

of where oceanic water originated from, in this case water coming

from the Atlantic and entering into the Artic basin.

New Insights from High Resolution and Long-Term Chemical Measurements with the MBARI In Situ Ultraviolet Spectrophotometer

L.J. Coletti, K.S. Johnson, C.M. Sakamoto, Z. Chase, J.A. Barth, J.G. Bellingham, F.P. Chavez, S.E. Fitzwater, P.G. Strutton, P.M. Walz and N. Tervalon

Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road Moss Landing, CA 95039; e-mail: johnson@mbari.org

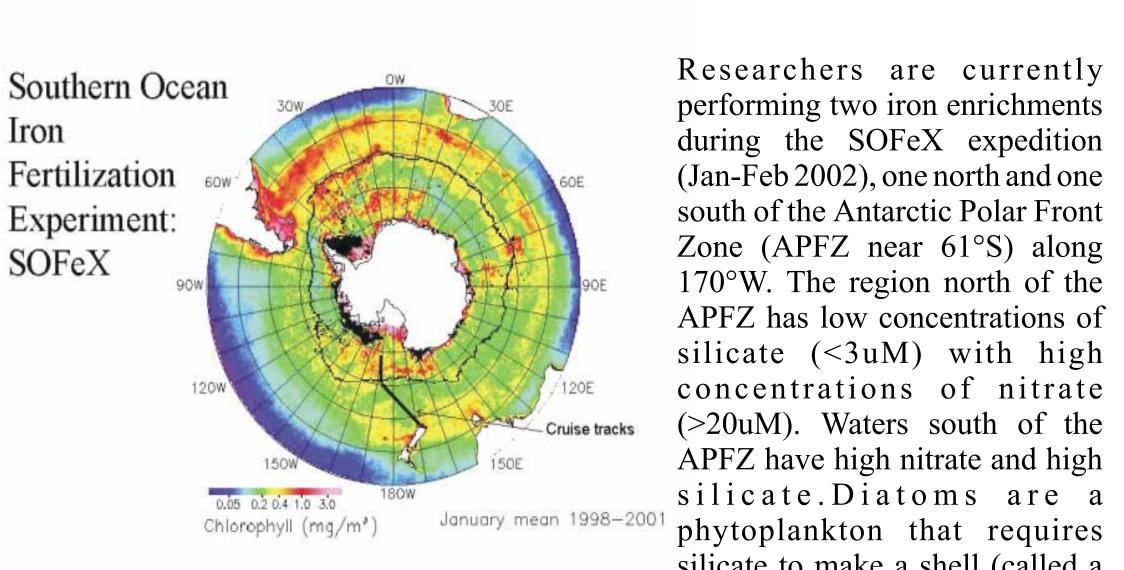


The MBARI ISUS in 4000m rated housing

A cross-shelf grid off undulating vehicle SeaSoar. Cold, salty, nitrate-rich subsurface water has been upwelled over the outer upwelling. Recent wind (from the south) downwelling of property isolines near the coast (< 25 km

offshore and 20 meters nearshore. ISUS reported (via RS232 connection to towfish CTD) in-situ nitrate values at a 1Hz rate

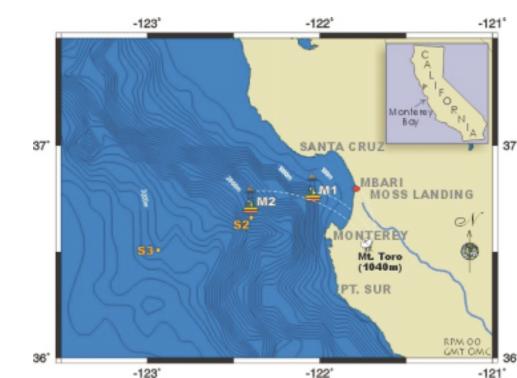
High Resolution Nitrate Profiling on the MBARI Trace Metal CTD/Rosette



Researchers are currently performing two iron enrichments during the SOFeX expedition (Jan-Feb 2002), one north and one south of the Antarctic Polar Front Zone (APFZ near 61°S) along 170°W. The region north of the APFZ has low concentrations of silicate (<3uM) with high concentrations of nitrate Cruise tracks (>20uM). Waters south of the APFZ have high nitrate and high silicate.Diatoms are a silicate to make a shell (called a

test). Diatoms remove most of the carbon dioxide from surface waters. Although both regions have high nitrate, diatoms may not grow north of the front due to Si limitation. I diatoms don't grow north of the front, where most of the high nitrate low chlorophyll (HNLC) water is found, then the Iron Hypothesis may not work. However, the experiment thus far seems to indicate that introducing iron into a HNLC region can indeed stimulate growth, currently (Feb 10) the North Patch (54°12'S 169°36'W) chlorophyll is at least 5 times higher than any chlorophyll concentration within 1000 km.

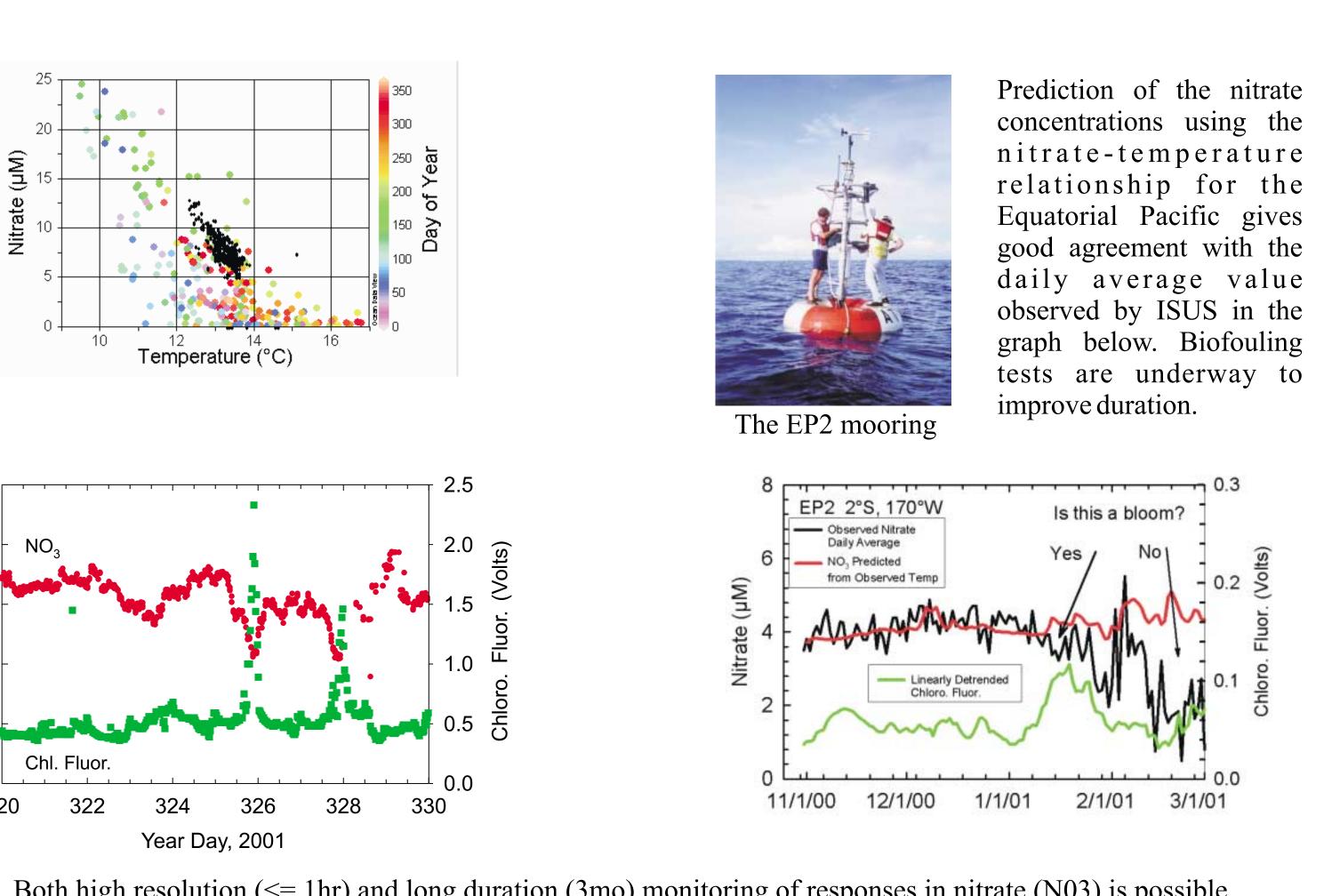
To measure in-situ nitrate three ISUS instruments are being used as part of this experiment; two are mounted from drifters operating in the enrichment areas ("patches") and monitor the surface values while a third is being used to provide high-resolution vertical profiles.

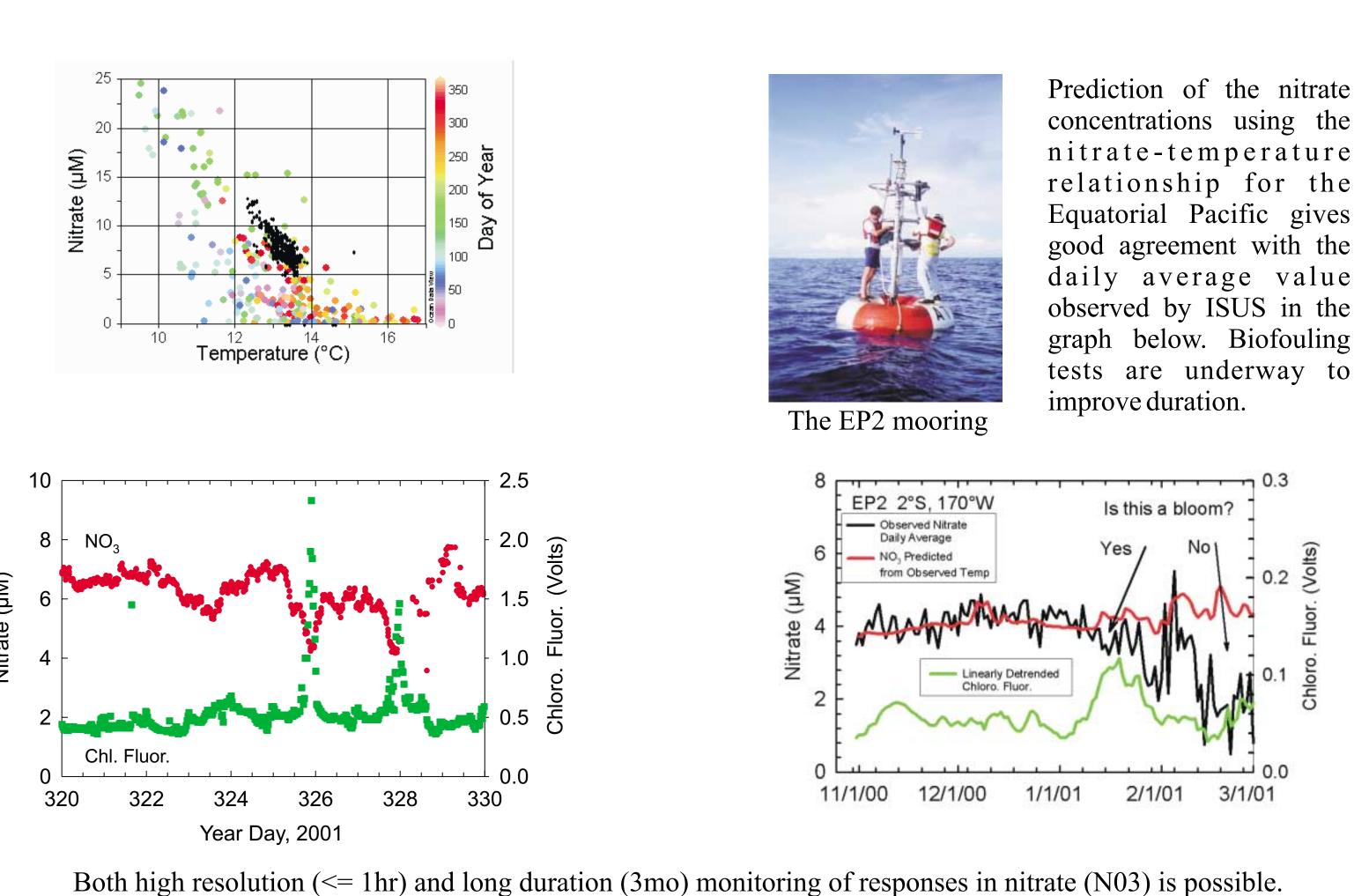


Location of MBARI M1 mooring

The temperature-nitrate and time relationship for multi-year M1 sample data matches well with ISUS data in the graph above right. The daily averaged ISUS data from Oct-Dec 2001 represented in black and multi-year M1 sample data shown in color.

Episodic events with associated nitrate consumption are shown during the same deployment period as above (Oct-Dec 2001) in the graph directly right. ISUS samples once an hour and can operate in this mode for over a year from a single battery pack.



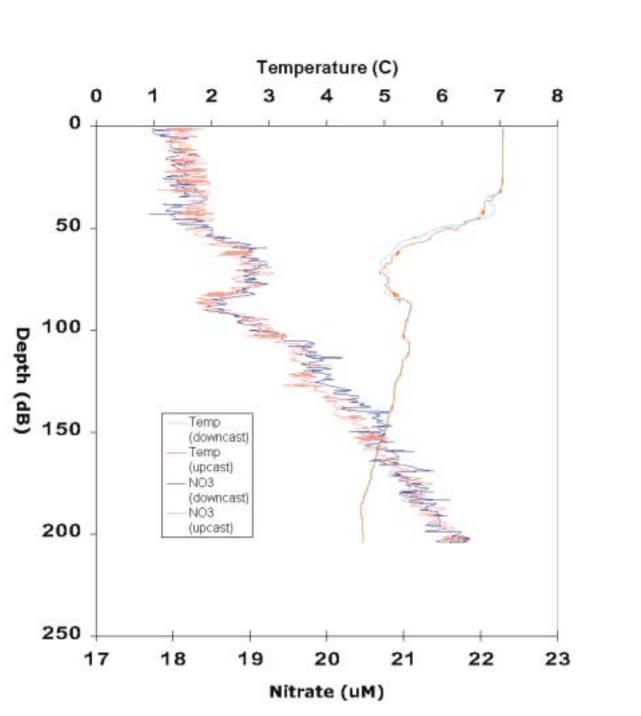


UV absorbance spectra for compounds of interest to oceanographers, including nitrate, nitrite, bisulfide (HS⁻) and bromide are shown at right at concentrations typical in the marine environment. In the past 40 years, there have been several analytical methods developed for the direct determination of these compounds based on their UV absorption, including an APHA standard method for nitrate analysis. These methods have not become widely used, in part because the analytical methods were usually based on measurements at a single wavelength. A measurement at a single wavelength does not allow chemicals with overlapping spectra to be differentiated. However, advances in the development of diode array spectrophotometers now make it simple to rapidly collect full spectra in the UV region. Spectral deconvolution techniques make it feasible to determine these compounds directly in seawater, without any interferences, and with no chemical manipulations. Robust, multispectral methods for nitrate determination in such difficult solutions as unfiltered waste water or ground waters have recently been developed (Thomas et al., 1990; Karlsson et al., 1995; Holm et al., 1997).





ISUS mounted in bottom cage



Vertical nitrate profile taken by ISUS at SOFeX CTD station 11 (55°57'S 177°52'W). ISUS collects and reports (via analog voltage connection to CTD) in-situ nitrate values at a 1Hz rate. High resolution nutrient profiles, previously unattainable at this rate, are now being used in field experiments to gain insight into nutrient structures.

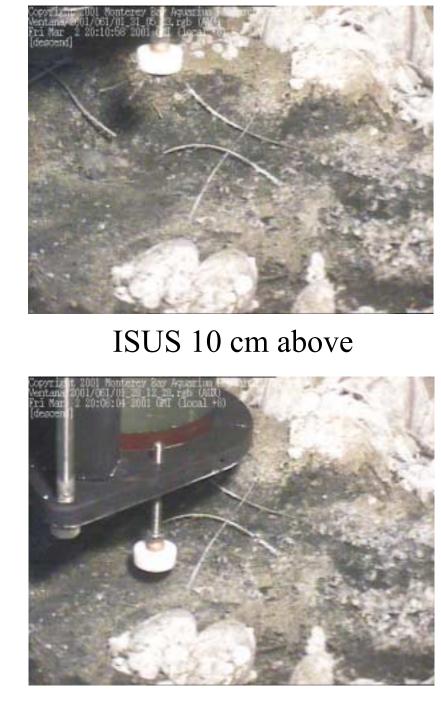


In Situ Profiling of Ambient Bisulfide (HS-) using the MBARI ROV Ventana

ISUS has been deployed from the MBARI ROV (Reomtely Operated Vehicle) Ventana over cold seeps with clam communities in the Monterey Bay at depths of 960m to measure ambient bisulfide. It was initially believed that no sulfides would be detectable in the water column, however, small scale vertical profiles (image sequence



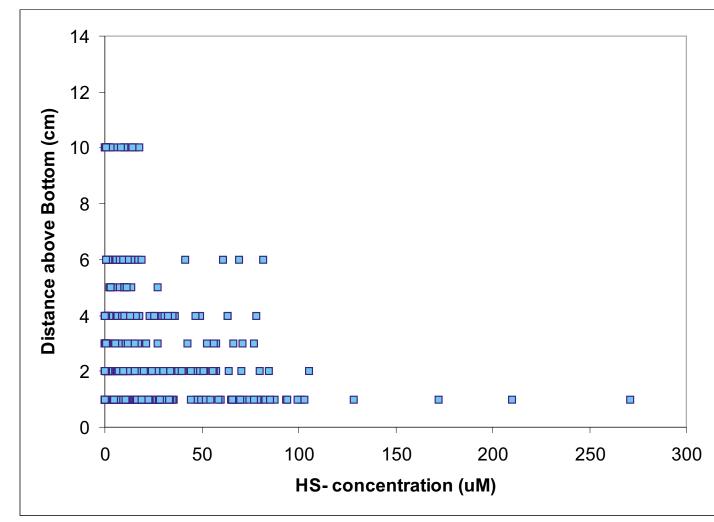
below) revealed that significant concentrations do exist directly over these seeps. The ROV was fitted with a special vertical profiler, built by MBARI personnel, that controlled the height of ISUS above the sediments.





ISUS 4 cm above

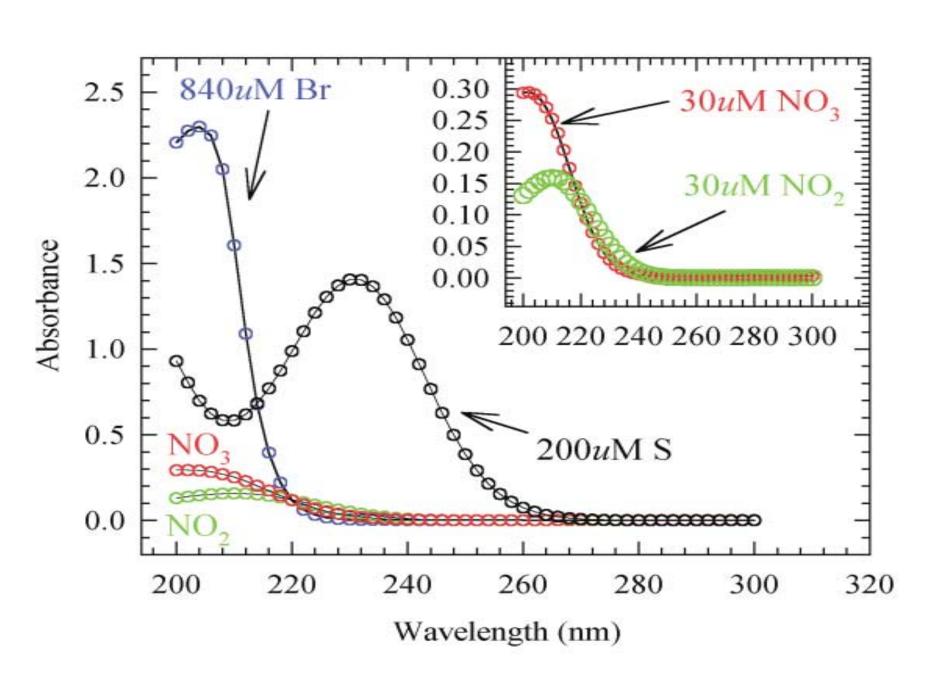
ISUS 2cm above



Distribution of bisulfide (HS-) concentrations above cold seep in Monterey Bay, California



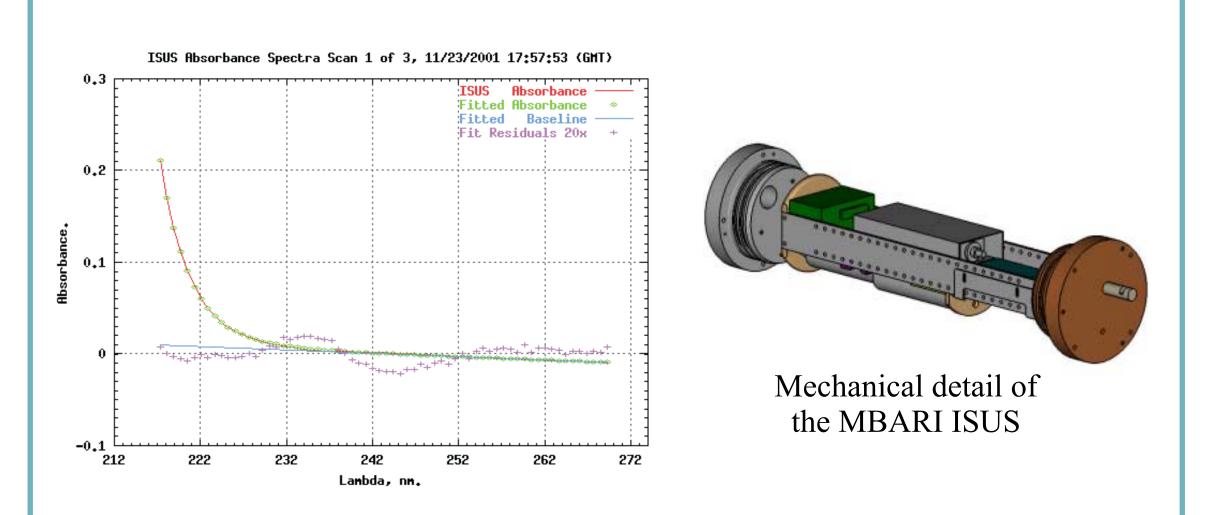
Background





Operation

An immersed optical reflection probe images UV light from a continuous wave, line-free lamp into a fixed volume of ambient solution. The UV light passes out through the solution to the probe's mirror, is reflected back through the solution to the probe's imaging optic and is finally reimaged for measurement. The measurement is made using a multi-element spectrometer with holographic grating (200-400nm). As UV light passes through the solution it is absorbed by the various dissolved compounds present. The spectrometer measures the absorbance spectra of the solution and the data are stored. Numerical methods are then applied to determine the concentrations of the constituent compounds. The graph below illustrates the typical shape of an absorbance spectra for surface seawater in Monterey Bay, California. The graph also contains the end products from the numerical analysis. The determined concentrations for this sample, calculating for nitrate and bromide, i.e., "optical salinity", were 3.8 uM and 33.13 pss respectively.



Conclusions

Optical measurements of nitrate and sulfide concentrations can be made in seawater to 4000m with a submersible, low power spectrophotometer. This approach can measure nitrate and sulfide at concentrations near 0.1 μ M. High resolution measurements (< 1 s) are possible from vertically profiling platforms. The instrument is stable and we plan to continue deploying it for both long term measurements from deep sea moorings and high resolution vertical profiles from various platforms.

References

Guenther, E. A., K. S. Johnson, K. H. Coale. 2001. Direct ultraviolet spectrophotometric determination of total sulfide and iodide in natural waters. Analytical Chemistry, 73: 3481-3487.

Johnson, K. S. and Coletti, L. J. In prep. In situ ultraviolet spectrophotometry for high reolution and long term monitoring of nitrate, bromide and bisulfide in natural waters.

Acknowledgments

This work was supported by NSF Grant OCE 9906983 and by a grant from the David and Lucile Packard Foundation to the Monterey Bay Aquarium Research Institute.