Comparison of two field sensors for the *in situ* measurement of Chlorophyll a in NYC Reservoirs

NYC Watershed Science and Technical Conference

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Questions to address:

• Why do we measure chlorophyll?
• How is chlorophyll measured?
• What instruments are being compared?
• How did the data compare?
• What are the conclusions?
• What are the next steps?
Why measure chlorophyll?

What is chlorophyll a?

- Chlorophyll allows plants (including algae) to photosynthesize, i.e., use sunlight to convert simple molecules into organic compounds. Chlorophyll a is the predominant type of chlorophyll found in green plants and algae.

Why is chlorophyll a important?

- Chlorophyll a provides an estimate of the amount of algae growing in a waterbody. It can be used to classify the trophic condition of a waterbody. Although algae are a natural part of freshwater ecosystems, too much algae can cause aesthetic problems such as green scums and bad odors, and can result in decreased levels of dissolved oxygen. Some algae also produce toxins that are an increasing public health concern worldwide.

What can chlorophyll a tell us about the condition of the water?

- One of the symptoms of degraded water quality condition is the increase of algal biomass as measured by the concentration of chlorophyll a. Waters with high levels of nutrients from fertilizers, septic systems, sewage treatment plants and urban runoff may have high concentrations of chlorophyll a and excess amounts of algae.
How can chlorophyll be measured?

Spectrophotometric Measurement (field or lab)

- Spectrophotometry measures how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution.

Fluorometric Techniques (field or lab)

- Fluorometry measures the amount of the fluorescence of emitted light from a sample once presented with a light source.

High-Performance Liquid Chromatography: HPLC (lab only)

- HPLC is used to separate the pigments from a complex pigment mixture using a solvent and measure them in the sub-microgram range using chromatography.
NYC DEP Lab method

High Performance Liquid Chromatography (HPLC)
  o Standard Methods for the Examination of Water and Wastewater, 10200-H 2011
  o NYC DEP lab instrument: Agilent 1200 HPLC

• Pros
  o Accurate
  o Precise
  o Comparable data
  o Direct measurement on concentration

• Cons
  o Expensive
  o Time consuming
  o Data not readily available
  o Limited number of samples
Field methods

• Pros
  o Higher frequency data
  o Data can be obtained near-real time
  o Less expensive

• Cons
  o Difficult calibrations
  o Biofouling
  o Difficult to compare data across data platforms
  o Estimate of concentration
What are you using to measure chlorophyll in your water?

A. HPLC
B. Field fluorometer
C. Field spectrophotometer
D. Combination of field sensor and lab methods
NYC DEP owns and operates a large supply of YSI EXO equipment

It is the primary field sonde in use during our routine stream and reservoir monitoring

It is also the field sonde on all the robotic monitoring buoys, and most stream huts
YSI Total Algae Probe

### YSI EXO Total Algae Sensor Specifications

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<tr>
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<th>Chlorophyll</th>
<th>Phycocyanin</th>
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<tbody>
<tr>
<td><strong>Range</strong></td>
<td>0 to 100 RFU or 0 to 400 ug/L Chl</td>
<td>0 to 100 RFU or 0 to 100 ug/L Chl</td>
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<tr>
<td><strong>Accuracy</strong></td>
<td>linearity: $r^2 \geq 0.999$ for Rhodamine WT across full range</td>
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</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>0.01 RFU or 0.01 ug/L chl</td>
<td>0.01 RFU or 0.01 ug/L chl</td>
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#### Optics

- **Chl Excitation**: 470 +/- 15 nm
- **PC Excitation**: 590 +/- 15 nm
- **Emission**: 685 +/- 20 nm
The AlgaeTorch is a fluorometer made for quick and easy total chlorophyll and cyanobacteria measurements.

Due to the fact that algae of the same division contain a similar quantity and quality of photosynthetic pigments, their fluorescence excitation spectrum (with a fixed emission wavelength at 680nm) is significant. Thus, it is possible to differentiate divisions of algae by their fluorescence excitation spectrum.

The bbe AlgaeTorch for algae differentiation uses 7 LEDs for fluorescence excitation. The LEDs emit light at 3 selected wavelengths (470nm, 525nm, 610nm).

An additional LED is used optionally for turbidity measurements based on the reflected light of any particles in the water. The turbidity measurement is based on backscattering. The calibration is done with Formazin.

The results are shown in FTU (Formazin turbidity units). This result is also used to perform a turbidity compensation of the chlorophyll measurement. Consequently, the chlorophyll measurement in turbid water is enhanced by the turbidity measurement.

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Ultrasonic Technology for Cyanobacteria Control:  
A Pilot Study on Two New York City Reservoirs  

NYC Watershed Science and Technical Conference  
September 12, 2018  

Kurt W. Gabel and Lori Emery  
New York City Department of Environmental Protection  Bureau of Water Supply
**2018 New Croton Reservoir**

- Site 8 CNC was the control site, without ultrasonic treatment
  - YSI EXO sonde with Total Algae Probe and BBE Moldaenke Algae Torch

**2019 Croton Falls Reservoir**

- Site 5 CCF was the treatment site, with ultrasonic
  - YSI EXO sonde with Total Algae Probe and BBE Moldaenke Algae Torch
2018 Site 8 New Croton Chla (ug/L)

- Torch Chla
- EXO Chla
- lab Chla
Poll Question

What is most important when choosing a field chlorophyll sensor?

A. Comparability to other methods

B. Accuracy

C. Precision
The agreement between the two different field sensors was not good. Factors causing variability in signal can be attributed to:

- Differences in optics
- Differences in calibration procedure
- Differences in algorithms in processing the raw signal
- Biofouling
- Temporal/spatial variation
- Interferences
- Correction factors
Optics

Each sensor includes optical components such as a light source, optical filters, and a photodetector.

• BBE Moldaenke Algae Torch
  o The algae torch is a single measurement device which allows for increased space on the platform for more robust components dedicated to measuring the chlorophyll signal.

• YSI Total Algae Probe
  o The YSI is a multi-parameter sonde, using the same platform to measure multiple different optical signals in the same housing.
The sensor needs to be calibrated to adjust for any drift in signal over time. Calibration differences are outlined below:

- **BBE Moldaenke Algae Torch**
  - Factory calibrated with cultured algae.
  - This may be the best calibration procedure, although only completed every 2 years.

- **YSI Total Algae Probe**
  - Calibrated on-site using stock made in house.
  - This procedure may occur more often than factory calibration, but may also introduce more error.
• Each sensor measures a raw signal which is then processed and converted into a more meaningful value.

• Vendor algorithms are proprietary, so we generally cannot compare each conversion across sensor platforms.
• Field sensors of any sort are at risk of biofouling from being deployed in natural waters for long time frames. Each sensor has wiper capability to minimize biofouling. Wipers are helpful in minimizing biofouling, but they can also cause interference if the wiper is parked inappropriately in front of the optics.

• BBE Moldaenke Algae Torch
  o The Algae Torch was equipped with an external wiper, programmed to wipe all sensors every 15 minutes.

• YSI Total Algae Probe
  o The YSI EXO sonde has a central wiper, which was programmed to wipe all sensors on a fixed frequency basis.
Spatial/Temporal Variation

- Measuring biological signals in situ is challenging due to the rapid changes that happen in natural conditions. The spatial variation is also highly heterogeneous in natural bodies of water.

- Algae Torch
  - The algae torch was deployed in close proximity to the sampling site, but not exactly side by side.

- YSI Total Algae Probe
  - The YSI sonde was deployed closest to where the sampling site is located.
Interferences

- Sensor interference needs to be considered when deciphering field sensor data. Forms of interference may include:
  - Turbidity
  - Ambient light
  - Other particulates in water
  - Stray signal from other optical probes in close proximity
Correction Factors

• BBE Moldaenke Algae Torch
  o Has ability to calibrate offset for distilled water and ultra-filtered water
  o Can be calibrated using yellow substances
  o Can be calibrated for algae fingerprints
  o Turbidity offset can be used, as well as slope for higher turbidity
  o Air pressure can be used to compensate for current air pressure
  o Temperature compensation from internal temperature probe
  o *Note: none of these correction factors were used in this study

• YSI Total Algae Probe
  o Temperature compensation from internal temperature probe
  o *Note: the best accuracy of pigment measurements can be obtained by user-built correlations between RFU and pigment concentrations measured by an independent method, and using samples from the site or sites of interest with representative algal populations.
In 2018 the Algae torch read consistently higher than the YSI and lab data but data seemed to have a correlation between the Algae Torch and YSI.

In 2019, the YSI did not respond to the algae bloom with high chlorophyll values but performed well during bench testing.

BBE Moldaenke Algae Torch

- **Pros**
  - Field rugged, factory calibrated with algal cultures, accurate and precise

- **Cons**
  - Expensive, not easily adapted to other sampling platforms or deployable in the field

YSI Total Algae Probe

- **Pros**
  - Field rugged, easily deployed, can store data internally, easily mounted on existing platforms and profilers, less expensive

- **Cons**
  - Less accurate, difficult to compare data with other measurements
Next Steps

We could like to conduct further bench testing using cultured algae in controlled environment to compare both sensors and see if the results are similar.

• BBE Moldaenke Algae Torch
  o Can we configure the Algae Torch to be deployed in reservoirs at fixed-depths easily?
  o Can we configure the Algae Torch to be used on our profiling buoys?

• YSI Total Algae Probe
  o Can we improve the measurement with different calibration techniques?
  o Can we make further correlations using the raw signal, or the RFU values?