

ISUS/SUNA Nitrate Measurements in Networked Ocean Observing Systems

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Sustaining measurements of water quality parameters in sensitive watershed habitats is challenging, particularly during critical periods such as spring blooms, and major run off events. Direct, in situ measurements of nitrate have been difficult to obtain until the development of the ISUS (In Situ Ultraviolet Spectrometer, Johnson & Coletti 2002) and more recently the next generation SUNA (Submersible Ultraviolet Nitrate Analyzer). These chemical-free optical sensors have now been operating in a wide range of challenging environments over the past five years. Performance evaluations of these instruments, lessons learned, and environmental insights obtained will be discussed, as well as results from these sensors under the recent ACT (Alliance for Coastal Technologies) Nutrient Sensor Technology Demonstration Program.

I. INTRODUCTION

Remote in situ time series measurements of nitrate in open and coastal oceans are critical inputs into water quality monitoring programs, harmful algal bloom early warning systems and large scale physiological modeling research. The original In Situ Ultraviolet Spectrophotometer (ISUS) optical nitrate sensor was developed by Ken Johnson and Luke Coletti at the Monterey Bay Aquarium Research Institute (MBARI) to provide robust, continuous long-term nitrate measurements from unattended, remote platforms [1]. The ISUS is a chemical-free optical sensor that utilizes the UV absorption characteristics of dissolved nitrate to measure in situ concentrations directly, without the need of reagents or incubations. More recently, Satlantic has leveraged the ISUS technology to produce a shallow water version called the SUNA (Submersible Ultraviolet Nitrate Sensor) optimized for near-shore and fresh water deployments. Both

the ISUS and SUNA utilize the broad spectral range required to accurately resolve nitrate absorption spectra in complex media such as marine, estuarine and fresh waters.

While the ISUS has had many demonstrated successes in long-term oceanographic deployments, estuarine and fresh water environments have been more challenging due to the greater potential for interfering species, contaminants and bio-fouling. Through the collaboration of a vast network of ISUS users, effective mitigation techniques have been developed and refined over the past several years. This paper summarizes the major challenges effecting in situ optical nitrate sensors, reviews performance evaluation results and suggests techniques for optimizing deployments to return robust and useful long-term nitrate data sets.



Fig. 1. ISUS nitrate sensor PVC version with copper bio-fouling guard (top) and stainless steel SUNA (below).

II. ISUS/SUNA Technology

Absorption of UV light in seawater is dominated by dissolved nitrate and bromide ions at wavelengths less than 240 nm. The intrinsic absorption spectra

of both species allows for direct measurement of each without the need for addition of chemical reagents. The optical sensing systems of both the ISUS and SUNA instruments are designed to accurately measure absorption spectra with a resolution of approximately 1 nm. In the ISUS, this is achieved using a stable UV light source, a fiber optic sensing probe and a precision spectrometer. The optical sensing system measures in situ absorption spectra, which are then separated into contributing species by a least squares fitting algorithm [1]. The implementation of the processing algorithm on the embedded processor delivers real-time nitrate concentration measurements at a rate of 1 Hz.

The onboard absorption curve-fitting algorithm uses laboratory calibrated instrument-specific extinction coefficients for nitrate and bromide to resolve the contributions of each. However, since the absorption properties of bromide ions are temperature dependent [2], a third temperature compensation factor is required to obtain maximum accuracy.

The SUNA nitrate sensor was developed in 2008 as a smaller, shallow water version of the ISUS sensor.

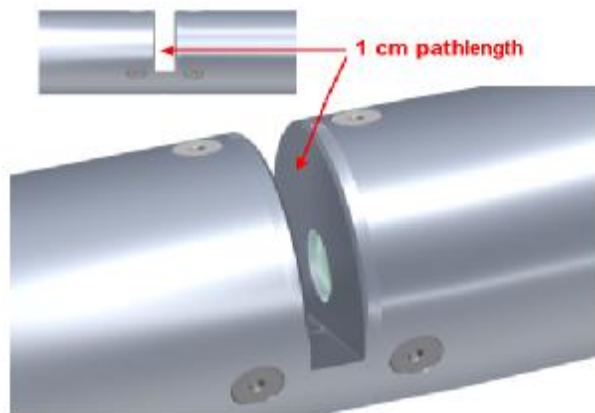


Fig. 2. Diagram of SUNA sample chamber with quartz window.

The main differences between the ISUS and SUNA are the replacement of the fiber-optic sensing probe with a straight-through quartz sampling chamber (Fig. 2) and the replacement of a single board computer with a microcontroller used for nitrate calculations only. That is, the SUNA does not have the onboard data storage or scheduling capabilities

of the ISUS. These capabilities were removed in an effort to offer a lower cost alternative for cases where an external data logger duplicates these features. Since the core optical sampling systems are identical, the SUNA achieves similar performance specifications as the ISUS.

III. Performance Evaluations

A. ISUS V3

The latest version of the MBARI-ISUS, the ISUS V3, was evaluated in the Alliance for Coastal Technologies (ACT) Performance Demonstration of in situ nutrient analyzers in 2007. The demonstration consisted of deployments in Resurrection Bay Alaska, Chesapeake Bay Maryland, and Monterey Bay California [3]. The Chesapeake Bay and Resurrection Bay deployments were one-month mooring deployments in contrasting environments, while the Monterey Bay operation consisted of an 8-hour horizontal surface survey.

The Resurrection Bay test site was in Humpy Cove (Fig. 3), a pristine glacial fiord characterized by relatively clear (average beam transmission 86%), low chlorophyll, low nutrient waters with limited anthropogenic inputs.



Fig. 3. ACT instrument mooring site at Humpy Cove in Resurrection Bay, Alaska.

Local nitrate levels were quite low for the duration of the deployment ($< 2 \mu\text{M}$), with small variations

successfully tracked by the ISUS V3 (Fig. 4). A pattern of higher variability at the beginning of the deployment gradually improved towards the end. This trend is typically reversed for long-term deployments as the calculated nitrate values can be affected by increased bio-fouling. Bio-fouling was not an issue during this 30-day deployment.

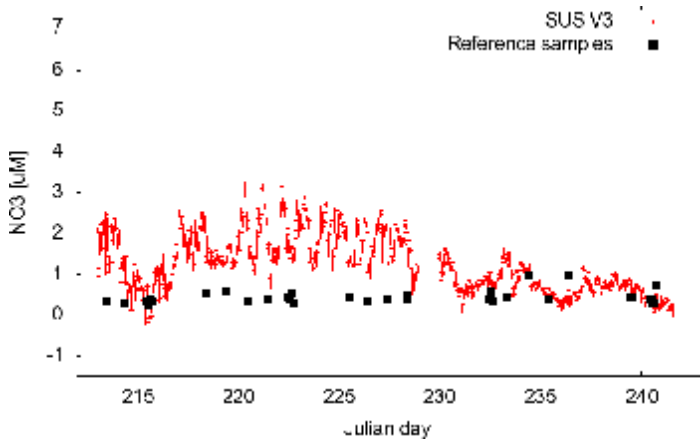


Fig. 4. Time series comparison of the Atlantic ISUS V3 measured nitrate versus laboratory measured reference samples.

The test site was very shallow (< 2m) with relatively low flow (compared to open coastal areas). The initial measurement variability may have been a result of the stirring of glacial silt which interfered with the optical sample before being eventually flushed from the bio-fouling guard. The ISUS V3 uses a passive copper bio-fouling guard with a 100 µm Nitex screen. While the guard successfully protected the ISUS from bio-fouling over the course of the deployment, it may have trapped fine silt particles stirred up from the shallow deployment activity. In such environments, removing the Nitex mesh and using the copper shield alone reduces the buildup of silt particles within the guard and improves results. Alternatively, a pumped flow-through cell can be installed to prevent both bio-fouling and sediment buildup in more challenging environments.

The ISUS V3 was also deployed for a 30-day mooring test at the Chesapeake Bay Laboratory (CBL) sampling pier in the Patuxent River (Fig. 5). The water quality at the CBL site was markedly different from that in Resurrection Bay. The Chesapeake site was characterized by optically dense water (average beam transmission of 52%) with high CDOM and chlorophyll concentrations five times greater than in Resurrection Bay.

Nutrient concentrations were also much greater with nitrate trending from 13.5 µM at the beginning of the deployment to 2.1 µM at the conclusion. Once again, despite the greater fouling potential at this site, the copper anti-fouling guard successfully protected the ISUS V3 sample probe from biological growth.



Fig. 5. ACT instrument mooring at the Chesapeake Bay Laboratory pier.

The ISUS V3 time series correctly resolved the episodic nitrate variations and overall hourly trend over the 30-day deployment (Fig. 6). However, the nitrate calculations produced by the ISUS V3 contain a consistent offset that is likely caused by the relatively high optical density of the water dominated by very high levels of CDOM (see section IV 'Lessons Learned' for more on CDOM interference).

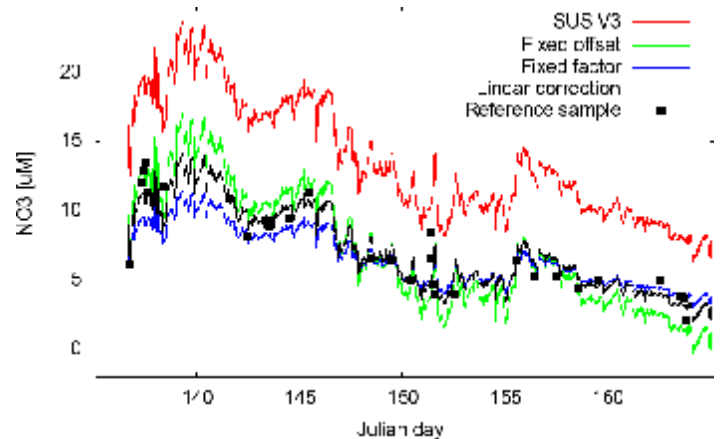


Fig. 6. Time series comparison of the Atlantic ISUS V3 measured nitrate versus ISUS corrected data and laboratory measured reference samples.

Absolute accuracy from the hourly time series was obtained by applying a correction factor calculated from the reference samples (Fig. 6). We evaluated three methods to correct the time series ISUS V3 data to match the discrete lab analysis values: (1) Assume there is a fixed offset between the in situ and laboratory data. This option produces an offset correction of $6.6 \pm 0.3 \mu\text{M}$. (2) Assume there is a fixed factor between the two data sets. This option produces a correction factor of $2.06 \pm 0.1 \mu\text{M}$. (3) Assume a linear relationship with a fixed offset and fixed factor so that $\text{NO}_3(\text{true}) = \text{Offset} + \text{Scale} * \text{NO}_3(\text{ISUS})$. The best fit is $\text{Offset} = -2.47 \pm 0.96$, $\text{Scale} = 0.71 \pm 0.07$.

In this case, all three methods provided excellent fits with the reference laboratory samples, indicating that the cause of the offset was consistent throughout the deployment. Absorption data from the ISUS V3 were examined for the 250 nm wavelength channel to see if the nitrate offset co-varied with absorption, possibly indicating a causal relationship with an absorbing species other than nitrate. No relationship was found however, further signifying that the ISUS V3 correctly resolved the relative changes in in-situ nitrate over the month long deployment.

The ISUS V3 was also successfully employed in a surface mapping application in Monterey Bay using a flow through system onboard the R/V John H. Martin. For this application, the anti-fouling guard used in the mooring deployments was replaced with a flow through chamber and the system was supplied with water pumped from a depth of 1 m [3]. The survey spanned a wide range of water quality conditions from the Elkhorn Slough to the coastal ocean with a two orders of magnitude variation in nitrate concentration. Although the computational noise was greater in the highly turbid harbour waters (beam transmission $< 20\%$), the real-time ISUS V3 nitrate measurements closely matched the wet chemistry derived reference samples over the entire range (Fig. 7).

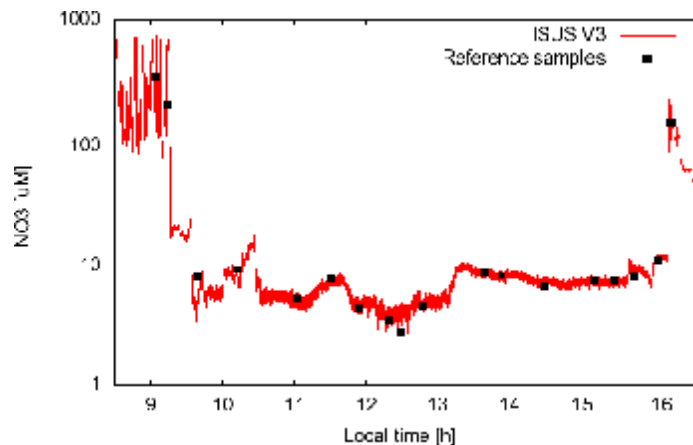


Fig. 7. Surface mapping time series of the Monterey Bay using the ISUS V3.

B. SUNA

The first SUNA prototype was deployed in the North West Arm of Halifax Harbour where Satlantic maintains a Land/Ocean Biogeochemical Observatory (LOBO) for testing and demonstration purposes [4]. In addition to measuring nitrate concentrations, the LOBO buoy system is outfitted with a suite of instruments which record time series measurements of salinity, temperature, CDOM, turbidity, dissolved oxygen and chlorophyll fluorescence on an hourly basis (Fig 8).



Fig 8. Land/Ocean Biogeochemical Observatory (LOBO) deployed in the North West Arm of Halifax Harbour, Nova Scotia.

The SUNA was first deployed on the LOBO buoy on February 8, 2008. For the first two months of the deployment, the ISUS V3 was also left on the LOBO to provide a cross comparison and

validation of in situ nitrate concentrations. As expected, the instruments agreed very closely, both tracking and identifying nitrate spikes associated with significant run-off events (Fig 9). This was to be expected since both instruments share key sensing components and computational algorithms. This test indicated that no instrument artifacts were introduced with the new optical design.

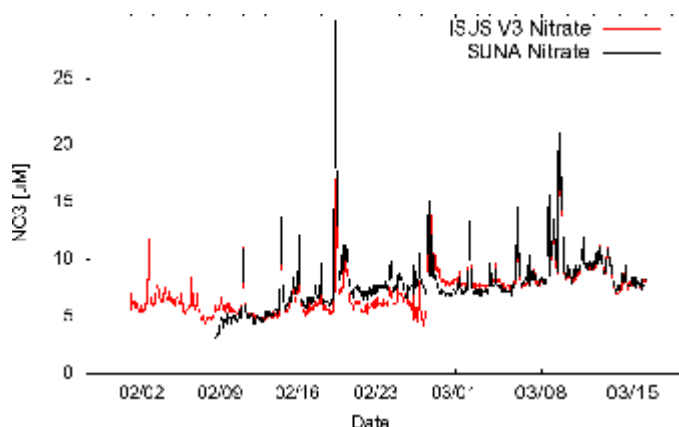


Fig. 9. Time series nitrate measurements (mM) from the North West Arm LOBO showing both the ISJ5 V3 (red) and the SUNA prototype (green).

More recently, the SUNA has been used to monitor the progression of the spring bloom in Halifax Harbour. A LOBO time series from the winter of 2009 demonstrates that the nitrate and fluorescence levels remained high and low respectively throughout the winter months (Fig. 10).

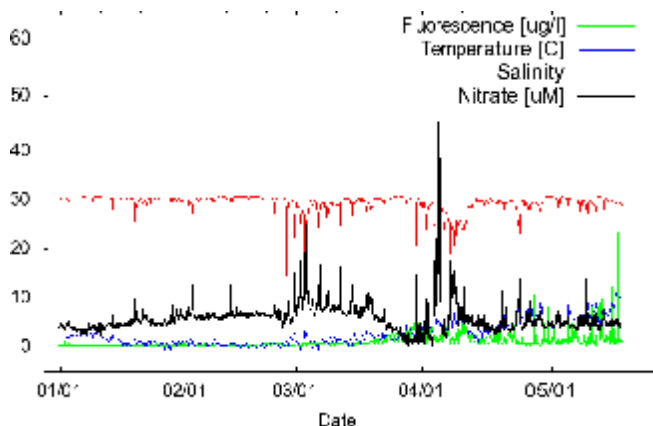


Fig. 10. Time series measurements from the LOBO buoy system (<http://lobo.satlantic.com>) showing the progression of the Spring Bloom.

Major run-off events caused by significant rain and snow melt caused major nitrate spikes towards the beginning of March. Then as day length and water temperature increased towards the end of March,

the in situ nitrate concentration was drawn down as the background fluorescence increased. Just as the bloom was developing however, a major rain and spring melt event (as evidenced by the salinity data) triggered a major injection of fresh water that caused a major nitrate spike. Since the North West Arm site is coastal with a 2m tidal range, high nitrate fresh water infusions diffuse relatively quickly. This is evidenced by both the salinity and nitrate time series data.

IV. Lessons Learned

A. Interfering species

One of the main challenges to obtaining accurate long-term nitrate time series data is the influence of interfering species. Interfering species come in two forms: spectrally neutral and spectrally variable.

Spectrally neutral interfering species such as fine silt and sediment affect each wavelength in the critical range of 217 nm to 240 nm equally. Because the nitrate calculation is derived from the shape of the absorption curve within this wavelength range, spectrally flat absolute changes in the magnitude of the absorption curves have no effect at low concentrations. At higher concentrations however, the light signal can be significantly reduced causing certain wavelengths to be close to the noise floor or completely extinct. In such cases, the fitting algorithms cannot compensate and the resulting nitrate calculation is significantly effected. To mitigate this effect, a new adaptive fitting algorithm has been implemented to exclude wavelengths that have a signal below an adjustable threshold. This new automatic wavelength adjustment has the potential to vastly improve results in highly turbid waters. Although this method has been tested and verified under laboratory conditions, it has not yet been verified under challenging field conditions.

Spectrally variable interfering species such as colored dissolved organic matter (CDOM) have variable absorption characteristics in the UV wavelength range. Although the absorption curve for CDOM increases exponentially with decreasing wavelength in the UV region, within the critical wavelength range used for the nitrate calculation, the absorption spectra is linear (Fig. 11). As a

result, at lower concentrations typically experienced in the open and coastal ocean, the absorption signal for CDOM is easily compensated for by the linear baseline correction of the fitting algorithm [1].

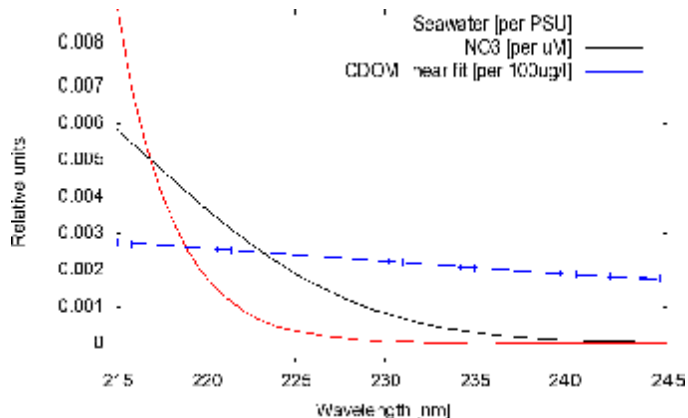


Fig. 11. Extinction coefficients for nitrate, bromide (Seawater) and CDOM (Suwannee River Fulvic Acid).

At higher CDOM concentrations typically found in nutrient rich estuaries and fresh water systems, the strong absorption can lower the overall signal to an extent that creates an offset in the nitrate calculation. This may have been the case in the Chesapeake Bay portion of the ACT performance evaluation (Fig. 6). In such cases, the ISUS V3 or SUNA still provide essential time series trends and capture the diurnal and episodic changes in concentration. The absolute accuracy of the nitrate data can then be corrected *post hoc* using discrete sample analysis. Work continues to parameterize the CDOM signal and incorporate it as an additional fitted parameter to improve the accuracy of the nitrate calculation. While this effort is ongoing, it is complicated by the variable nature and composition of CDOM from various sources.

B. Temperature dependence of Bromide Extinction Coefficients

One area of accuracy improvement that has recently shown significant progress is in correcting offsets caused by the temperature dependence of bromide extinction coefficients. As mentioned in Section II, bromide ions absorb strongly in the critical range of the UV spectrum and are therefore calibrated for and fitted in the nitrate calculation

algorithms. The research team from MBARI have recently recognized the importance of the temperature dependence of bromide extinction coefficients on the accuracy of the nitrate calculation. As a result, they devised, tested and verified a methodology for applying independently measured temperature and salinity data to accurately determine the portion of the measured absorption spectra attributed to bromide [5]. Consequently, comprehensive instrument packages which include ISUS V3 or SUNA instruments with conductivity and temperature probes, as on the LOBO buoy system, offer the potential for significant post processing accuracy improvements (Fig 12).

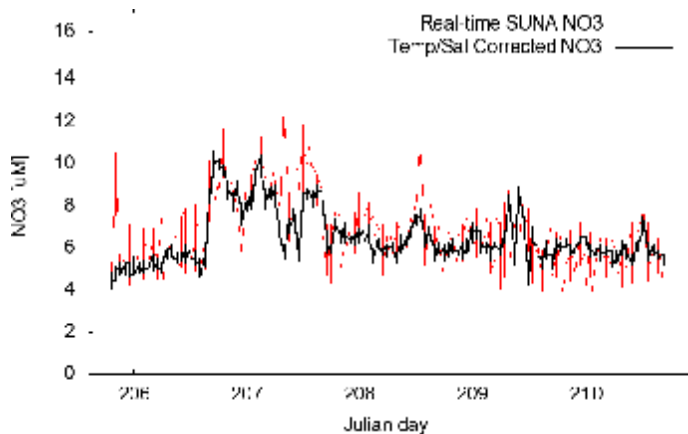


Fig. 12. SUNA nitrate data collected from the North West Arm LOBO system, raw and re-processed with the temperature/salinity correction.

An initial version of the temperature-salinity correction algorithm has been tested with recent data from Satlantic's North West Arm LOBO system. A short-term nitrate time series from the LOBO mounted SUNA was re-processed using concurrent temperature and salinity data also logged by the LOBO. Because the salinity and temperature data are known, the absorption curve fitting algorithms need only solve for nitrate and a linear baseline, reducing the number of fitted variables from five to three. This approach significantly improves the precision of the nitrate calculation, reducing the measurement standard deviation of the test data set from 0.8 to 0.2, or a four-fold improvement.

The next step in this development is to include this correction capability in ISUS V3 and SUNA post-

processing software as well as future versions of the LOBOViz software.

V. Summary

In summary, advances in in-situ optical sensor technology have improved both the accuracy of measurements as well as duration of deployments while opening the technology to broader applications and sensing environments. Through further characterization of common interfering species and improved algorithms incorporating ancillary environmental data, achievable accuracy will continue to improve.

References

- [1] K.S. Johnson, and L.J. Coletti, "In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide, and bisulfide in the ocean", *Deep Sea Research I*, **53**, 561-573, 2002.
- [2] V. Di Noto, M. Mecozzi, "Determination of Seawater Salinity by Ultraviolet Spectroscopic Measurements". *Applied Spectroscopy*, V51, N9, p 1294, 1997.
- [3] "Performance Demonstration Statement Satlantic ISUS V3 Nitrate Sensor". Alliance for Coastal Technologies TD08-02, 2008.
- [4] A.J. Comeau, M.R. Lewis, J.J. Cullen, R.S. Adams, J. Andrea, S. Feener, S.D. McLean, K.S. Johnson, L.J. Coletti, H.W. Jannasch, S.E. Fitzwater, C. Moore, A.H. Barnard, "Monitoring the Spring Bloom in an Ice Covered Fjord with the Land/Ocean Biogeochemical Observatory (LOBO)", *Proceedings of Oceans 2007*.
- [5] C.M. Sakamoto, K.S. Johnson, L.J. Coletti. "Improved Algorithm for the Computation of Nitrate Concentrations in Seawater using an in situ Ultraviolet Spectrophotometer", *Limnology and Oceanography: Methods* 7, 132-143, 2009.