

Real-Time Monitoring of Nitrate in Estuaries with the MBARI ISUS

The MBARI ISUS (In-Situ Ultraviolet Spectrometer) is a real time, chemical free system designed to overcome the traditional challenges associated with nitrate analyses in coastal and estuarine waters. ISUS provides easy, accurate, and continuous nitrate concentration measurements that are essential to the study of physical, chemical, and biological processes in natural waters (Figure 1).



Figure 1 - ISUS Deployment Florida Bay

ISUS was developed by the Monterey Bay Aquarium Research Institute (MBARI) in California. The technology is based on the absorption characteristics of inorganic compounds in the UV portion of the spectrum. These compounds absorb light in the UV with a unique signature, which can be resolved very accurately using a 256 channel spectrometer inside the instrument. Using a unique algorithm developed by MBARI, the system can measure nitrate in the most challenging of conditions, even in waters with very high concentrations of dissolved and particulate materials.

How can the ISUS retrieve accurate values for nitrates under such a large range of conditions, with different sediment and CDOM sources? The algorithm developed by MBARI is very effective at

removing this by using what we refer to as a baseline correction (Figure 2, Figure 3). When the

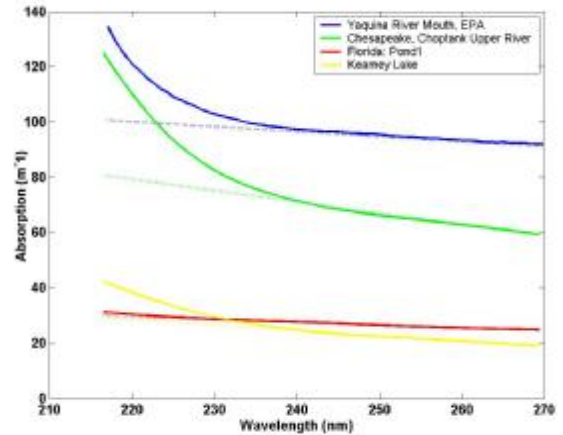


Figure 2 - Measured Spectra Showing Baseline

instruments are calibrated in the lab, the molar absorptivity of nitrate and bromide are calculated from a regression of 16 calibration samples over a range of nitrates, salinities and temperatures. This

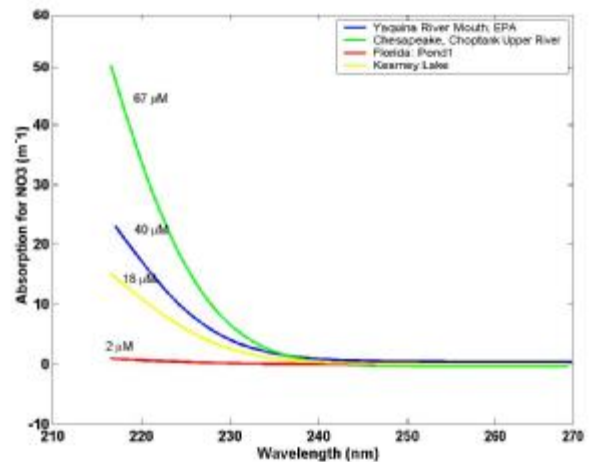


Figure 3 - Corrected Spectra Showing Computed Nitrate

information is stored internally in the system calibration file and is used for the real-time calculations. Field measurements are made using a

UV spectrometer, measuring the absorption spectra every 0.9nm, from 200 to 400nm. By using classical least square analysis over this large number of spectral channels (Johnson and Coletti, 2002), the baseline is computed, and the concentrations of bromide and nitrate are computed to reconstruct the measured spectrum. Accuracy is typically within $2\mu\text{M}$ or 10% of the nitrate reading, whichever is higher. Since the analysis is made statistically over a large number of spectral channels, the system can measure nitrate over a very wide range ($0\text{--}2000\mu\text{M}+$) and with very high levels of dissolved and particulate materials without interference in the accuracy of the results. This is all transparent to the user as the actual computation only takes the instrument internal computer a few milliseconds and outputs the concentration directly. For highly unusual conditions, the analysis algorithm can be adjusted by the user or by post processing using the original data set

Extensive validation of the system has been done by Dr. Ken Johnson and Luke Coletti at MBARI (Johnson and Coletti, 2002) for open ocean and coastal applications. Satlantic has collected data from various locations around the globe to create an extensive validation set for the system. The results include nearly 150,000 nitrate realizations, validated by periodic water sample analyses that use traditional autoanalyzer techniques. Although it is impractical to process samples with the same temporal and spatial resolution possible using the ISUS, these samples show the solid performance of this system over a wide range of conditions. Since the original design was principally validated in the open ocean, there was considerable interest in the performance in coastal areas and estuaries with high dissolved organic and particulate concentrations. We designed an extensive validation program specifically for estuaries in challenging conditions, including: Chesapeake Bay, the Everglades, an Oregon coastal estuary, and Nova Scotia peat drainage basins. The results are very impressive and show the temporal and spatial scales that can be addressed with real-time nitrate measurements.

The Chesapeake data set alone represents 15,000 measurements over a 160km transect (Figure 4) from up the Patuxent River, across the Bay and up the Choptank River. Real-time nitrate measurements, collected continuously every 2

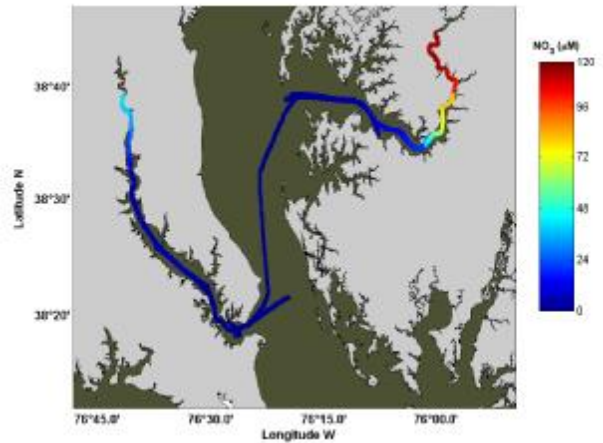


Figure 4 - Chesapeake Bay ISUS Nitrates

seconds, varied over the transect from 3 to $120\mu\text{M}$. The system also logged salinity, temperature, chlorophyll fluorescence, CDOM fluorescence, dissolved oxygen, pH and turbidity in a flow-through tank on deck. During the transect, the turbidity varied from 1 to 25NTU (Figure 5),

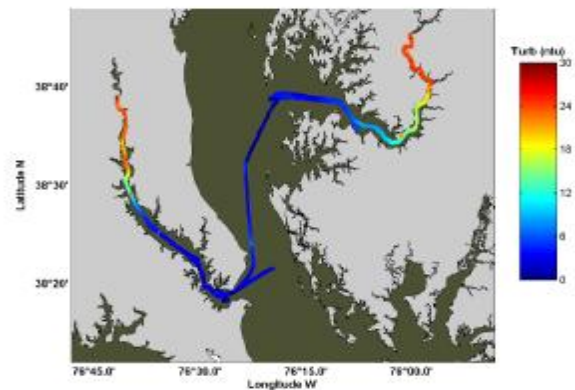


Figure 5 - Chesapeake Bay Turbidity

CDOM varied from 2-120+ QSU (the sensor actually saturated in the upper Choptank

River) (Figure 6), and the salinity varied

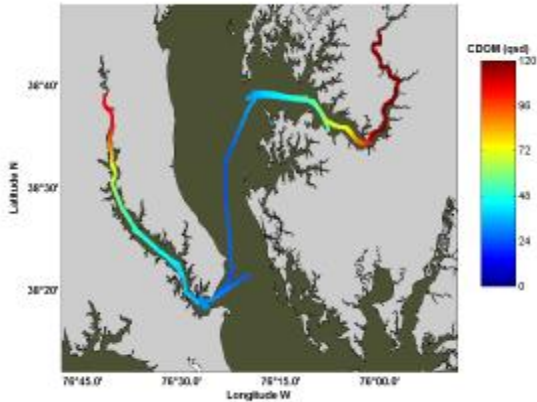


Figure 6 – Chesapeake Bay CDOM

from 0.3 to 15 psu . Over 50 validation samples were collected and processed by the autoanalyzer at the UMD HPL lab: the match with the real time data collected over this huge range was within $1.8\mu\text{M}$ (1σ) (Figure 7). At one point at the upper Choptank River site, the ISUS system was not even visible in

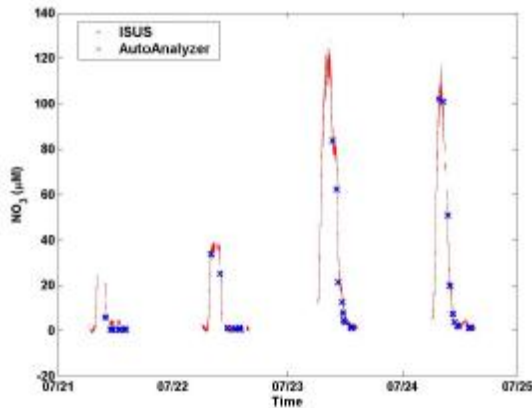


Figure 7 - Validation Sample Analysis

the 30cm deep tank it was in due to the combination of high CDOM and high turbidity (Figure 8), while still measuring accurate nitrate values.

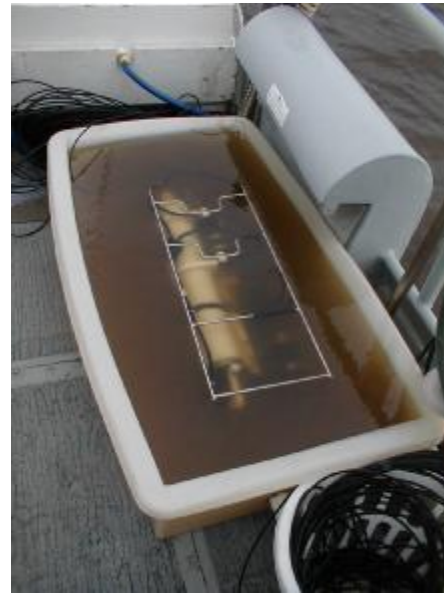


Figure 8 - ISUS in Flow Through Tank - Upper Choptank R.

In the Everglades, the system was towed along side of a small boat while navigating through the mangroves. CDOMs of up to 100 QSU were observed, nitrates varied from about 0-3 μM and were retrieved to within $1\mu\text{M}$ of validation samples processed at the SFWMD lab. It was even able to detect (in real time) a rapid gradient in nitrate (even at these low levels) caused by a subsurface flow (Figure 9).

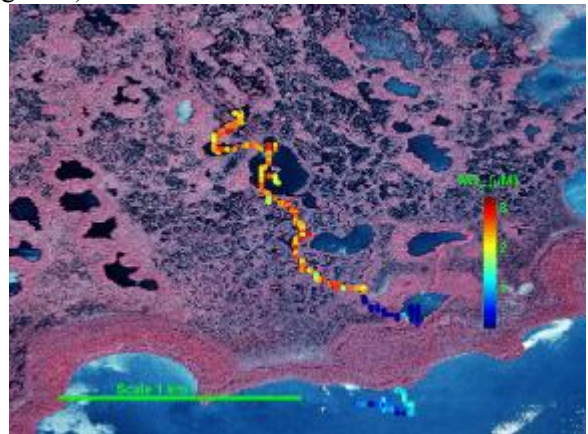


Figure 9 - ISUS Transect in Talyor Slough

In Yaquina Bay, Oregon, the system is moored at the EPA Pacific Coastal Ecology Branch dock, monitoring nitrates every 30 minutes for the past 3 months. This data demonstrates the temporal variability of estuaries that cannot be visualized by periodic water sampling using traditional methods (Figure 10). This work is part of a CRADA between

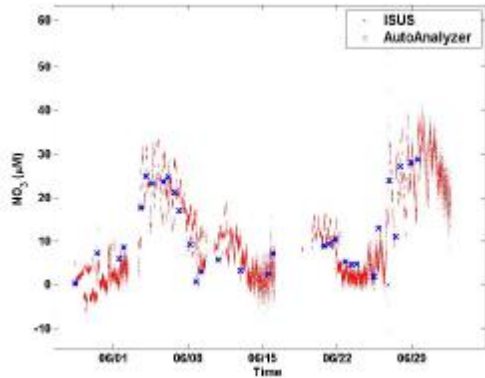


Figure 10 - EPA Test Mooring in Yaquina Bay

Satlantic and the EPA to provide real time monitoring of nutrients in coastal and estuarine waters.

MBARI has also tested the system in Elkhorn Slough, next to their facility in Moss Landing, California. Agricultural run-off into this system at low tide results in very high nitrate concentrations (over 800µM) and very high sediment loads (up to 60NTU). The ISUS performance was excellent under these conditions (Figure 11).

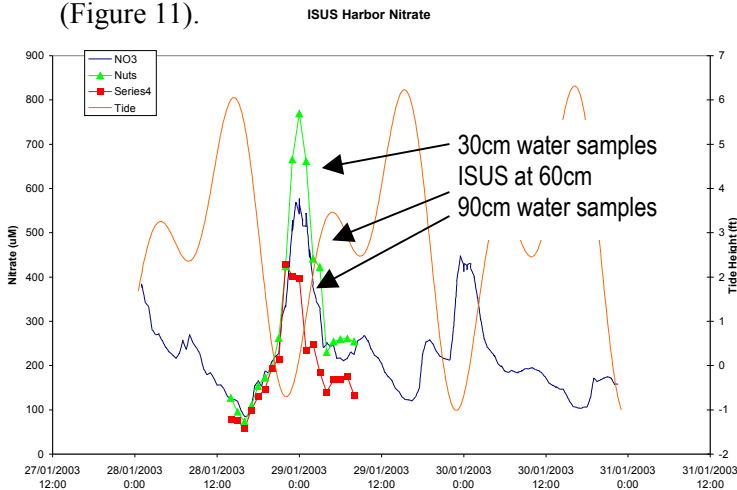


Figure 11 - ISUS Data From Elkhorn Slough

Lab testing has included samples of up to 14,000µM, showing the flexibility of the UV technique used by the ISUS.

The ISUS has been deployed in a wide range of environments and operational modes (buoys, profilers, towed vehicles, ROVs, flow-through systems and bench top). It has a number of interfaces that allow it to be easily integrated into a wide range of platforms and in special configurations, it can be used to merge multiple sensors into one data stream, such the system we used for our work in Chesapeake Bay (Figure 12).

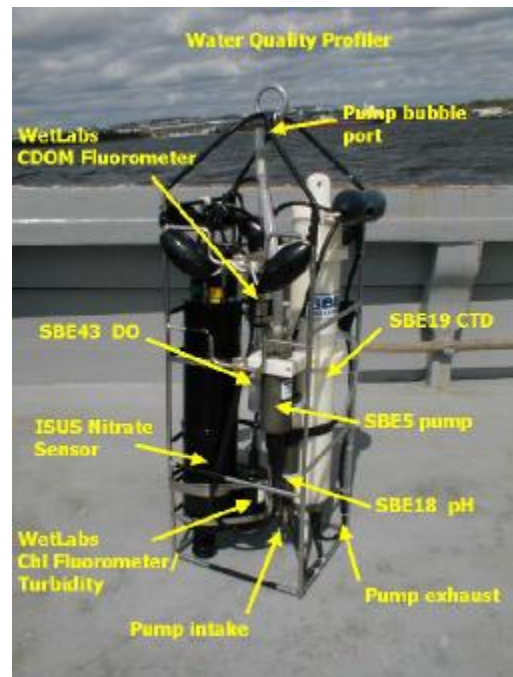


Figure 12 - ISUS Integrated as Water Quality Profiler

ISUS has proven to be stable, sensitive, and have the endurance to operate for extended periods with low maintenance, and no chemicals. The data sets collected have been able to demonstrate visualization of nutrients variability in the environment on temporal and spatial scales never before possible. Contact our team today to discuss your application and learn how our systems can help you solve your most challenging monitoring problems.