CASE STUDY
Measuring Nitrate in Puget Sound using Optical Sensors

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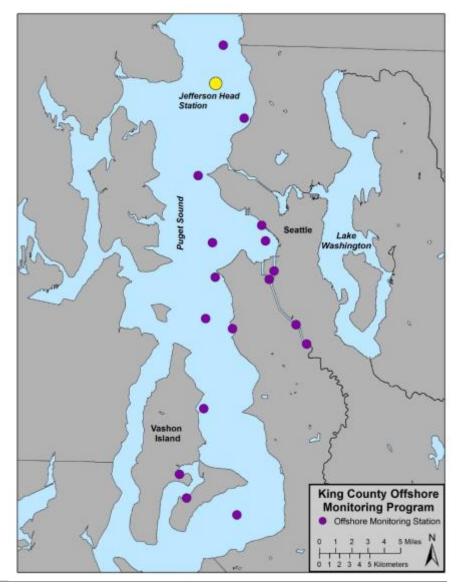
Field validation case study   October, 2017

The King County Dept. of Natural Resources and Parks (in Seattle, WA USA) conducts long-term marine monitoring to assess baseline conditions and trends in Central Puget Sound. Routine nutrient data, including nitrate, have been collected since 1994. Twice monthly observations are collected at several marine stations in Puget Sound (Figure 1), using a suite of biogeochemical sensors while concurrently collecting discrete water samples at multiple depths. This example enables the direct comparison of nitrate concentrations made with the SUNA nitrate to those made with traditional wet chemistry methods.

Figure 1: The yellow circle shows the location of Jefferson Head Station and the purple circles show the location of the other offshore stations (total of 18 sites) monitored by *King County Dept. of Natural Resources & Parks*.

A shipboard profiling carousel is outfitted with sensors to measure temperature, salinity, depth, dissolved oxygen, transmissivity, fluorescence, and nitrate. Five water sampling bottles mounted on the carousel are used to collect discrete measurements of bacteria levels (Fecal coliform indicators and Enterococcus), nutrient levels (dissolved inorganic nitrogen, total nitrogen, orthophosphate, and silica), pigment levels (Chlorophyll-a and Pheophytin-a), and physical parameters (dissolved oxygen, salinity, and total dissolved solids). This paper focuses on the SUNA nitrate sensor and discrete samples of nitrate + nitrite nitrogen collected at Jefferson Head Station (the yellow circle on Figure 1) on April 4th 2017. For information about the other sensors or to access the data, please visit the King County Marine Monitoring Group's webpage: http://green2.kingcounty.gov/marine/

The SUNA V2 is configured with a 10mm path length and is controlled by a Sea-Bird 25plus CTD (Conductivity, Temperature and Depth). The CTD collects measurements in real-time during the downcast and upcast and triggers the acquisition of discrete water samples by closing the sampling bottles at specific depths during the upcast. These bottle samples are then used to measure the nitrate concentration in the water using a colorimetric analysis method (NEMI METHOD, SM4500-NO3-F). The SUNA V2 nitrate sensor was calibrated with nitrate spiked seawater at Sea-Bird Scientific's state of the art sensor development labs. Absorbance spectra were corrected for seawater bromide using *in situ* temperature and salinity data following Sakamoto et al. [1].

Figure 2 (Following page) shows the vertical profile of the water column at the Jefferson Head station and the relationship between temperature (red line), salinity (blue line) and nitrate concentration (black line) versus depth. In the upper water column (<30 m), the nitrate concentration is very low because it is rapidly consumed by phytoplankton which are fueled by the penetration of the sun rays into the seawater. Below this, the nitrate concentration is larger because upwelling replenishes nutrient concentrations from deeper, nitrate-rich water. Figure 3 shows the SUNA V2 nitrate data from the upcast (blue circle) and downcast (red circle) along with the *in situ* discrete nitrate bottle samples (green star). Differences between the upcast and the downcast can be attributed to vertical movement of water. The reproducibility of the sensor is demonstrated by the negligible hysteresis between the upcast and downcast. The SUNA V2 nitrate sensor accuracy was also excellent, to within ±0.18 µM of nitrate when compared to discrete bottle samples taken from 20-300m depth (the accuracy specification of a 10mm cell SUNA V2 with T and S correction is ±2 µM). Nitrite is included in the bottle samples and can contribute from 0-2.2 µM of the total nitrate + nitrite. The 1m bottle sample had poor agreement with the reported value from the SUNA V2 nitrate sensor (Δ3.5 µM from bottle sample). This could either be due to high variability in the surface layer, as the SUNA and the bottle samples are not collocated.

Conclusion

With the appropriate calibrations and corrections, the SUNA nitrate sensor is a robust tool to measure nitrate concentrations in oceanic and freshwater environments. In this case study, SUNA measurements from Puget Sound corrected for bromide match the accuracy of measurements made with traditional wet chemistry techniques to within ±0.18 µM. While care must be taken when processing SUNA data, updates to the reference spectrum and seawater corrections can be applied by the user with Sea-Bird Scientific's UCI graphical data processing software if concurrent temperature and salinity measurements are available. These corrections help SUNA measurements made in seawater approach those made with discrete measurements while retaining the high vertical resolution of optical based chemical sensors. Scientists and engineers at Sea-Bird Scientific continue to refine SUNA technology, calibrations and processing to minimize sensor drift and interference from other chemical species for greater accuracy and precision in a wider range of environments.
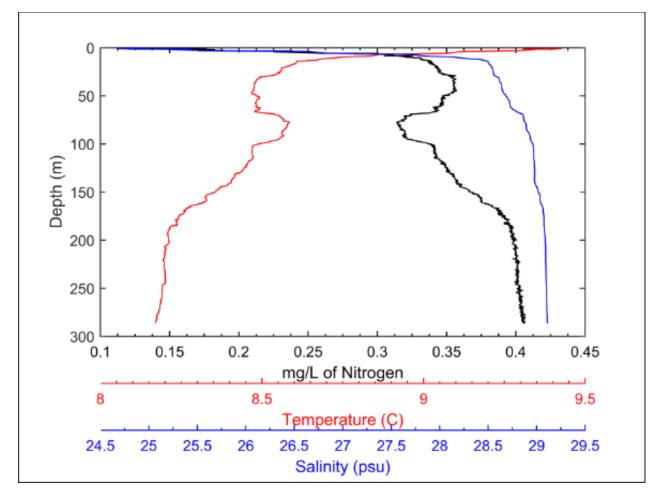
Figure 2: Vertical profile (downcast) of temperature (red), salinity (blue), and nitrate concentration (black) in the water column at Jefferson Head Station on April 4th, 2017.
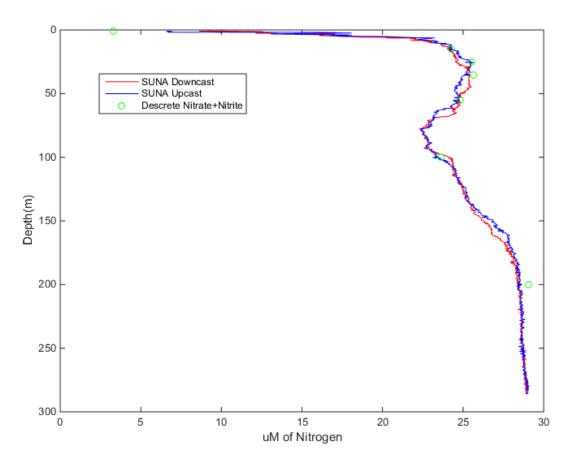
Figure 3: Vertical profile (upcast) in blue and downcast in red) of nitrate in the water column at Jefferson Head Station on April 4th, 2017. Discrete nitrate concentration taken during the upcast are shown as green circle.

References

Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer - Sakamoto - 2009 - Limnology and Oceanography: Methods - Wiley Online Library." [Online]. Available: http://onlinelibrary.wiley.com/doi/10.4319/lom.2009.7.132/full.