Continuous Monitoring for Nutrients: State of the Technology and State of the Science

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U.S. Department of the Interior
U.S. Geological Survey
Continuous Monitoring

- 24/7 data collection
- Wide range of constituents with direct or proxy measurements
- Intervals of seconds to hours
- Capture all events
- Remote access and control of sensors

Mississippi River at Baton Rouge
Applications

- Monitoring for drinking water and wastewater
- Load assessment
- Source identification
- Event detection
- Real-time decision support

Sacramento River above Freeport
The need for real-time, continuous nitrate...

Des Moines Water Works nitrate removal system:
- $4 million installation (1992)
- $7,000 per day to operate
## Water quality sensors

<table>
<thead>
<tr>
<th>Parameter(s)</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>“The big five”</td>
<td>Temperature, pH, conductivity, dissolved oxygen, turbidity</td>
<td>Field ready</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Determined by UV light absorption. Used for assessing management practices and assessing aquatic eutrophication.</td>
<td>Field ready</td>
</tr>
<tr>
<td>Dissolved organic matter</td>
<td>Correlated with colored dissolved organic matter fluorescence (FDOM). An important constituent related to drinking water quality, metals transport and ecosystem health.</td>
<td>Field ready</td>
</tr>
<tr>
<td>Algal pigments</td>
<td>Chlorophyll and other algal pigments (phycocyanin, phycoerythryn) for assessment of aquatic productivity and harmful algal blooms.</td>
<td>Field ready</td>
</tr>
<tr>
<td>Phosphate, ammonium</td>
<td>Wet chemical sensors for nutrients</td>
<td>Field ready / testing</td>
</tr>
<tr>
<td>Backscatter, particle size</td>
<td>Related to suspended sediment concentration, type and size. An important habitat index, important for modeling watershed processes and predicting sedimentation.</td>
<td>Field ready / testing</td>
</tr>
<tr>
<td>Multi-wavelength absorbance and fluorescence</td>
<td>Custom measurements used for measuring specific constituents such as oil, pathogens, wastewater content, and mercury by proxy as well as for source tracking in complex systems.</td>
<td>Testing</td>
</tr>
</tbody>
</table>
Variety of designs and costs
Optical sensors

Measure the interaction between light and optically-active constituents in the water
Wet Chemical Nutrient Sensors

Field deployable, wet chemical sensor using standard colorimetric methods (molybdenum blue; similar to EPA 365.5)

**Wetlabs Cycle P Sensor**

<table>
<thead>
<tr>
<th><strong>Detection Limit</strong></th>
<th>≤0.0023 mg/L PO₄-P</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum Concentration Range</strong></td>
<td>0-1.2 mg/L PO₄-P</td>
</tr>
<tr>
<td><strong>Maximum Sampling Rate</strong></td>
<td>30 minutes</td>
</tr>
<tr>
<td><strong>Samples Per Reagent</strong></td>
<td>~ 1000</td>
</tr>
</tbody>
</table>

USGS
Guidelines and Protocols

- Instrument characterization
- Guidelines for use in a variety of environments
- Continued interactions with manufacturers
USGS Continuous Nitrate Monitoring

- 90+ sites nationwide (operated in 24 states)
- Extensive network in the Mississippi River Basin
- Most nitrate monitoring (>80%) funded by cooperators

http://waterwatch.usgs.gov/wqwatch/
Optical nitrate: from bench to field

- Spectrophotometer: Measures the intensity of light after passing through a solution
- Similar to Standard Method 4500-NO3- B (APHA, AWWA, WEF, 1995)

- Miniaturized components
- Rugged housings
- Efficient power handling
- No (or few) moving parts
- Internal dataloggers and controllers
- Anti-fouling systems
- On-board data processing

Top: chemwiki.ucdavis.edu; Bottom: TM1D5
Accurate Measurements

- Consider the type of technology (ISE, wet chemical, optical)…then buy optical.
- For UV sensors, **keys to accurate measurements:**

Minimize fouling
Accurate Measurements

- Consider the type of technology (ISE, wet chemical, optical)...then buy optical.
- For UV sensors, **keys to accurate measurements:**
  
  **Measure the right wavelengths**

  ![Graph showing absorbance vs. wavelength for different chemicals]

  - Absorbance except Br⁻
  - 840 μM Br⁻
  - 50 μM I⁻
  - 50 μM H₂S
  - 30 μM NO₃⁻

  **Get the right path length**

  
  
  \[ A = -\log(I/I_o) = 2\log_{10}\%T = \varepsilon c L \]
Accurate Measurements

- Consider the type of technology (ISE, wet chemical, optical)…then buy optical.
- For UV sensors, **keys to accurate measurements:**

  **Get the right algorithm**

  - Proprietary algorithms
    - Based on field and lab data
  - Calibration types
    - Global
    - Application-specific (wastewater, seawater, etc.)
    - Local
  - Compensation for interferences

  Same sensor, same solution, different algorithm!
Accurate Measurements

- Consider the type of technology (ISE, wet chemical, optical)...then buy optical.
- For UV sensors, **keys to accurate measurements**:
  - Compare to lab data
    - Validate against lab samples ("gold standard"?)
    - Make bias corrections if needed and appropriate

![Graph showing correlation between sensor and lab nitrate measurements](image)
Mississippi River Continuous Nitrate

- Strong correlation between in situ and discrete nitrate (depth- and width-integrated)
- Nitrate “flush” in spring 2013 (following 2012 drought)
- Dynamic nature, not well correlated with Q
- Estimated error ~ ± 4%

Mississippi River at Baton Rouge (USGS gage 07374000)
Can we improve load estimates?

- Differences in modeled vs. sensor loads of up to 30% in the spring (sensor > model)
- Order of magnitude lower uncertainty in the sensor vs. model loads
- Loads below the 10th and above the 90th percentiles during this period


(Pellerin et al., submitted)
Re-assess the role of in-stream N retention?

- May help refine SPARROW aquatic decay coefficients (especially in a dynamic model)
- Help with estimating groundwater N loading?

Alexander et al., 2000
Exploring nutrient uptake?

Evidence for draw down of N (and P) to support algal production?

Stage (ft)
15
16
17
18
19
20
21
22
23

Nitrate (mg N/L)
0.06
0.08
0.10
0.12
0.14

Phycocyanin (RFU)
0
50
100
150
200

Discharge
Nitrate
Phycocyanin

8/11/12  8/12/12  8/13/12  8/14/12
Thoughts on the “Nutrient Challenge”

1. “Accuracy” and “sensitivity” should not be sacrificed in order to reduce up-front costs for sensor purchase
   - Instrument specifications are topic of active discussion
   - “Regulatory” and “low cost” may not go well together

2. Costs to maintain instruments should be considered in any vision for a broader nutrient monitoring network
   - Costs to manage sensors and data often $20-30K per site per year

3. Additional discussion needed on how to collect, deliver, store, and use data of known quality in national network of nutrient monitors
Fluorescence sensors

- **DOM** – 1000s of compounds, operationally defined by filter size, ~ 50% carbon
  - Transports nutrients and metals, base of microbial foodwebs, disinfection byproduct formation

- **CDOM** – colored or chromophoric DOM that absorbs light in the UV and VIS range

- **FDOM** – fraction of CDOM that absorbs in the UV (~370 nm) and emits at longer wavelengths (~460 nm)
  - Highly sensitive, commercially-available, good proxy for humic material

Quinine sulfate (QS) in 0.05 H₂SO₄ measured with a commercial FDOM sensor (ex. ~370 nm, em. ~460 nm)
Benchtop vs. field fluorometer

**Benchtop**
- Excitation – emission matrix fluorescence (EEMs)
- Several thousand pairs of ex/em measurements
- Compositional indicators (e.g. ratios like fluorescence index)
- Can control matrix effects (e.g. filter, dilute, warm to room temperature, etc.)

**Field sensor**
- Developed for oceanography
- Single excitation – emission peak (but customizable)
- Can be paired with other fluorescence wavelengths
- Relatively inexpensive ($2-7K)
- Data “around the clock”
- Subject to matrix effects

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**Peak A** (humic-like)

**Peak B** (protein-like)

**Peak T** (protein-like)

**Peak D** (fulvic-like)

**Peak C** (humic-like)

**EEM (excitation-emission matrix fluorescence)**

**Algal pigments, dyes**
Challenges

- Fouling
- Drift
- Power
- Communication
- Interferences
- Sensor design
- Units
Characterize sensors

- Evaluate and develop corrections for interferences
  - Suspended particles / turbidity
  - CDOM
- Need common methodologies and real-world standards

Downing et al., LO Methods, in press; also USGS-CUAHSI In Situ Optical Sensor Workshop Summary (OFR 2012-1044)
FDOM vs. DOC

Raw and corrected sensor data from Sleepers River, Vermont

\[ y = 0.0069x + 0.0696 \]

\[ R^2 = 0.9367 \]
Data comparability

- Differences in ex/em and bandpass between manufacturers
- Field FDOM data in quinine sulfate equivalents (QSE) can differ dramatically
How is DOC transport affected by large events?

- Large DOC response after leaf fall and muted responses during snowmelt
- Variability from storm to storm, snowmelt periods, etc.

![Graph showing DOC transport](image)
Agricultural watersheds: DOM sources

DOM transport in the Willow Slough agricultural watershed shows an early peak in turbidity, but a delayed and prolonged response of DOM reflecting agricultural field runoff (Saraceno et al., 2009).
Diurnal DOM dynamics – San Joaquin River, CA

- Supports TMDL to reduce the amount of oxygen demanding substances and their precursors in the San Joaquin River

- DOM composition can change even if DOC concentration doesn’t…

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Spencer et al. 2007, Pellerin et al. 2009

In Situ FDOM (QSE)

DOC (mg/L)

FDOM

Discrete DOC


In Situ FDOM (QSE)
Proxies: methylmercury

“Surrogate” measurements for high resolved methylmercury (MeHg) flux from a tidal wetland, Browns Island, CA

Bergamaschi et al., 2011
Chlorophyll fluorescence

- **Interferences**
  - Particles, CDOM, temp

- **Calibration/Validation**
  - Monoculture
  - Dyes

- **Environmental variability**
  - Algal species
  - Photoquenching

- **Units**
  - Relative fluorescence units
  - ug/L of ???

**USGS Techniques and Methods Report on Fluorometers to be published in 2015**

Roesler and Barnard, 2014
Is continuous water quality data “big data”?

- “Enhanced” water quality monitoring stations becoming more common
- 100s to 1000s of measurements per day (compared to 12-18 per year)
- New parameters being added all the time (PO₄, NH₄, phycocyanin, particle size, …)
Advancing the QA of WQ Data

Loggernet

Datalogger

WQ sensors

AQ server

Fault detect

Burst-stats QA/QC

AQ

Site diagnostics

- Smart use of trips to the field
- Diagnostics for failing sensors
  - Improve data quality
  - Automated SMS messages
- Autosampling triggered by event detection (discrete samples)
- Use of metadata directly from sensors

USGS OWI/OWQ (Brad Garner, Jordan Read)
Campbell Scientific SE-108 Submersible Datalogger

- “Plug-and-play” integration for data loggers
  - Pre-wired for up to 8 sensors including SUNAs, EXOs, and a variety of other sensors
  - Currently a custom “proof-of-concept”; next version would be smaller, have more flexibility (e.g. any sensor to any port) and could include modems or bluetooth
- Cost ~ $7,500 each
- Current version is submersible; a standard enclosure version is also a possibility
New Instruments

- **Wastewater proxy**
  - Target low UV fluorescence as unique indicator of wastewater presence
  - Indicators for the potential presence of pathogens and bacteria (S. Corsi, WI WSC)
- **Wastewater sensor**
- **Ammonium**
- **Algal composition**
- ...
Rapid Deployment Systems

Event response

- Wastewater
- Oil and grease
- Nutrients
- Sediments (amount and type)
- Disinfection by-products
- ?

Hurricane Sandy
11 billion gallons of untreated and partially treated wastewater

Rim Fire
4th largest wildfire in California, in the primary drinking water supply for ~ 2 million people

Deepwater Horizon
Release of 4.9 million barrels of oil into the Gulf of Mexico

McNutt et al., 2011: US Coast Guard
How would we build a nationally-consistent, real-time, continuous nutrient monitoring network that:

1. Meets monitoring and regulatory needs (drinking water quality, TMDLs, edge-of-field loads, coastal issues)

2. “Accelerates the pace of discovery” (*White House Big Data Research and Development Initiative*)

3. Has some long-term “stability”

4. Improves our efficiency (from data collection to decision support)?
National Consistency

- **Data and databases**
  - common protocols
  - centralized databases
  - data uncertainty
  - Tools to automate QA
  - ...

- **Statistics and model**
  - spatial modeling
  - projections of future quality
  - ...

- **Information products**
  - real-time “watches”
  - data access portals
  - information products
  - tools available to everyone
  - ...

Thanks!

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(Andy Zeigler)