UF Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

Technical Report: SeaBird SUNA V2 Calibration for high CDOM and Saltwater Environments

Stefano Biondi, M. Sc., University of Florida

stefano.biondi@ufl.edu

1. Background and Objectives

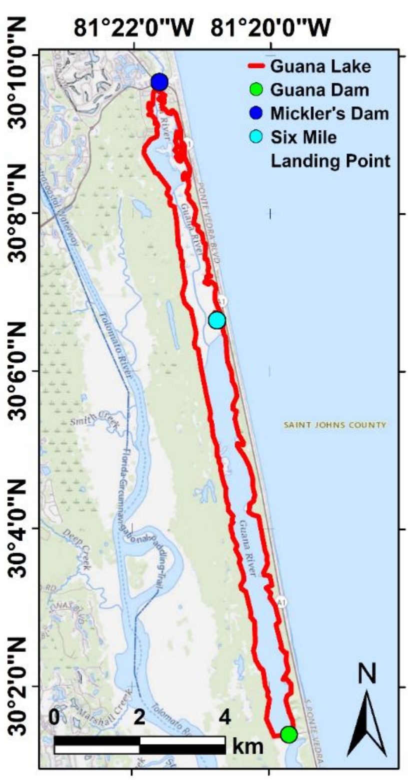


Figure 1. The Guana Lake, which boundaries are defined by the continuous red line. The Lake is connected to the Guana River in the south, through the Guana Dam (green dot) and in the north, through the Mickler's Dam (blue dot). The Six Mile public landing point is also indicated in the map (light blue dot). On the background, the USGS National Map.

Estuaries worldwide are increasingly impacted by eutrophication, largely driven by human activities. Fertilizer runoff and septic system leaks disrupt natural nutrient cycles, increasing nutrient concentration in water bodies. Urban runoff, rich in nitrates (NO_3) from fertilizers, contributes to nutrient surpluses that promote excessive biomass growth (Smith et. al, 2019). The Guana Lake (Figure 1), an impounded estuarine system located in Ponte Vedra, FL, is experiencing urbanization effects, leading to nutrient accumulation within its waters (Dix et al., 2019). To investigate nutrient dynamics in Guana Lake, we focused on detecting both organic and inorganic nitrogen concentration in the water. Over the course of one year, we conducted monthly surveys, collecting water samples and deploying the SeaBird SUNA V2 optical sensor to measure NO_3 concentrations and capture seasonal variations in N levels. However, the optical sensor's performance is influenced by ion interactions and light availability. Hence, accurate calibration is crucial. In fact, the Guana Lake is influenced at its southern end (green dot in Figure 1) by the tide, which makes the salinity in the Lake fluctuate. Additionally, freshwater input is provided at its northern end at Mickler's weir, which carries high levels of Colored Dissolved Organic Matter (CDOM). This report aims to show the laboratory methodology used to calibrate the SUNA V2. The results will provide rating curves for an easier post processing of data collected with the SUNA V2 in environments with strong gradients in salinity and CDOM.

2. Methods and Instrumentation

In this section are illustrated the methods for water sampling and the procedures used to calibrate SUNA V2.

2.1 In situ water sampling

Water was sampled at the same four locations every survey. At each sampling location, a dark leak-proof high-density polyethylene (HDPE) bottle was used to collect a water sample of 500 ml. Bottles were cleaned and sterilized before each survey. Samples were manually grabbed at a depth of 0.5 m, and bottles were labeled with the date, time, and number of the sample (progressive, starting from 1 each day). NO_3, TKN and $\mathrm{NH_4}$ samples were filtered through a 0.45-μm filter (using filtration towers that have been acid-washed before the sampling day) and acidified to pH<2 with $\mathrm{H_2SO_4}$ at the location. Bottles were stored on ice until the end of the daily survey. At the end of the day, samples were stored at a temperature of 4°C, as required by the lab performing the analysis. Samples were delivered to the UF/IFAS Analytical Services Laboratories for Nitrogen concentration analysis. According to the procedure indicated in their ANSERV Lab's QA Manual, they were delivered to ANSERV Lab acidified, at a temperature of 4°C, and in 20 ml scintillation vials. The ANSERV Lab's QA Manual includes information on the MDL/PQL the method of analysis for the bottle samples collected in the field, the calibration procedures of their instruments, and their Chain of Custody procedures. Details on the ANSERV Lab and the nutrient concentration analysis they perform are reported in the Laboratory Analysis section.

2.2 Seabird SUNA V2 specifics

The Sea-Bird Scientific SUNA V2 is an in-situ sensor designed for real-time nitrate monitoring across diverse aquatic environments. It utilizes ultraviolet (UV) absorption technology to measure nitrate concentrations. The sensor features a titanium housing rated for depths up to 500 meters. Furthermore, it offers a standard 10 mm optical pathlength, with an optional 5 mm pathlength available for environments with high turbidity. The SUNA V2 is equipped with adaptive sampling and a universal real-time nitrate processing algorithm. Additionally, it is equipped with a bio wiper for fouling control and internal data logging with 2 GB memory, which allows long-term monitoring.

Figure 2: the SeaBird SUNA V2 Nitrate sensor.

2.3 Calibration

Here are shown the calibration methods for Saltwater and Colored water environments.

2.3.1 Saltwater Environment

To perform calibration in saltwater environment we created a high concentration standard with 100 mg Sodium Nitrate in a 1L volumetric Flask of Ultra DI water. Then, a mass balance for dilution was applied. This reads:

$$C_1V_1 = C_2V_2 \quad ,$$

Where C_1 is the initial concentration (100 mg/L) with Volume V_1 (1 L) and C_2 is the final concentration at volume V_2. We then analyzed 7 nitrate concentrations: 0, 0.1, 0.2, 0.5, 1, 2, and 6 mg/L.

Figure 3: Calibration set up. The SUNA is powered thanks to an external battery and connected to a vacuum pump to push water through the lens and allow continuous reading.

2.3.2 Colored water environment (high CDOM)

We collected a 5-gallon field water tank, with 9 ppt salinity and C_1 = 0 mg/L. Then, we filled a volumetric task with a 100 mg/L solution of ultra-DI water as we did for the salinity correction. In this case, A concentration of 0 mg/L refers to field water with no NO_3 addition. The first test always involved just field water, after which NO_3 was added. The first reading with just ultra-DI water was 0.4 µM. Then we created the standards by diluting the NO_3 concentrations as we did in *section 2.3.1*. Additionally, salinity standards were added to analyze different combinations of CDOM and Salinity in the samples. In this case, the dilution in smaller flasks was not done by using DI water, but the initial saltwater standard. The rinse process, though, was done by using DI water.

3 Results

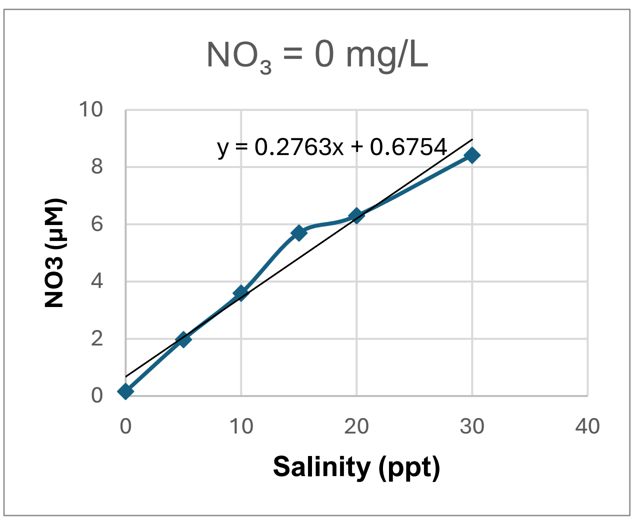
In this section the results of the experiment are illustrated through charts and plots.

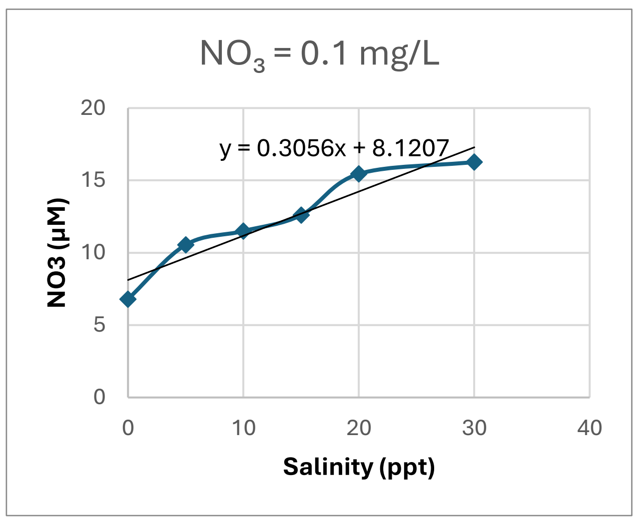
3.1 Saltwater Environment with varying NO_3 concentrations

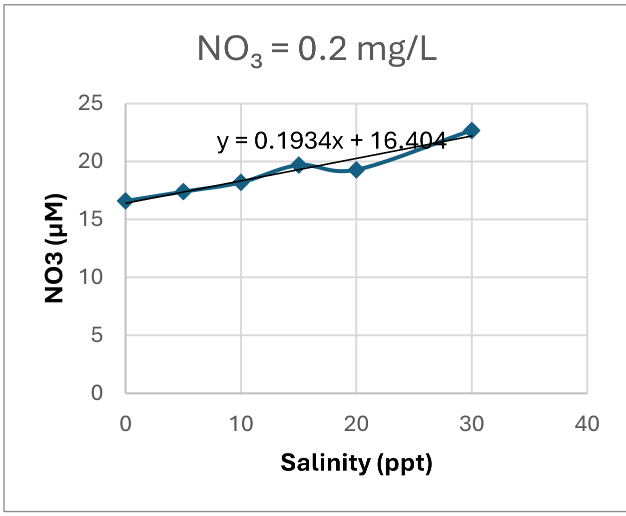
Table 1 illustrates the overall results for all the experiments carried out in the lab. The second column is (expected value at 0 ppt) shows the conversion from mg/L to μM.

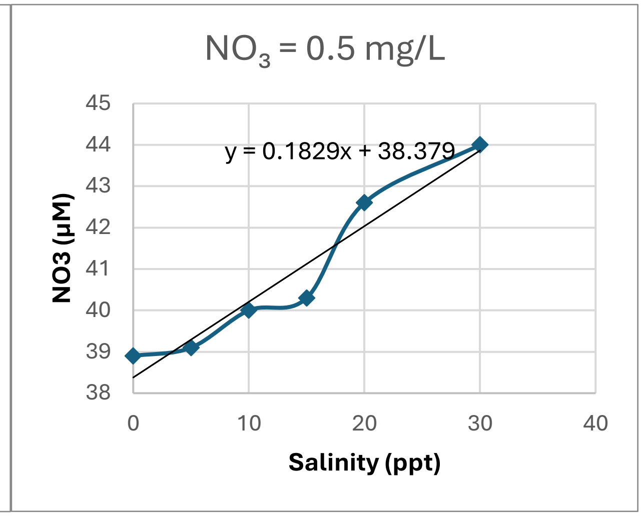
sample conc NO_3 (mg/L)	expected value at 0 ppt (μM)	measured values (μM)					
		0 ppt	5 ppt	10 ppt	15 ppt	20 ppt	30 ppt
0	0	0.16	1.98	3.6	9.7	6.3	8.42
0.1	7.1	6.8	10.55	11.5	12.6	15.45	16.27
0.2	14.4	16.6	17.4	18.2	19.7	19.3	22.7
0.5	35.7	38.9	39.1	40	40.3	42.6	44
1	71.4	71.7	78.1	76.8	77.2	81	80.5
2	142.8	141.2	146	158.3	147	148	172
6	482	421	422	425.7	424	424	421

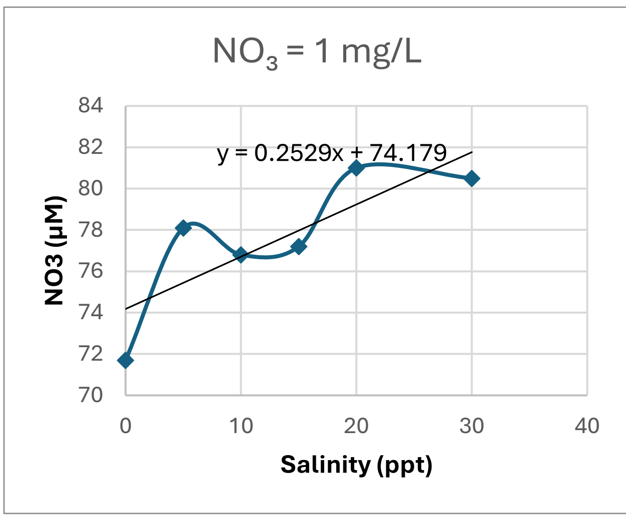
Table 1: experiments results

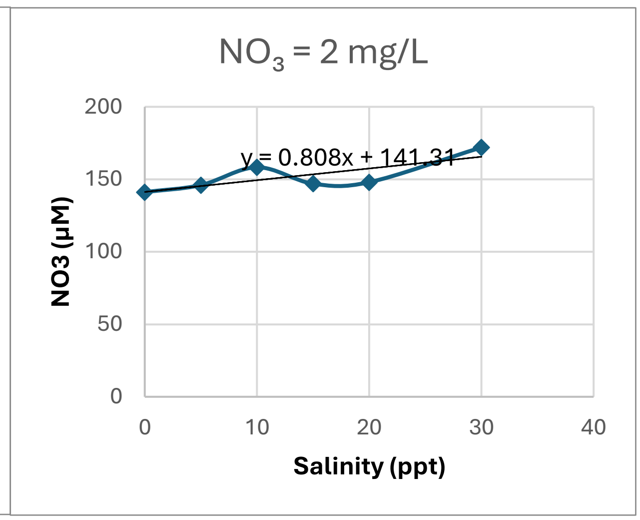












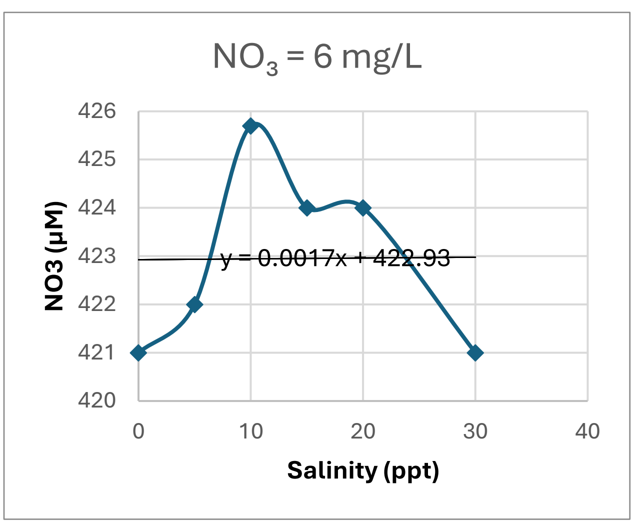


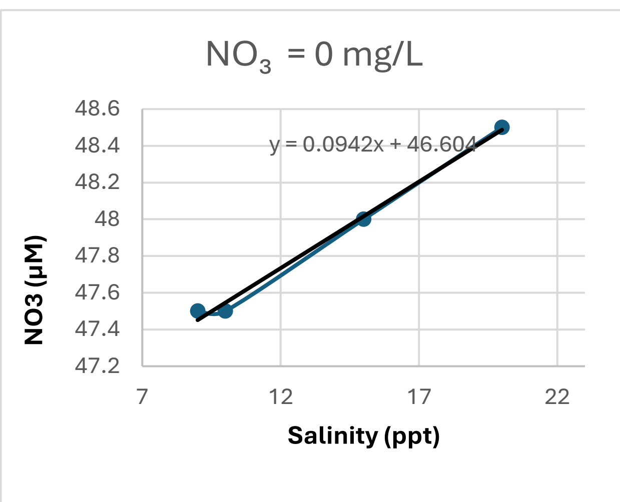
Figure 4: Measured NO_3 concentration with varying concentration C_2

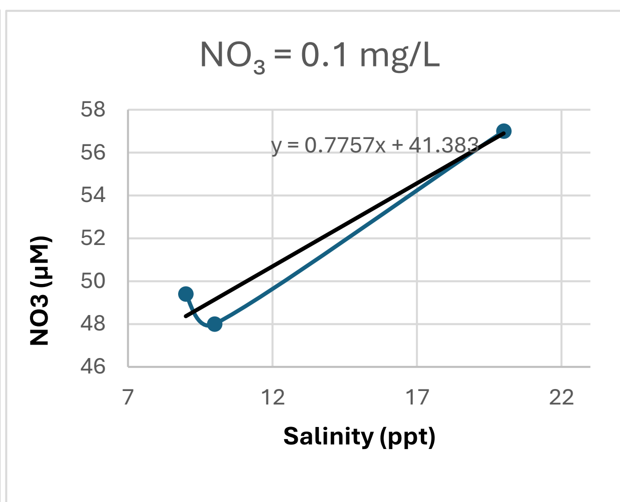
The plots illustrate the SUNA V2 sensor's nitrate measurements across varying salinity levels (0–30 ppt) and NO_3 concentrations (0 mg/L, 0.1 mg/L, 0.2 mg/L, 0.5 mg/L, 2 mg/L, and 6 mg/L). For the lower nitrate concentrations (0, 0.1, 0.2, 0.5, and 1 mg/L), the sensor shows a consistent trend line with a slope between 0.18 and 0.3. This indicates that the increase in ion detection by the sensor due to salinity should be corrected by approximately 18-30% for every unit increase in salinity (expressed in ppt). This correction is necessary to account for the influence of salinity on the sensor's readings at these lower concentrations. For higher nitrate concentrations, the sensor exhibits limitations in detection. In the case of 2 mg/L, there is significant oscillation in the readings, leading to a more uncertain trend line that complicates the conversion process. This suggests that the sensor's accuracy decreases at higher nitrate levels, making it less reliable for precise measurements in this range. The highest concentration case (6 mg/L) reveals that the SUNA V2 reaches a detection limit of around 420 µM. It is important to note that a concentration of 6 mg/L is highly unlikely in environments like Guana Lake, where dense vegetation would likely utilize such a high nitrate level as a resource.

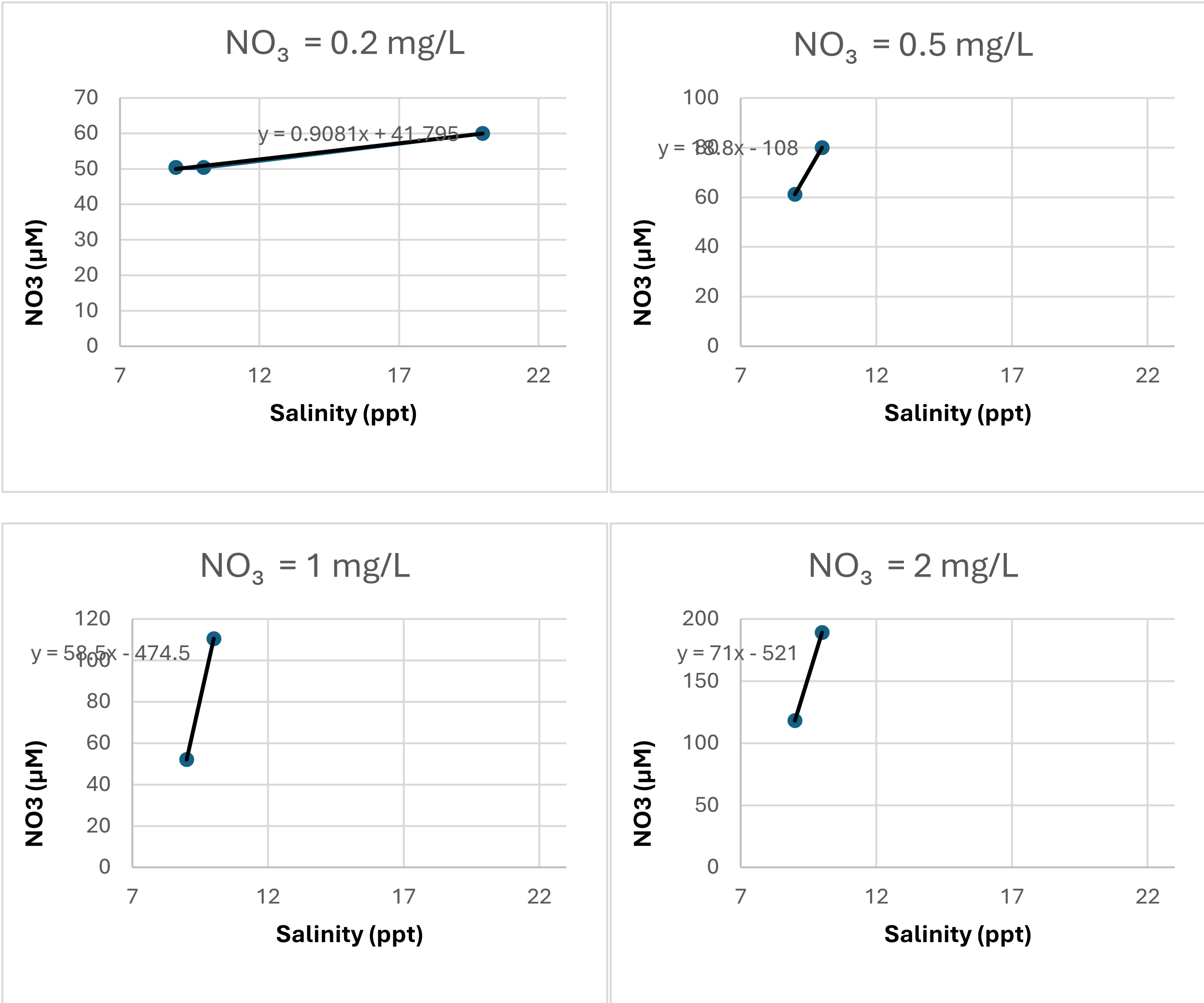
3.2 Colored water environment with varying NO3 concentrations

sample conc (mg/L)	expected value at 0 ppt (µM)	measured values (µM)				
		9 ppt	10 ppt	15 ppt	20 ppt	30 ppt
0	0	47.5	47.5	48	48.5	ND
0.1	7.1	49.4	48	ND	57	ND
0.2	14.4	50.4	50.4	ND	60	ND
0.5	35.7	61.2	80	ND	ND	ND
1	71.4	52	110.5	ND	ND	ND
2	142.8	118	189	ND	ND	ND
6	482	319	449	468	ND	ND

Table 2: overall data for colored water analysis







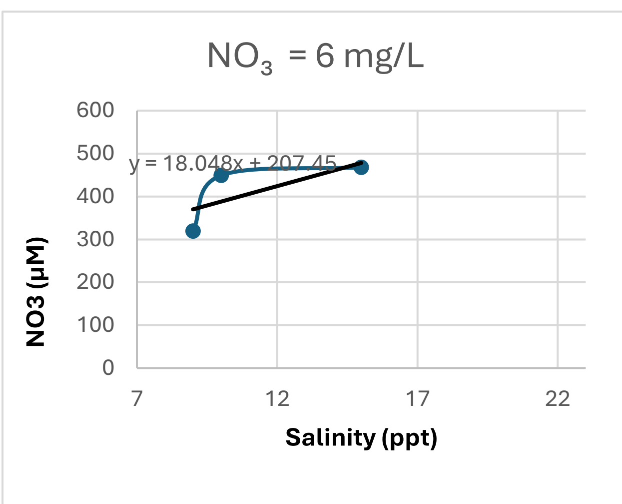


Figure 5: Measured NO_3 concentration with varying salinity and different C_2.

The SUNA V2 sensor struggles to detect NO_3 ions accurately because the coloration can interfere with the optical detection mechanism. In fact, the presence of colored dissolved organic matter (CDOM) or particulates can absorb or scatter the deep UV light used by the sensor, reducing the amount of light that reaches the detector. One significant limitation is the threshold (15 ppt) at which the salinity in colored water becomes too high for the sensor to function effectively. At this point, no correction can restore the sensor's accuracy. To address this issue, one potential solution is to shorten the optical path length of the sensor. This modification would allow for better light penetration in highly colored water, enabling the sensor to provide an estimate of NO_3 concentrations. However, this approach comes with trade-offs: it sacrifices the sensor's ability to detect low concentrations of NO_3 and requires careful field documentation to ensure that samples collected with the spacer are correctly interpreted. In general, the calibration was unsuccessfully performed with field water.

4. Conclusions

The Seabird SUNA V2 sensor was deployed in an estuarine environment exhibiting significant gradients in salinity and colored dissolved organic matter (CDOM). Given the influence of these parameters on nitrate (NO_3) detection, a calibration procedure was implemented to account for their effects. Two key processes were investigated: the relationship between NO_3 concentration and varying salinity levels, tested using both deionized (DI) water and field water (9 ppt). The results indicated that increasing salinity in DI water resulted in a 20-30% increase in ion detection during NO_3 measurements. However, in field water, the presence of organic particles introduced variability that compromised the reliability of the readings, preventing the establishment of a clear rating curve.

This study provides a preliminary calibration framework for the SUNA V2 in high-salinity environments and underscores the need for further research to quantify the impacts of CDOM and organic matter on sensor performance.

5. Acknowledgements

The author acknowledges Dr. AJ Reisinger for his technical consultation and for providing access to laboratory instrumentation at the University of Florida. Special thanks are extended to Jenna Reimer for her assistance in the preparation and analysis of CDOM samples.

6. Reference

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