COLLABORATIVE SCIENCE FOR ESTUARIES WEBINAR SERIES





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Refining Techniques for High-Frequency Monitoring of Chlorophyll



National Estuarine Research Reserve System Science Collaborative Date: Tuesday, April 19, 2022 Time: 3:30-4:30 PM ET

Refining techniques for high-frequency monitoring of chlorophyll *a* in the National Estuarine Research Reserve System

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NATIONAL ESTUARINE RESEARCH RESERVES



Great Lakes

- 1. Lake Superior, Wisconsin
- 2. Old Woman Creek, Ohio

Northeast

- 3. Wells, Maine
- 4. Great Bay, New Hampshire
- 5. Waquoit Bay, Massachusetts
- 6. Narragansett Bay, Rhode Island
- 7. Connecticut

Mid-Atlantic

- 8. Hudson River, New York
- 9. Jacques Cousteau, New Jersey
- 10. Delaware
- 11. Chesapeake Bay, Maryland
- 12. Chesapeake Bay, Virginia

Southeast

- 13. North Carolina
- 14. North Inlet-Winyah Bay, South Carolina
- 15. ACE Basin, South Carolina
- 16. Sapelo Island, Georgia
- 17. Guana Tolomato Matanzas, Florida

Gulf of Mexico

- 18. Rookery Bay, Florida
- 19. Apalachicola, Florida
- 20. Weeks Bay, Alabama
- 21. Grand Bay, Mississippi
- 22. Mission-Aransas, Texas

West

Tijuana River, California
Elkhorn Slough, California
San Francisco Bay, California
South Slough, Oregon
Padilla Bay, Washington
Kachemak Bay, Alaska

Pacific

29. He'eia, Hawai'i

Caribbean

30. Jobos Bay, Puerto Rico

PROPOSED

Bay of Green Bay, Wisconsin Louisiana

System-Wide Monitoring Program









Chlorophyll a



Image credit: https://slideplayer.com/slide/3922722/



Bricker et al. 2007. Effects of Nutrient Enrichment In the Nation's Estuaries: A Decade of Change. NOAA Coastal Ocean Program Decision Analysis Series No. 26. National Centers for Coastal Ocean Science, Silver Spring, MD. 328 pp.

Monthly Discrete Monitoring



Extracted Chlorophyll *a*



μg/L

In situ chlorophyll a





Image credit: www.ysi.com

In situ chlorophyll a

Valuable for

- Short-term plankton dynamics
 - Light, tides, flow, storms, etc.
- Bloom detection



In situ chlorophyll a





Image credit: www.ysi.com

Chlorophyll Catalyst Project



Purpose:

Assess the YSI EXO TAL sensor performance and make recommendations for the NERRS regarding inclusion of high-frequency, *in situ* chlorophyll *a* measurements in the SWMP

Dec 2020 – Feb 2022





NATIONAL ESTUARINE RESEARCH RESERVES



Great Lakes 1. Lake Superior, Wisconsin 2. Old Woman Creek, Ohio Northeast 3. Wells, Maine 4. Great Bay, New Hampshire 5. Waquoit Bay, Massachusetts 6. Narragansett Bay, Rhode Island 7. Connecticut Mid-Atlantic 8. Hudson River, New York 9. Jacques Cousteau, New Jersey 10. Delaware 11. Chesapeake Bay, Maryland 12. Chesapeake Bay, Virginia Southeast 13. North Carolina 14. North Inlet-Winyah Bay, South Carolina 📩 15. ACE Basin, South Carolina 16. Sapelo Island, Georgia 17. Guana Tolomato Matanzas, Florida Gulf of Mexico 18. Rookery Bay, Florida 19. Apalachicola, Florida 20. Weeks Bay, Alabama 21. Grand Bay, Mississippi 22. Mission-Aransas, Texas West 23. Tijuana River, California 24. Elkhorn Slough, California 25. San Francisco Bay, California 26. South Slough, Oregon 27. Padilla Bay, Washington 28. Kachemak Bay, Alaska Pacific 29. He'eia, Hawai'i 📩 Caribbean 30. Jobos Bay, Puerto Rico PROPOSED Bay of Green Bay, Wisconsin Louisiana

Question 1: How do temperature, turbidity, and FDOM influence CHL-A fluorescence (RFU) measured with the YSI EXO TAL sensor?



Methods – Interference Experiments





Turbidity experiment at North Inlet



Turbidity standard



FDOM standards



FDOM experiment at Lake Superior

Results – Turbidity Effect



Results – Temperature Effect



Results – FDOM Effect



Question 2: How can we best predict extracted CHL-A (µg/L) from the suite of YSI EXO sensors?





Methods – Field-Based Comparisons





He`eia



Padilla Bay



Wells



Methods – Lab-Based Comparisons



He'eia



North Inlet-Winyah Bay

Mission Aransas

Results - Comparisons



n = 1255

Results - Comparisons



Results - Comparisons



Methods – Data Analysis

Main question

How can we best predict extracted CHL-A (μ g/L) from the suite of YSI EXO sensors?

<u>Models</u>

- both national and site-specific
- Ordinary Least Squares Linear Regression using data from comparisons

Chl_extracted ~ chl_RFU + reserve + season + turb + FDOM + temp + interactions...

- Square root transformation
- AICc to pick "best" model

Chl_extracted ~ chl_RFU + reserve + season + turb + temp + interactions... Chl_extracted ~ chl_RFU

• R² & prediction error to compare to "best" model

Results – Data Analysis



Tank + ISCO

Full model, best AICc

- m_ols Full model without FDOM
 - **RFU only**

Conclusions

- Temperature, turbidity, and FDOM influence CHL-A (RFU) readings from the YSI EXO TAL sensor.
- Correcting CHL-A (RFU) using data from the accessory sensors is not straightforward.
- Overall, when CHL-A (RFU) and extracted CHL-A were measured simultaneously, linear models of CHL-A RFU explained 35% of the variance in extracted CHL-A. Predictive capability increased when other sensor data and only lab-based comparison data were included (R² = 0.79).
- The amount of variance not explained by the model is likely a combination of species composition, chlorophyll degradation, light history, and interferences
- Site-specific factors are important in determining the strength and the drivers of the relationship between CHL-A (RFU) and extracted CHL-A.

Recommendations

- We recommend NERRS begin implementing high-frequency chlorophyll monitoring system-wide, but this sensor is not a direct substitute for extractive CHL-A analysis.
- Recommendations for whether and how NERRs and others choose to implement the EXO TAL sensor depend on the chlorophyll monitoring goals for each individual station and resources available.

Considerations

- All CHL-A methods have caveats when estimating phytoplankton biomass (e.g., photoacclimation, quenching).
- There is more potential for erroneous readings with *in-situ* CHL-A because of interferences.
- Monthly CHL-A measurements are not frequent enough to capture short-term plankton dynamics.
- Potential applications for real-time *in-situ* CHL-A data
 - More research (ecosystem metabolism, HAB prevention, etc.)
 - HAB early detection, rapid response (if telemetered)
- Costs
 - TAL sensor \$3,150
 - FDOM sensor \$2,394
 - Calibration time
 - Waste

Project Page



https://nerrssciencecollaborative.org/project/Dix20



Recommendations



Q&A

Q: Did you consider using other manufacturer's sensors, especially those that account for LED degradation?

• **A**: No, our project was specifically interested in testing the YSI sensors at multiple reserve sites, but that would be a good next step for future work.

Q: Have you needed to develop site-specific relationships between grabs and sondes?

- **Erik** Yes, we showed there was a site interaction in the overall model, and so the relationship varied across site including the degree to which interfering substances impacted the model.
- **Nikki** each of us only looked at individual sites, each of us will now need to go to our other sites and do the same thing.

Q: Based on your experience, could we establish a list of lakes/reservoirs that are suitable (i.e., lower TSS, CDOM) for such monitoring with in situ chlorophyll-a sensors?

• A: We talked about that a little bit. We did end up recommending a threshold of about 2 micrograms per liter. If you have really low chlorophyll, we think there's probably too much noise-to-signal ratio to predict extracted chlorophyll.

Q: How does the cost of adding a fluorescence sensor package compare to increased grab sampling, say going from 1/month to 4/month?

A: It depends on whether you do your chlorophyll analysis in-house or pay a lab to do it. Ultimately, there's no way you're going to get anywhere close to the frequency you get with these sensors if you're collecting by hand; not to mention having access blocked by storms or other events.

Q: Can you explain more about what "light history" is and why it might be an interference in this study?

• A: Phytoplankton cells can reduce chlorophyll if there is a lot of light, and vice versa, to adapt to their conditions. We don't think it was a significant source of interference in our project as we had everything acclimated to dark tanks when we did our lab based comparisons.

Q: For the consideration of measurements, was consideration of the turbidity categorized (i.e. differentiating between soil particles, algae, microbes, etc.)?

• A: That digs a bit deeper than we could do in this first crosssystem assessment. Our goal is really to use a standard, albeit natural, source of turbidity to get a first cut and see how it varied across systems.



Q: Is the strength of the relationship between extracted and in situ chlorophyll-a also impacted by the signal to noise ratio? For example, North Inlet-Winyah Bay NERR has a strong relationship with more instances of elevated chlorophyll a, whereas He'eia NERR has a poor relationship but also low chlorophyll.

 A: We didn't actually test for a statistical relationship, but we think probably yes based on the general pattern we observed, with some deviations (e.g., Old Woman Creek, OH had one of the highest values of chlorophyll but one of the lowest correlations). We'd have to test it – there were other variables such as FDOM and turbidity that act as compounding interferences.

Q: Was any measurement performed after a celestial event (such as a solar flare) or atmospheric event (i.e. a big downpour or snow day)?

• **A**: Not that I know of. We all tried to sample across a full range of natural variability in the season, but unfortunately, no solar flares.

Q: Can you say a bit more about the calibration process?

• A: The calibration was based on what YSI recommends as a two-point calibration using a rhodamine fluorescent dye, and then kind of a mixture of our SWMP protocols as far as rinsing and cleaning. In the YSI manual they also have instructions on how you can perform a one-point calibration with zero, so pure water. Consistent with SWMP protocols, we generally follow the manufacturer's recommendations.

Q: Even if there is not always a strong relationship between extracted and in situ chlorophyll, do you still think it is a good proxy for something ecologically relevant? We have found that in situ chlorophyll-a changes in meaningful ways to other environmental factors.

• A: We think so. It's especially valuable being able to get measurements on the hourly to daily time scale. The question is: when you get spikes or really elevated values, you don't know for sure if that's turbidity or an FDOM spike that's inflating those values. So it's more like an early warning system for letting you know there could be something there.

Comments

This was really great, folks. I'm impressed with your work and the site-specific relationships were very encouraging; I'd even say surprising. I look forward to seeing more!

Great presentation and project! will be super helpful, I think, for us in Great Bay Estuary, since we had a particular high r-square. Thank you very much!

Adjustment Example



Results – Data Analysis



| | | | | | | | | | | | | | | | fdom_qsu. | | |
|-------------|------|--------|------------|------------|--------|--------|---------|---------|--|------------|--------|------|--------|---------|-----------|--|--|
| prediction | | | | | | | | | X.Intercept fdom_qsu. fdom_qsu. fdom_qsu. sensor_rfu sensor_rfu sensor_r | | | | | | | | |
| model | R2 | _error | sensor_rfu | ı fdom_qsu | turb | season | reserve | temp | | sensor_rfu | temp | turb | .temp | .turb | .turb | | |
| best_AIC | 0.79 | 25.7 | 0.231 | 0.0032 | 0.1254 | NA | + | 0.0266 | 1.15 | 0.0013 | -6e-04 | NA | 0.0172 | -0.0265 | NA | | |
| no_fdom_ols | 0.77 | 26.7 | 0.414 | NA | 0.1085 | + | + | -0.0214 | 1.33 | NA | NA | NA | 0.0102 | -0.0238 | NA | | |
| rfu_only | 0.41 | 49.1 | 0.388 | NA | NA | NA | NA | NA | 2.18 | NA | NA | NA | NA | NA | NA | | |

Results – Data Analysis



| fdom | qsu. |
|------|------|
| _ | |

| | | | prediction | L | | X.Intercept fdom_qsu. fdom_qsu.t fdom_qsu.t sensor_rfu. sensor_rfu. sensor_rfu. | | | | | | | | | |
|---------|-------------|-------|------------|------------|----------|---|--------|--------|--------|------------|-----|-----|---------|---------|------|
| Reserve | model | R.2 | error | sensor_rfu | fdom_qsu | turb | season | temp | | sensor_rfu | emp | urb | temp | turb | turb |
| ELK | best_AIC | 0.782 | 29.3 | 0.365 | 0.0242 | -0.0201 | + | 0.2324 | -1.216 | -0.012 | NA | NA | NA | NA | NA |
| ELK | no_fdom_ols | 0.775 | 29.9 | 0.497 | NA | 0.0247 | + | 0.2605 | -1.448 | NA | NA | NA | -0.0105 | -0.0166 | NA |
| ELK | rfu_only | 0.531 | 39.2 | 0.41 | NA | NA | NA | NA | 2.161 | NA | NA | NA | NA | NA | NA |