Session D3: UV Sensors: Nitrate

Room B117-119
8:00 – 9:30 am

0179
D3-1

Nitrate Analysis by UV Spectrophotometry – An Unbiased Comparison of Four Models

Teri Snazelle and Janice Fulford

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Four commercial UV spectrophotometer nitrate analyzers, SAtlantic SUNA, TRIOS Props, HACH Nitratax, and S::CAN spectrolyzer were tested at the UGSG/HIF to confirm the stated manufacturer's specifications. The Props and Spectrolyzer, use a deuterium lamp and split the light to provide a reference signal. The SUNA model uses a Xenon lamp and does not split the light beam. Unlike the other models tested that measure absorption from approximately 200 to 380 nm, the HACH Nitratax measure absorption at 201 and 350 nm. All models were put through basic in-house laboratory tests for accuracy, drift, and detector saturation. The models were then deployed locally, and their accuracy was evaluated against grab samples analyzed by a laboratory benchtop UV/VIS spectrophotometer. The units' anti-fouling mechanisms were also evaluated and documented.

0245
D3-2

Benefits of High Resolution *In situ* Monitoring of Nitrate in Aquatic Systems

Brian Bergamaschi, Brian Pellerin, Jacob Fleck, JohnFranco Saraceno, Bryan Downing and Tamara Kraus

US Geological Survey, Sacramento, Calif., USA

Physical dynamics in rivers, wetlands, and estuaries drive important biogeochemical processes related to fluxes of nitrate, yet our ability to quantify these processes has been hampered by difficulties inherent in collecting samples at temporal or spatial scales appropriate to the drivers of change in the system. Commercially available instruments that measure nitrate *in situ* are changing our understanding of nutrient dynamics because they allow us to make measurements at intervals ranging from seconds to hours over periods of months to years. We have used *in situ* nitrate sensors in a variety of locations to monitor nitrate dynamics at high temporal and spatial resolution to elucidate processes affecting nutrient flux, nutrient uptake, and nutrient sources. We will present examples of how such measurements can offer powerful new insights into sources and processing of nitrate. One example demonstrates how measurements at high temporal resolution are useful for examining nutrient cycling in a tidal environment. Measurement of biogeochemical variation and flux in estuarine environments, where tidal dynamics dominate, is impractical over the diurnal to spring-neap time- scales necessary to accurately quantify flux. We will also present a number of examples showing how variations in nitrate concentration help to identify source as well as better understand environmental processing, and biogeochemical processing, thus augmenting and extending ecological investigations and improving our assessments of flux.

0280
D3-3

Quantifying the Effects of Particle and Organic Matter Interference on Several Commercially Available *In situ* Optical Nitrate Sensors

John Franco Saraceno, Brian A. Pellerin, Bryan D. Downing and Brian A. Bergamaschi

US Geological Survey, Sacramento, Calif., USA

Commercially available reagentless *in situ* nitrate analyzers are enabling researchers to make accurate nitrate concentration measurements at the time scales (short intervals for long periods in near real time) at which processes responsible for nitrate variability occur. These measurements have the potential to improve nutrient models, improve flux estimates and warn and alert managers of poor water quality. Oceanographers have made optical nitrate measurements successfully in the open ocean for years, but as researchers move inland, potential interferences such organic matter and suspended sediments become a significant concern.

In this study we compared the nitrate estimates of several off of the shelf optical nitrate analyzers (HACH Nitratax, Satlantic SUNA, scan spectrolyser) on nitrate standards (1 mg/L N) spiked with high levels of standard sediment and organic matter mixtures characteristic of the full range of riverine conditions. For the sediment interference experiment, we suspended enough IHSS standard Elliot Silt Loam to reach an equivalent suspended sediment concentration of 2 g/L which resulted in a turbidity of about 600 FNU.

Nitrate measurements were collected in a flow through fashion while the slurry was sequentially filtered (0.2 µm) until no sediment remained. In order to assess the interference of DOM on the optical determination of nitrate, we sequentially added the IHSS Suwanee River DOM standard (IHSS 1R101N) to a nitrate standard until the concentration of DOC reached approximately 30 mg/L.

Preliminary results indicate a wide degree of variability in sensor output driven by sensor differences in path length, excitation wavelength(s) and post processing algorithm. Specific details as well as correction algorithms will be presented.

Optical nitrate analyzers operate by measuring the UV absorbance of nitrate in a water sample. Unfortunately, UV absorbance is not unique to nitrate; salts such as bromide, organic matter and sediments, in particular, can also absorb UV light when present in high concentrations.

We have used in situ nitrate sensors in a variety of locations to monitor nitrate dynamics at high temporal and spatial resolution to elucidate processes affecting nutrient flux, nutrient uptake, and nutrient sources. We will present examples of how such measurements can offer powerful new insights into sources and processing of nitrate. One example demonstrates how measurements at high temporal resolution are useful for examining nutrient cycling in a tidal environment. Measurement of biogeochemical variation and flux in estuarine environments, where tidal dynamics dominate, is impractical over the diurnal to spring-neap time-scales necessary to accurately quantify flux. We will also present a number of examples showing how variations in nitrate concentration help to identify source as well as better understand environmental processing, and biogeochemical processing, thus augmenting and extending ecological investigations and improving our assessments of flux.

0333

D3-4

Using Optical Sensors to Measure Nitrate Concentrations in Iowa's Rivers

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Optical sensors are being used to monitor nitrate concentrations at 15- to 30- minute intervals in Iowa rivers with watershed sizes ranging from about 570 to more than 32,000 km^2. Sensors measure dual wave-length ultraviolet absorption in a 1-, 2-, or 5-mm path. Installation of the first sensors was in 2008 on the Raccoon River with additional sensors being installed in the Iowa and Cedar Rivers in 2009. Sensors are cleaned and calibrated every 4-6 weeks. Sensors are removed from the river to clean sediment, biological growth, and lime-scale then calibrated with a zero and 10.0 mg/L standards. Water samples are collected at the sensor location during servicing and sent to the US Geological Survey's (USGS) National Water Quality Laboratory for analysis of nitrate concentration to verify sensor performance. In large rivers, integrated cross-sectional samples are collected to adjust for variability across the river.

Nitrate data are transmitted to the USGS ADAPS database and are displayed on a real-time basis on a web page. Raw data are reviewed and adjusted to compensate for sensor and cross sectional bias before being finalized in the database. Mean daily nitrate concentrations are published in the USGS annual water data report and are available to download from the ADAPS database. The 15-30 minute values are available on the Web for 120 days, and then retained indefinitely in the database.

These nitrate data are used to monitor rapidly changing concentrations in rivers used as a source of municipal water supply or as a wastewater receiving body. The data are used to better quantify the effects of land use changes due to farming and conservation practices. These nitrate data along with measured streamflow provide information to calculate an unbiased estimate of nitrogen transport, with improved accuracy as compared to load computations using traditional, regression-based estimation with periodic samples. Initial results have shown hysteresis in nitrate concentrations as streamflow increases and then decreases after a storm event. Nitrate concentrations vary diurnally during periods of stable baseflow in the summer when algae and aquatic plants are rapidly growing.