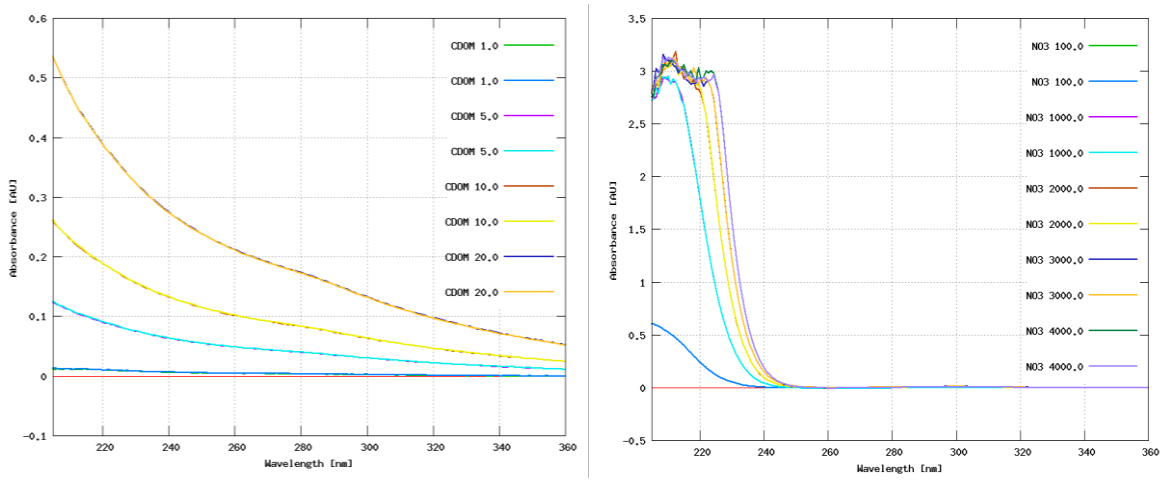
CDOM Interference on Nitrate Measurements

SUNA Operating Principle

The nitrate concentration of a water sample is calculated from the ultraviolet (UV) absorption. In a pure water sample, the concentration is proportional to the measured absorption. Natural bodies of water consist of a mixture of many substances, some of which absorb in the same wavelength range as nitrate. The challenge is to delineate nitrate from the other absorbers, but substances can only be delineated when their spectral signature is sufficiently distinct from nitrate.

Figure 1a. Shows the absorption spectrum of fulvic acid over various concentrations (mg/L) and 1b. nitrate absorption.



The model used to determine nitrate fits for 4 parameters: nitrate, bromide, a temperature coefficient and a linear baseline correction that accounts for all additional absorbing species. If the sample's absorption is high (default cut-off = 1.3 AU), the model can no longer be used effectively to fit parameters or determine nitrate concentration. SUNAV2 outputs a root mean square error parameter which indicates the quality of the models fit to the absorption curves.

CDOM Absorption Properties

Colored Dissolved Organic Matter (CDOM) is one of the main substance classes absorbing in the same UV range as nitrate. (Other significant absorbers are seawater, bromide, bisulfite, and suspended particles). CDOM is a mixture of many chemicals, and thus differs across locations and times, usually depending on its origin. Thus, there is no universal characterization of the UV absorption of CDOM.

CDOM Impact on SUNA Nitrate Concentration

The UV absorption spectra of CDOM differ across the types of CDOM. Some types of CDOM are closer in their absorption to nitrate than others. Types of CDOM that absorb similar to nitrate will cause a larger

bias than those that absorb dissimilar. Thus, the concentration of CDOM alone cannot predict the magnitude of the bias.

Quantifying and Correcting CDOM Impact

Under ideal conditions, CDOM would be isolated from all other absorbers, and its absorbing properties determined in isolation. A more realistic approach is to independently determine the content (nitrate, salinity, CDOM) of several water samples (presuming CDOM is stable over time), and determine the CDOM induced bias on the nitrate concentration.

FDOM: Fluorescent Dissolved Organic Matter is a subset of the Colored DOM pool and can be used as a proxy for CDOM (presuming stable composition over time). Most FDOM sensors use a 370 nm excitation source targeting more humic substances, which may not be representative of absorption in the nitrate range (~220 nm).

Absorption: SUNA V2 also outputs the absorption at 350 nm and 254 nm (A350 & A254). These wavelengths are outside the nitrate absorption range and can be used to estimate the impact of CDOM. As aforementioned if absorption is high (>1.3 AU), the SUNA will not be able to collect adequate light to make a measurement.

RMSE: The Root mean square error parameter output by SUNA V2 can be used to estimate how well the nitrate spectral fitting is, this should generally be less than 1E-3. If it is higher there is spectral shape (likely due to CDOM) impacting nitrate estimation adversely.

Pathlength: SUNA V2 comes in both a 10 mm and a 5 mm pathlength version. Because absorbance is directly proportional to pathlength, halving the pathlength provides a tolerance of about twice the background absorption.