merit (limit of detection, accuracy, precision, and linear range) for an ISUS nitrate sensor on a profiling float are dependent on the user's ability to provide postdeployment corrections to the data and an ability to assess sensor drift in time. As noted for the four floats considered here (5145, 5143, 6401, and 5146), initial offsets ($\text{ISUS} - \text{AA}$, where AA are samples analyzed on ship or shore by automated analyzer) in the

surface nitrate concentrations of 0.4, 4.2, 0.1, and $4.2\text{ }\mu\text{mol L}^{-1}$, respectively. This range is fairly typical. Without a means to correct the nitrate for these offsets, the initial accuracy is rather limited. However, these offsets can be corrected to within about 10%, which suggests an initial accuracy near $0.4\text{ }\mu\text{mol L}^{-1}$ or better. Once a sensor receives an initial correction, it is also clear that additional changes can occur. Drift rates on the order of $1\text{ }\mu\text{mol L}^{-1}\text{ yr}^{-1}$ are fairly typical (Fig. 9), although lower rates are also found (Fig. 8). As seen in Figs. 5 and 8, it is possible to compensate for these changes by comparison with nitrate at a depth where the concentration can be considered relatively constant. Over multiyear periods, these drift corrections may introduce an additional uncertainty as large as $1\text{ }\mu\text{mol L}^{-1}$. This uncertainty is directly dependent on the quality of the climatology or other constraints on a reference nitrate concentration. An independent estimate of long-term accuracy is supported by the differences between ISUS and ship-board measurements shown in Fig. 8b. The mean difference ($\text{ISUS} - \text{AA}$) over 3 yr is -0.5 ± 0.8 (1 SD) $\mu\text{mol L}^{-1}$.

Sensor precision can be estimated from the variability in the mixed layer. Over short time periods this precision is on the order of $\pm 0.1\text{ }\mu\text{mol L}^{-1}$, but this degrades over longer time periods because of sensor drift. The precision of all the corrected data over 2.5 years at HOT is on the order of $\pm 0.4\text{ }\mu\text{mol L}^{-1}$ in the mixed layer and at 1000 m [see the online supplementary material to

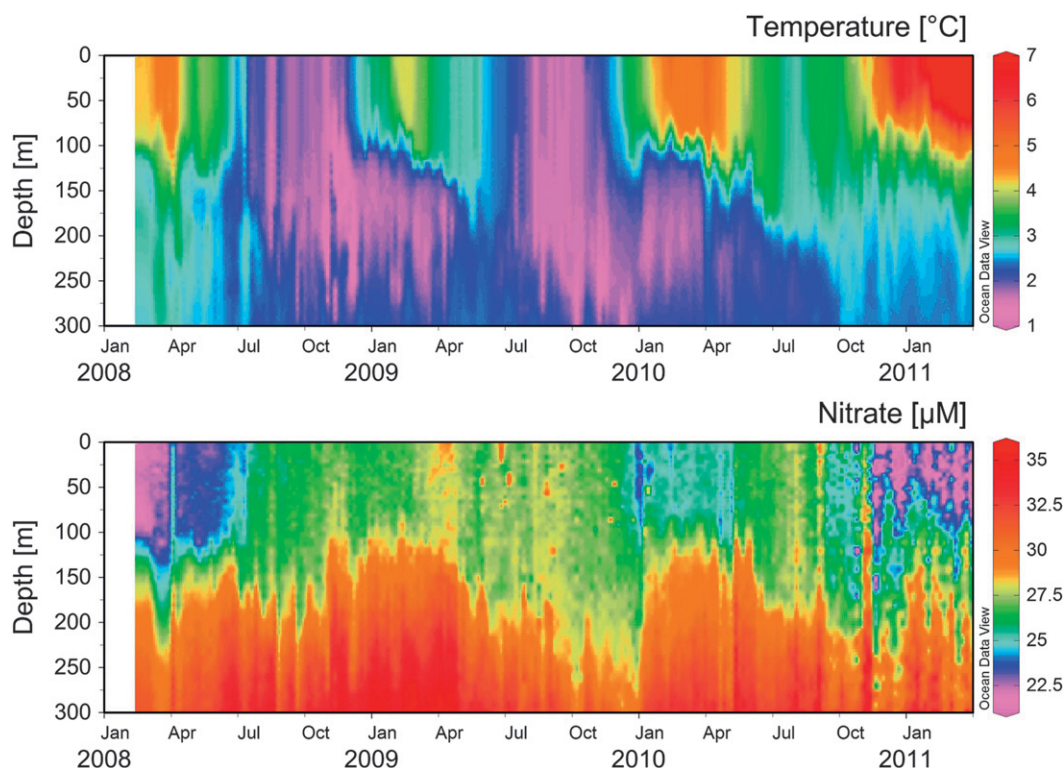


FIG. 11. (top) Temperature and (bottom) corrected nitrate concentration in the upper 300 m measured by profiling float 5146 in the Indian Ocean sector of the Southern Ocean. Nitrate was corrected as for float 5143 by adjusting values to match a hydrocast at deployment ($\text{Nitrate}_{\text{corrected}} = (\text{Nitrate}_{\text{raw}} - 4.78)/0.977$). No drift correction was made until the float grounded at Kerguelen in mid-2010. After that point, all nitrate values were adjusted with the difference between the observed and predicted nitrate at 650 m.

Johnson et al. (2010)]. Similar precision is seen for 3 yr of data from 1000 m at OSP (Fig. 8d). Finally, the sensor response is linear over the entire oceanographic nitrate concentration range, as shown in Fig. 4.

5. Conclusions

The development of reagent-free optical nitrate sensors now allows long-term observations of ocean nutrient chemistry from autonomous platforms, such as profiling floats (Johnson et al. 2009). Integration of the ISUS nitrate sensor into APEX profiling floats has produced an extremely useful platform and sensor combination that is providing unparalleled views of nutrient cycling in the ocean. This capability enables a variety of carbon cycle processes to be quantified. For example, the sensor can easily resolve the seasonal cycle in nitrate at high latitudes (Fig. 8). The nitrate uptake is directly coupled to carbon production (Wong et al. 1998, 2002). Such a capability will allow high-quality in situ measurements of net community production and carbon export in these waters using the observed annual cycle in nitrate concentration (MacCready and Quay 2001; Wong et al. 1998).

Small sensor drifts and offsets in nitrate concentration are apparent in oligotrophic, low-nutrient waters (Fig. 5). These errors in nitrate concentration appear as constant offsets over the entire vertical profile. If nitrate concentrations at the surface or at depth can be assumed to be constant during a deployment, then the error at the reference depth can be added back to the entire profile and a much higher-quality set of nitrate data is obtained. Such a procedure has already been used to study nitrate acquisition mechanisms in oligotrophic waters near Hawaii (Johnson et al. 2010). This would enable a quality-controlled dataset with greater accuracy than the original to be produced in most ocean locations.

Acknowledgments. This work was supported by the David and Lucile Packard Foundation, NSF Grant 0825348, NOPP/Office of Naval Research Grant N00014-09-10052, and NOAA Grant NA17RJ1232, part 2 to the University of Washington. Dale Ripley and Rick Rupan at the University of Washington contributed immensely to this work. We thank personnel at the Hawaii Ocean Time-Series program for deployment of floats at HOT, Steve Emerson for deployment at OSP, and Kevin Speer for

deployment in the Southern Ocean on the CLIVAR I06 cruise. We gratefully acknowledge the Hawaii Ocean Time-Series Program and the Line P program at the Institute of Ocean Sciences (Canadian Department of Fisheries and Oceans) for providing rapid, online access to their data. MBARI has licensed the design of the ISUS and receives royalty payments for commercial sales of the instrument.

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