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

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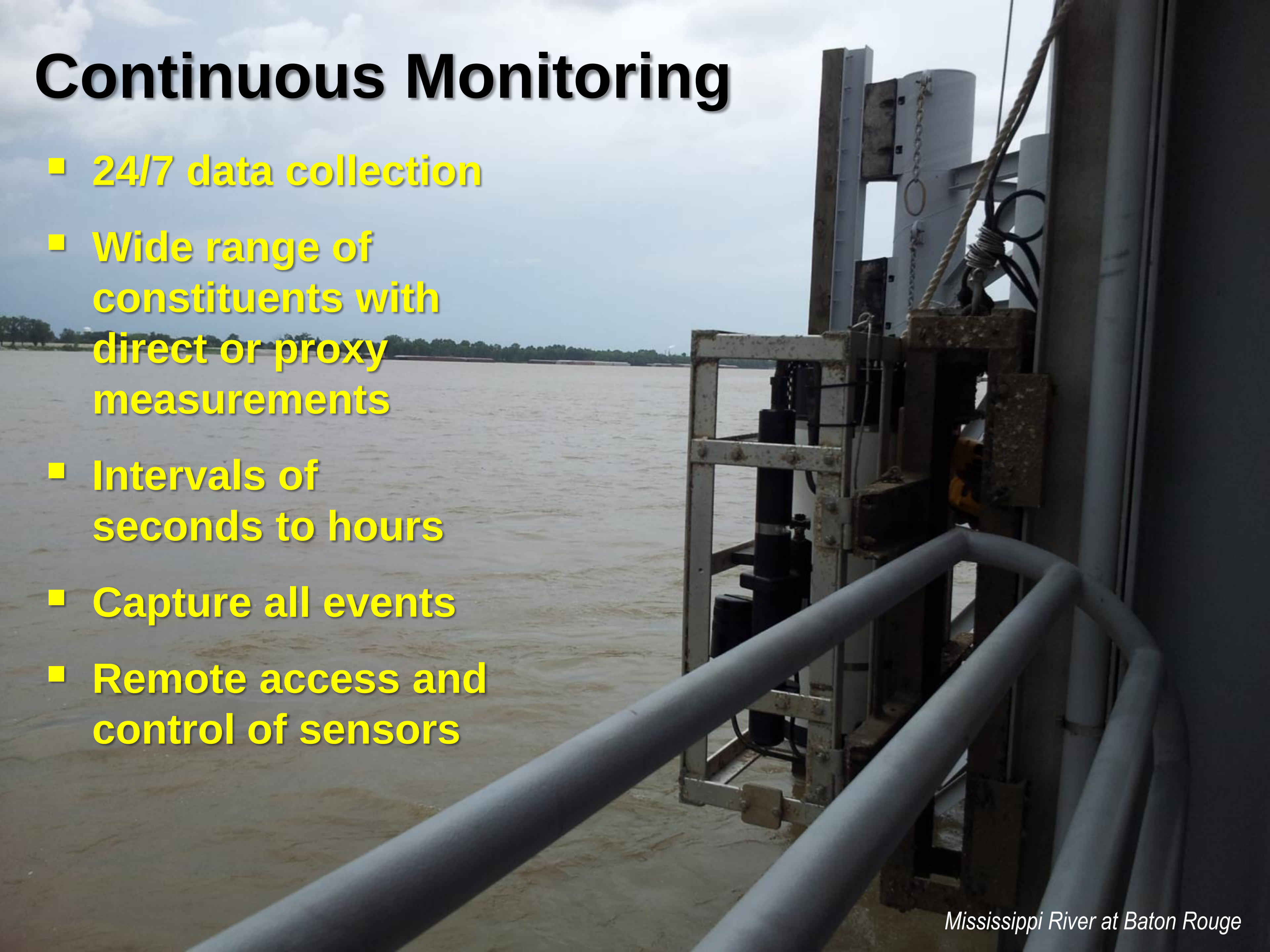
NWQMC Meeting, 7/30/14

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

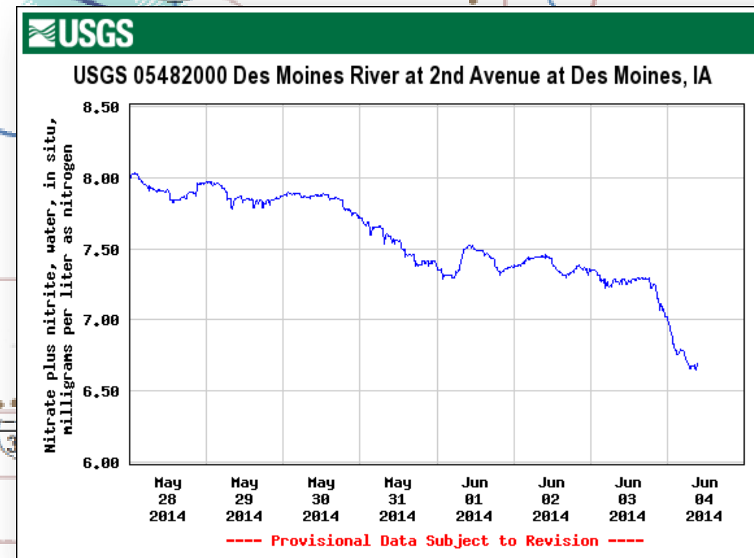
- Monitoring for drinking water and wastewater
- Load assessment
- Source identification
- Event detection
- Real-time decision support
- …

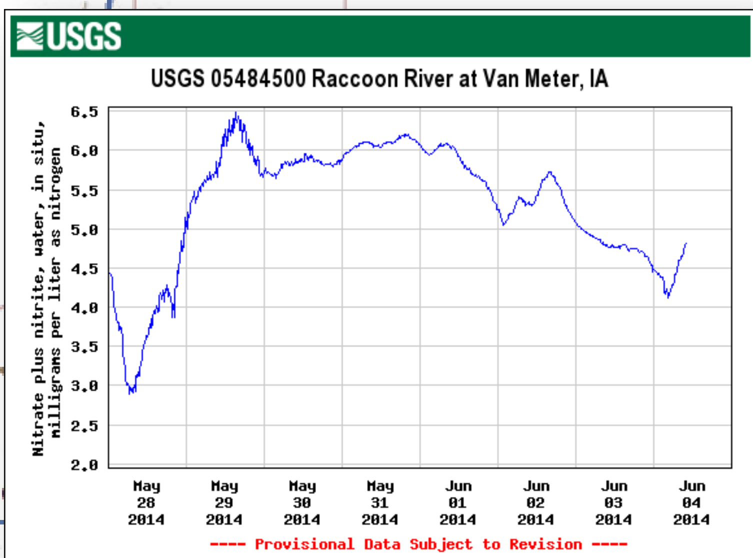
Sacramento River above Freeport

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

Parameter(s)	Description	Status
"The big five"	Temperature, pH, conductivity, dissolved oxygen, turbidity	Field ready
Nitrate	Determined by UV light absorption. Used for assessing management practices and assessing aquatic eutrophication.	Field ready
Dissolved organic matter	Correlated with colored dissolved organic matter fluorescence (FDOM). An important constituent related to drinking water quality, metals transport and ecosystem health.	Field ready
Algal pigments	Chlorophyll and other algal pigments (phycocyanin, phycoerythryn) for assessment of aquatic productivity and harmful algal blooms.	Field ready
Phosphate, ammonium	Wet chemical sensors for nutrients	Field ready / testing
Backscatter, particle size	Related to suspended sediment concentration, type and size. An important habitat index, important for modeling watershed processes and predicting sedimentation.	Field ready/ testing
Multi-wavelength absorbance and fluorescence	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.	Testing

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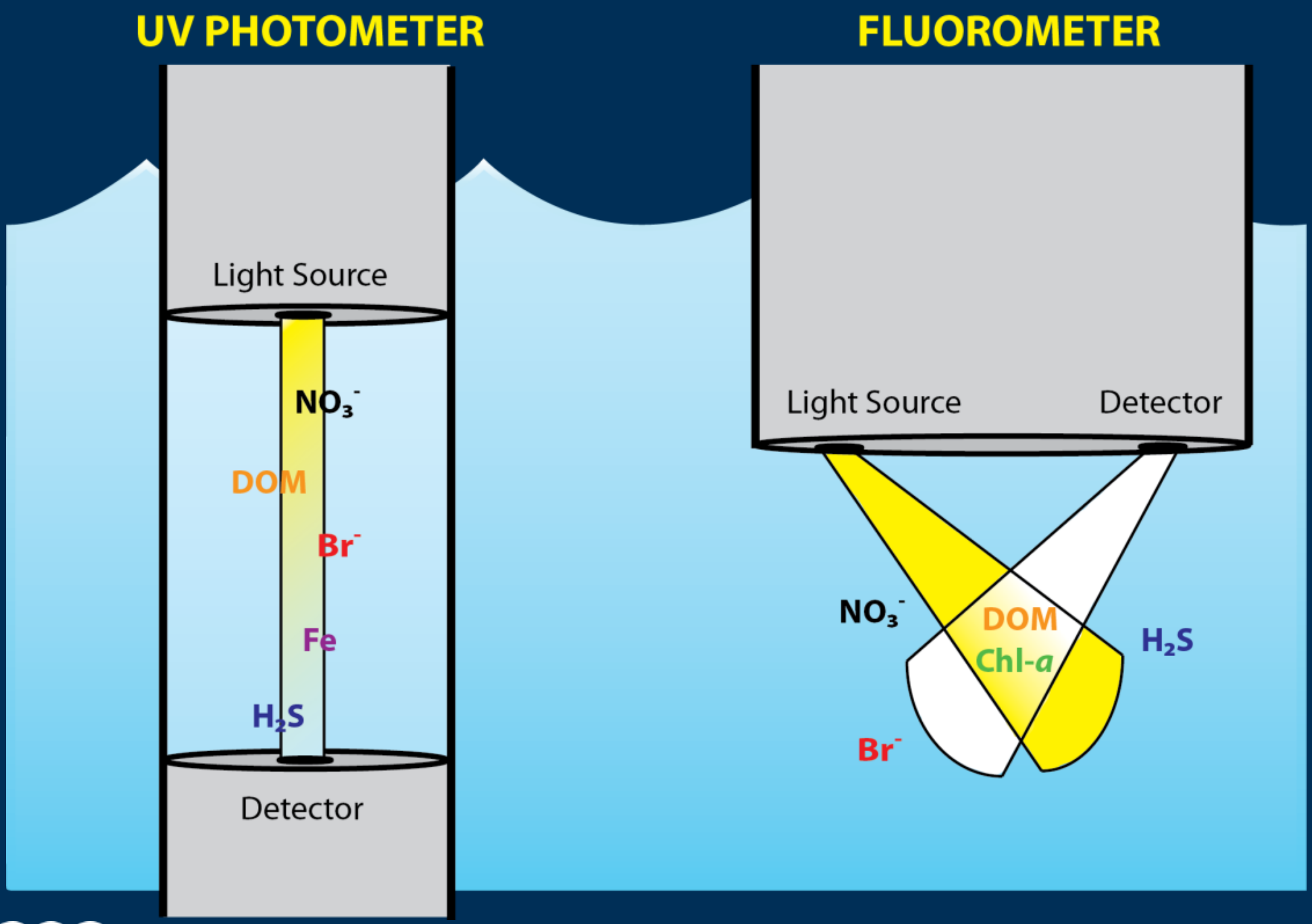
Variety of designs and costs

Optical sensors

Measure the interaction between light and optically-active constituents in the water



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Wet Chemical Nutrient Sensors

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

Wetlabs Cycle P Sensor	
Detection Limit	≤0.0023 mg/L PO_4-P
Maximum Concentration Range	0-1.2 mg /L PO_4-P
Maximum Sampling Rate	30 minutes
Samples Per Reagent	~ 1000

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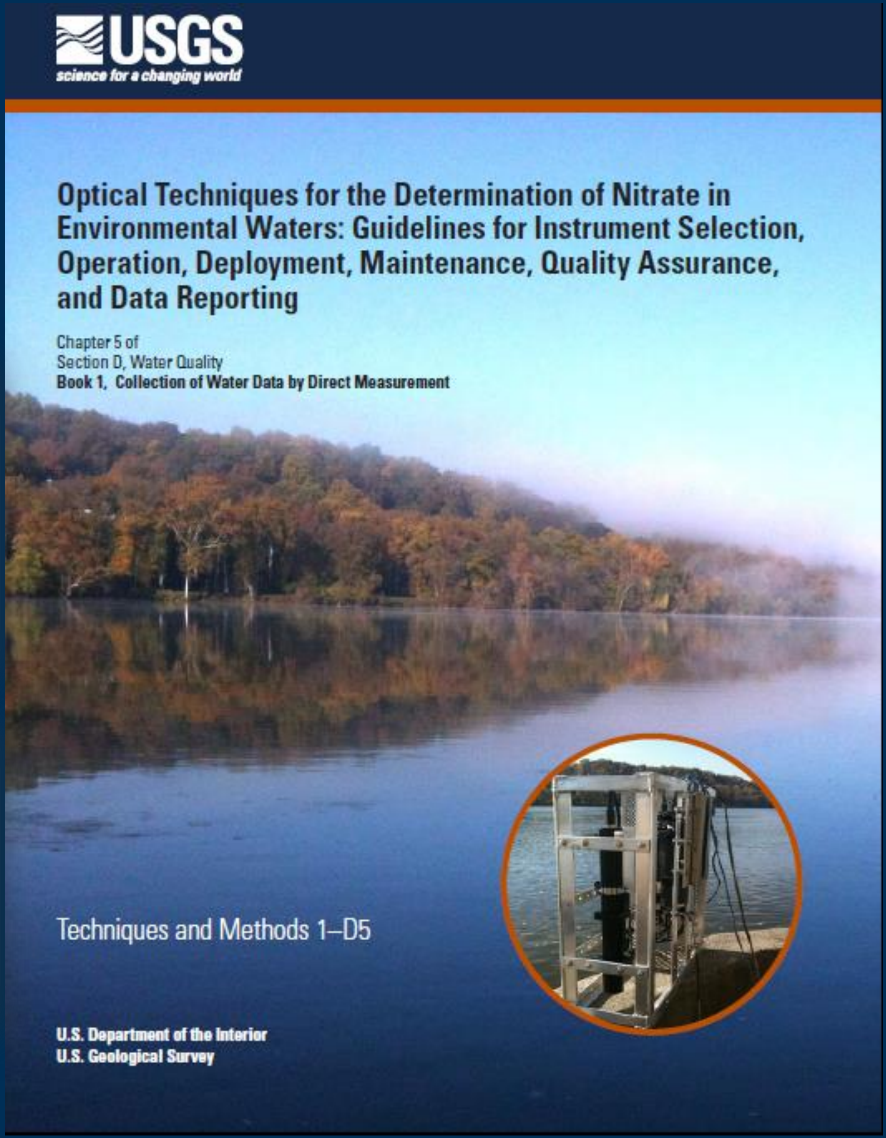
Guidelines and Protocols

- Instrument characterization
- Guidelines for use in a variety of environments
- Continued interactions with manufacturers



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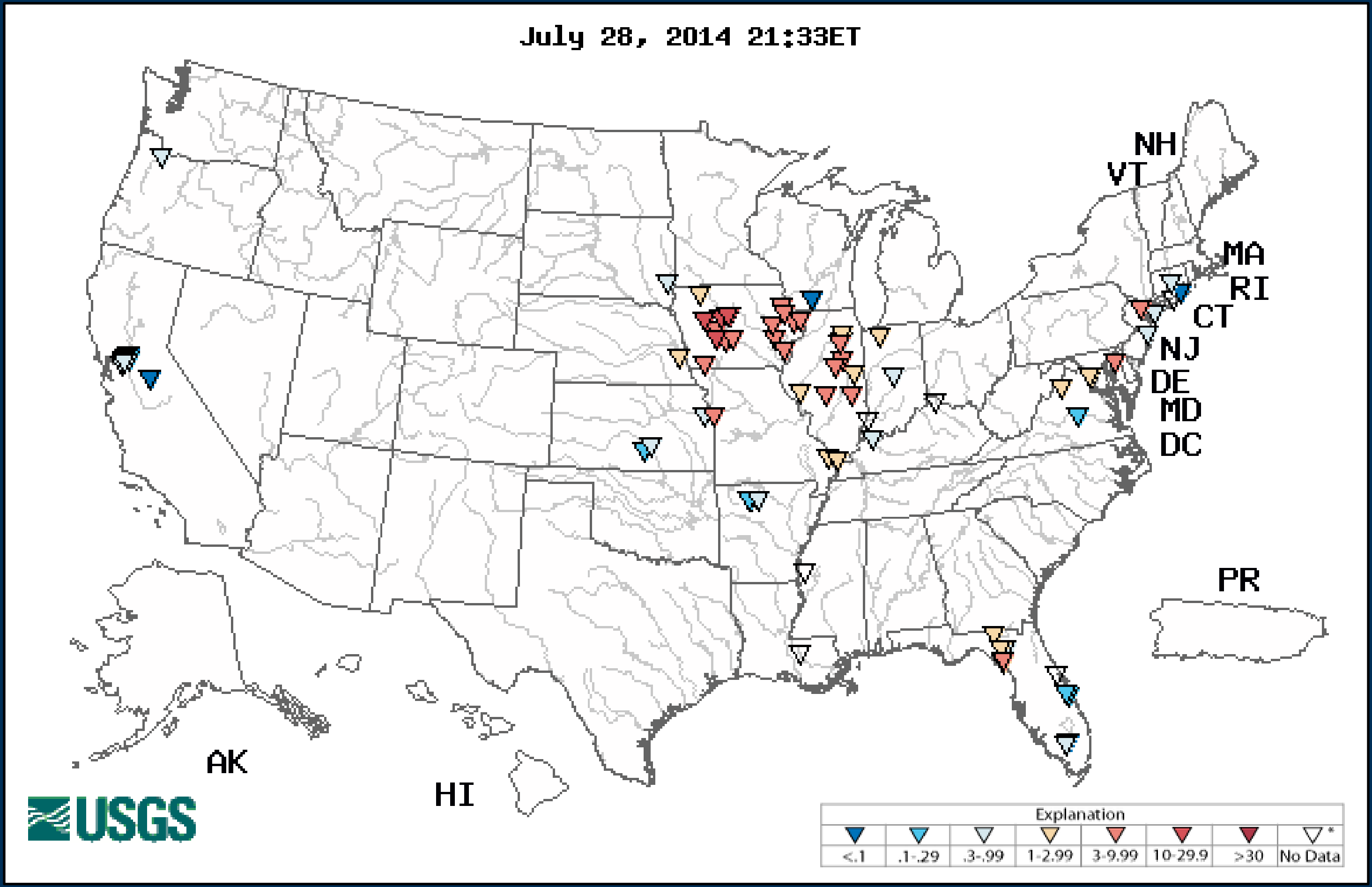
pubs.usgs.gov/tm/01/d5

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

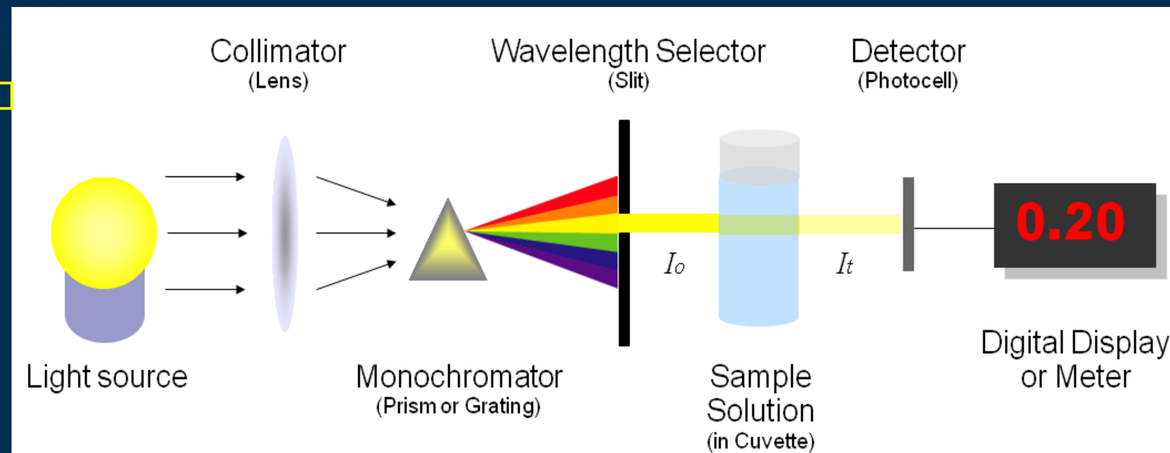


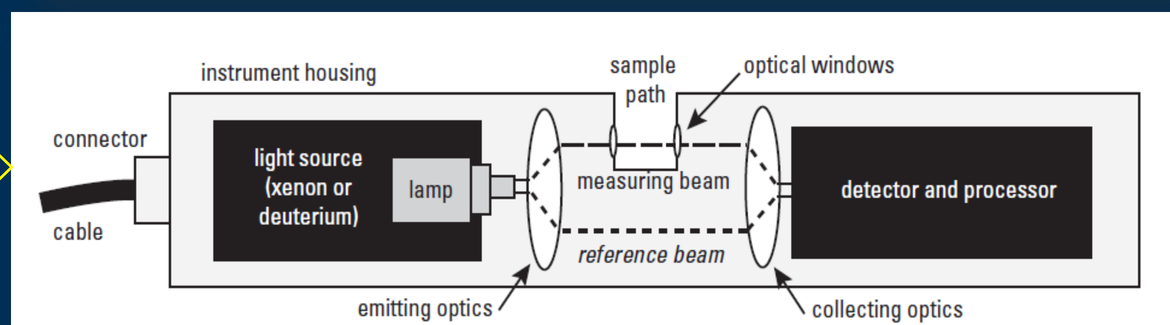
http://waterwatch.usgs.gov/wqwatch/

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





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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**:

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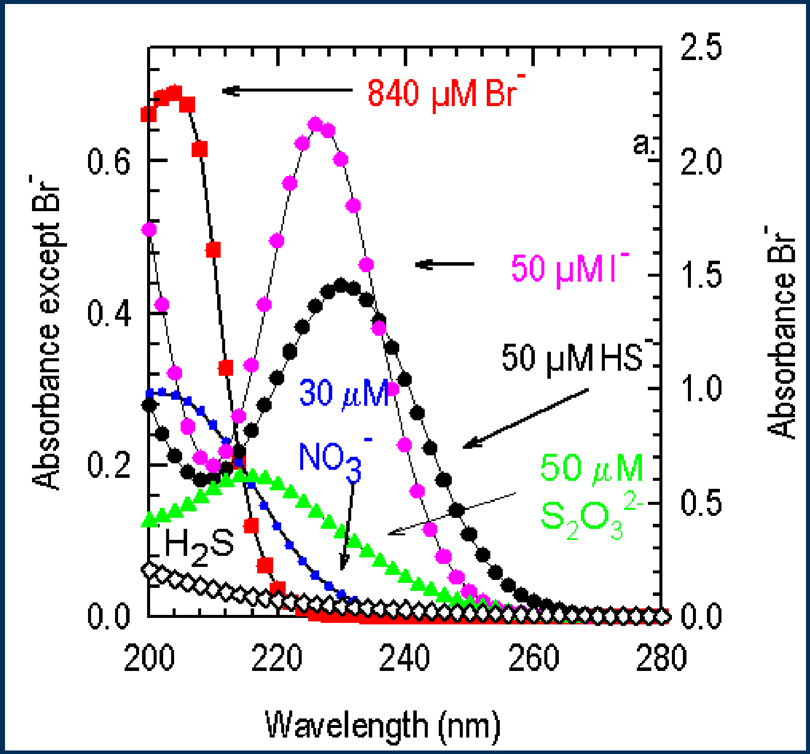
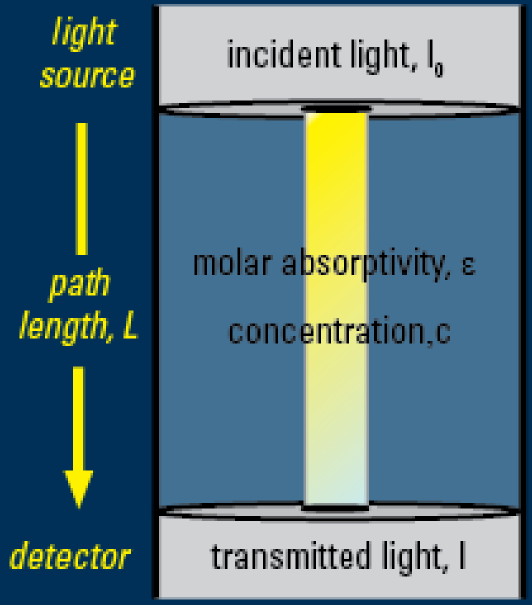
- For UV sensors, **keys to accurate measurements**:

Measure the right wavelengths



Get the right path length



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

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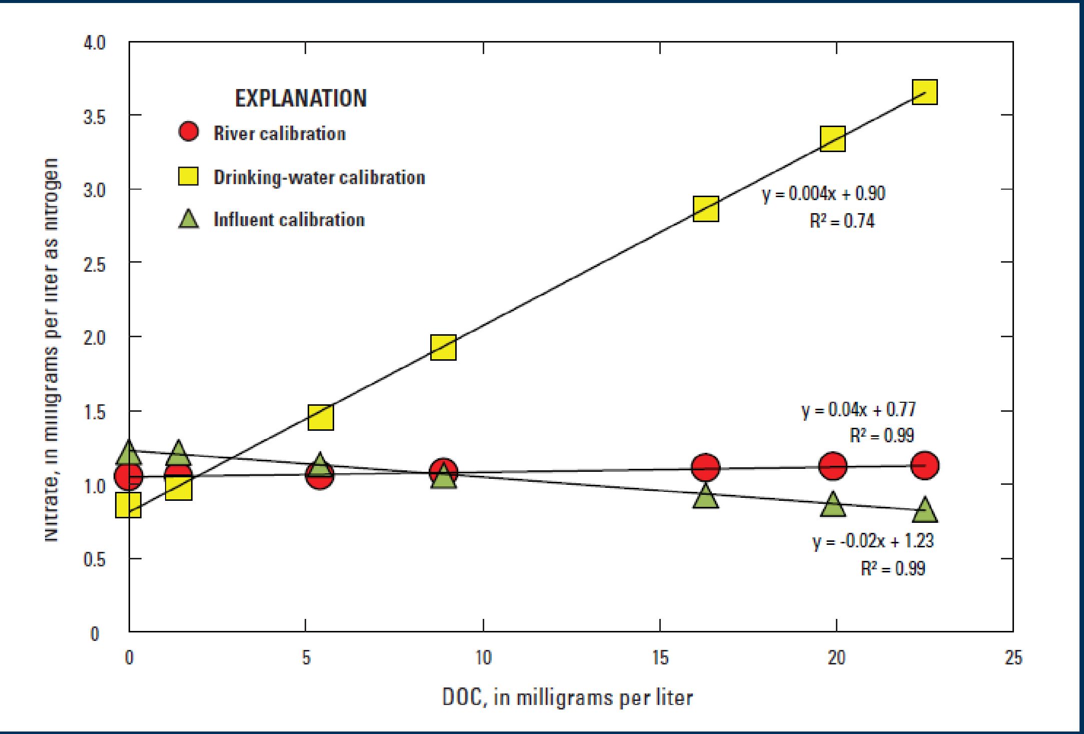
Accurate Measurements

- 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!

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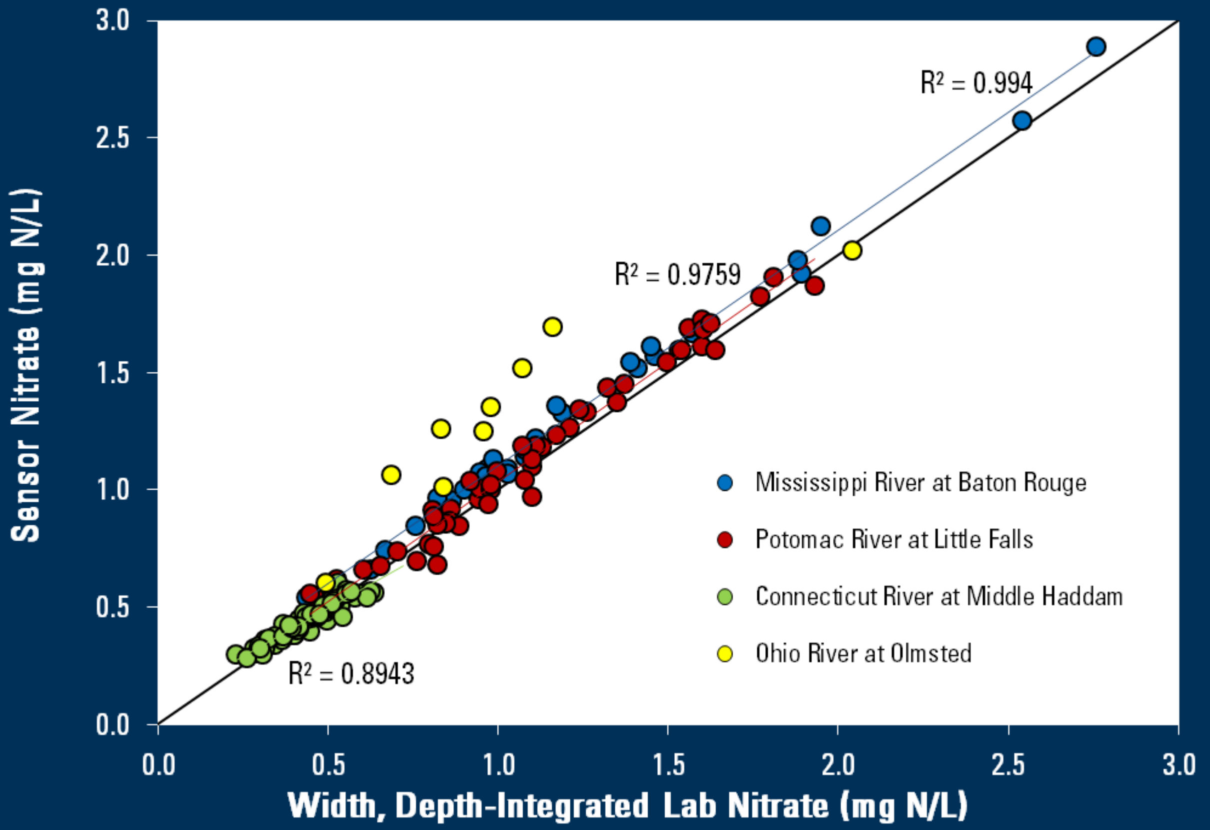
Accurate Measurements

- 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**



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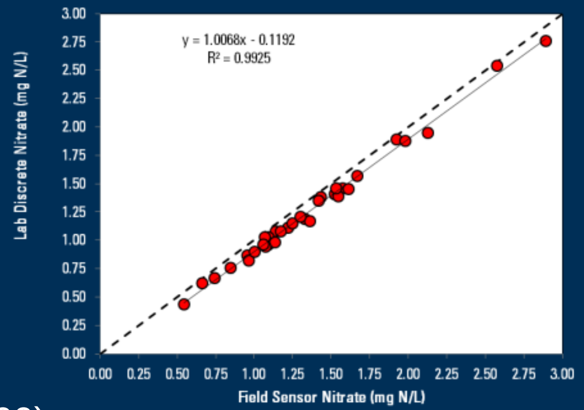
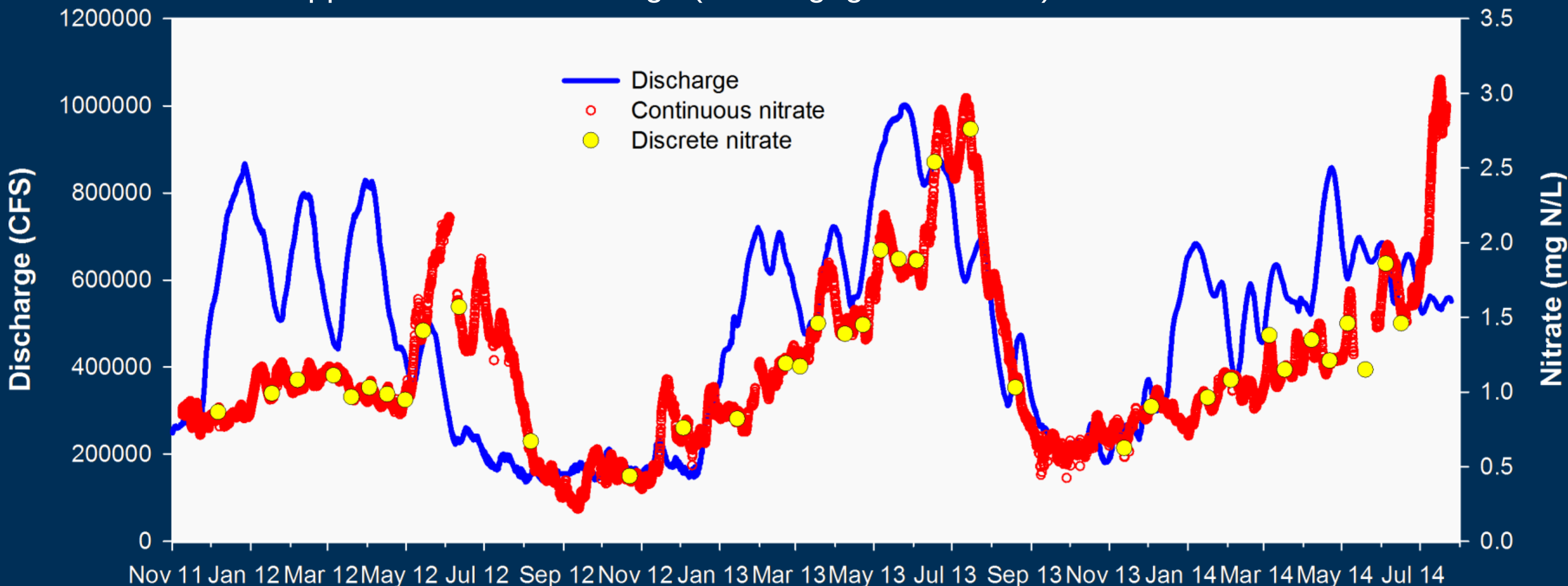
Mississippi River Continuous Nitrate

- 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%





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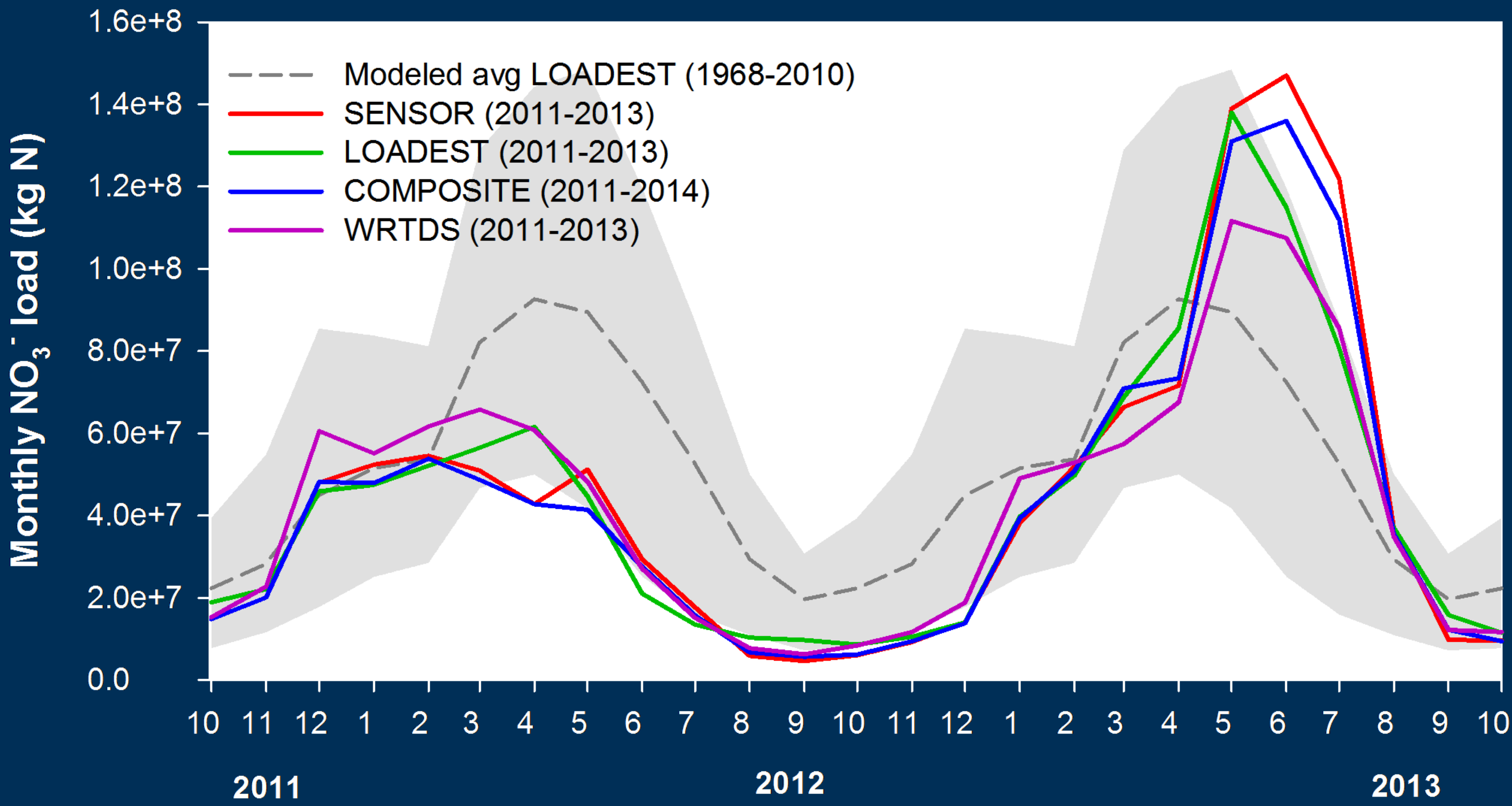
Can we improve load estimates?

- 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)

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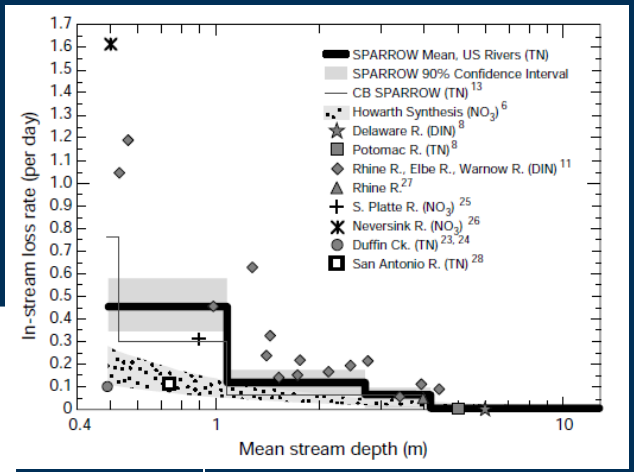
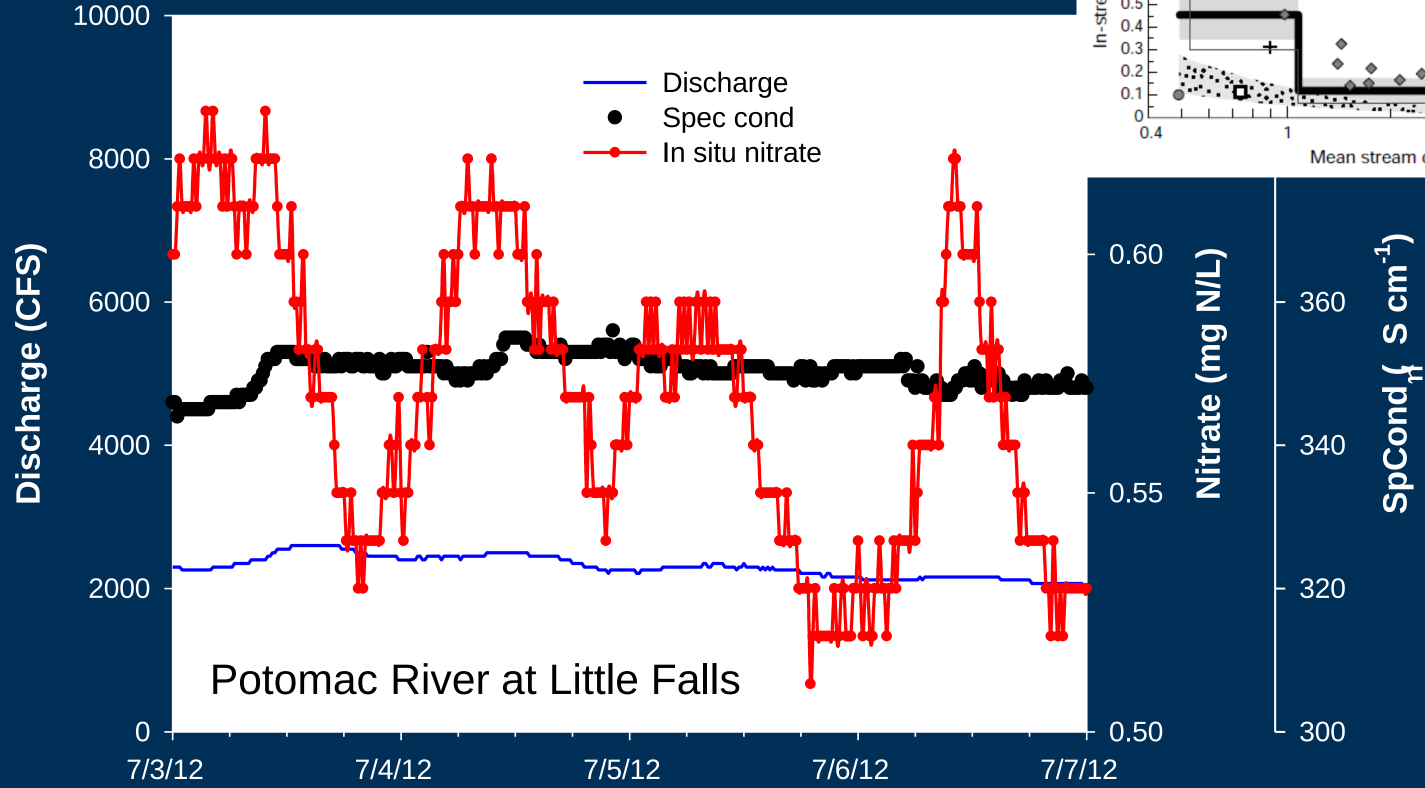
LOADEST data from St. Francisville, continuous data from Baton Rouge;
http://toxics.usgs.gov/hypoxia/mississippi/flux_ests/delivery/index.html; * http://www.gulfhypoxia.net/

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





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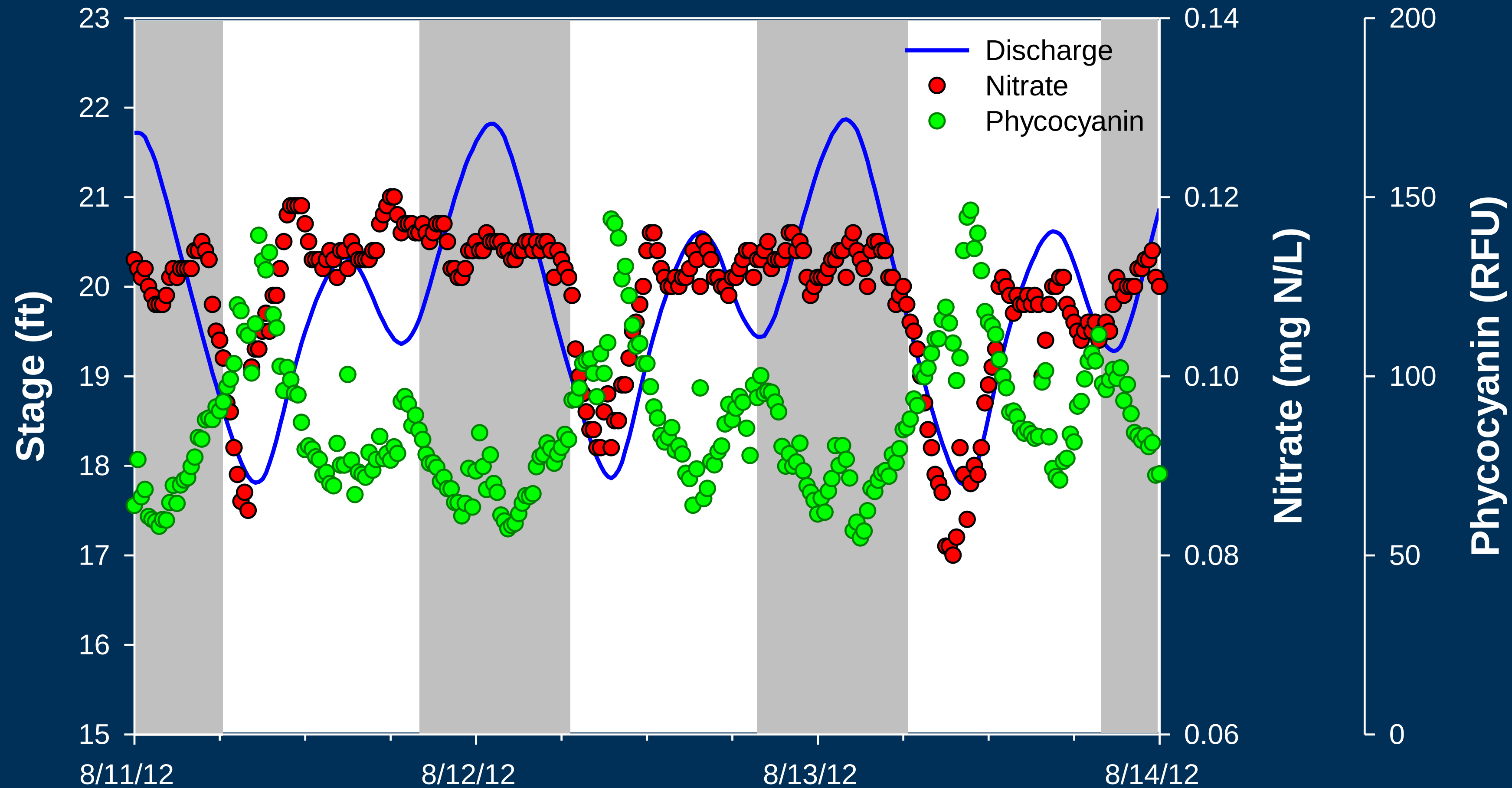
Exploring nutrient uptake?

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



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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 <u>known quality</u> in national network of nutrient monitors

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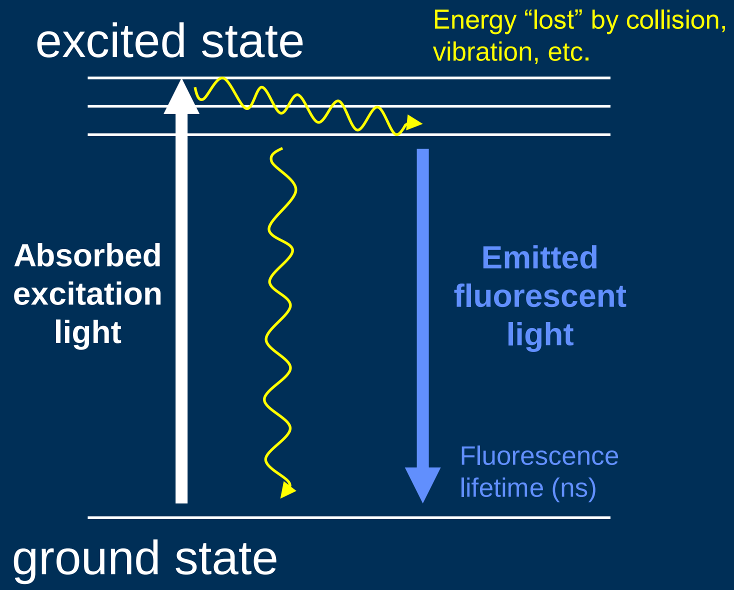
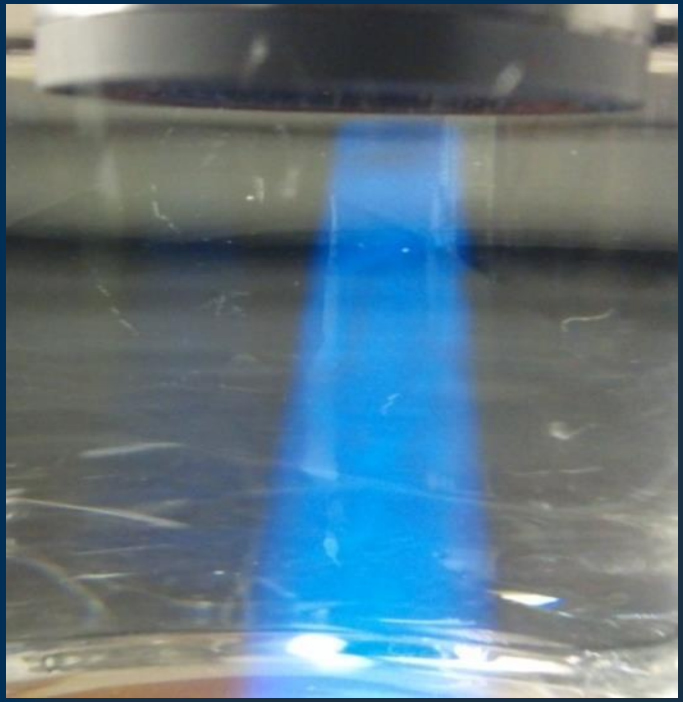
Fluorescence sensors

- **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*





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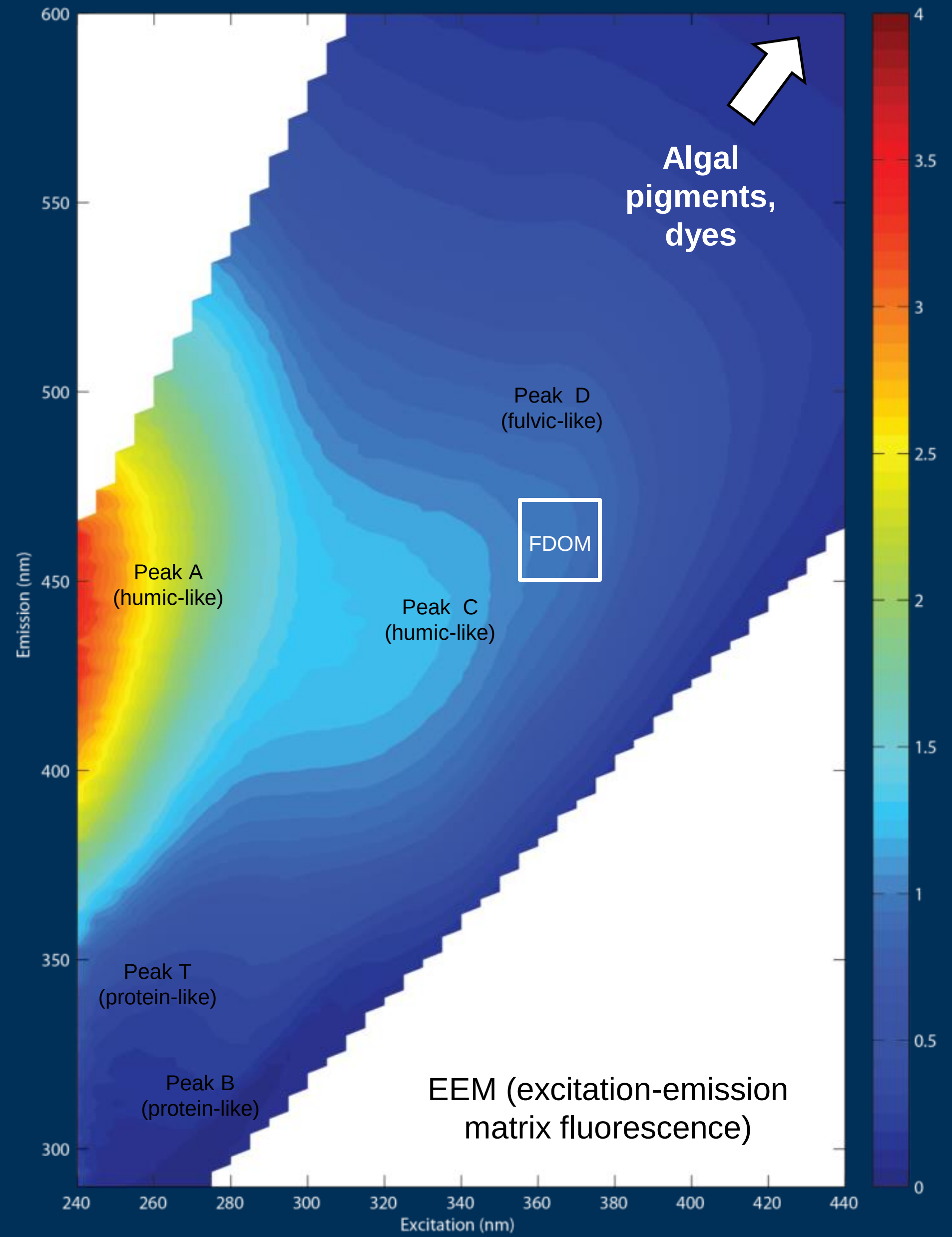
Quinine sulfate (QS) in 0.05 H_2SO_4 measured with a commercial FDOM sensor (ex. ~370 nm, em. ~460 nm)

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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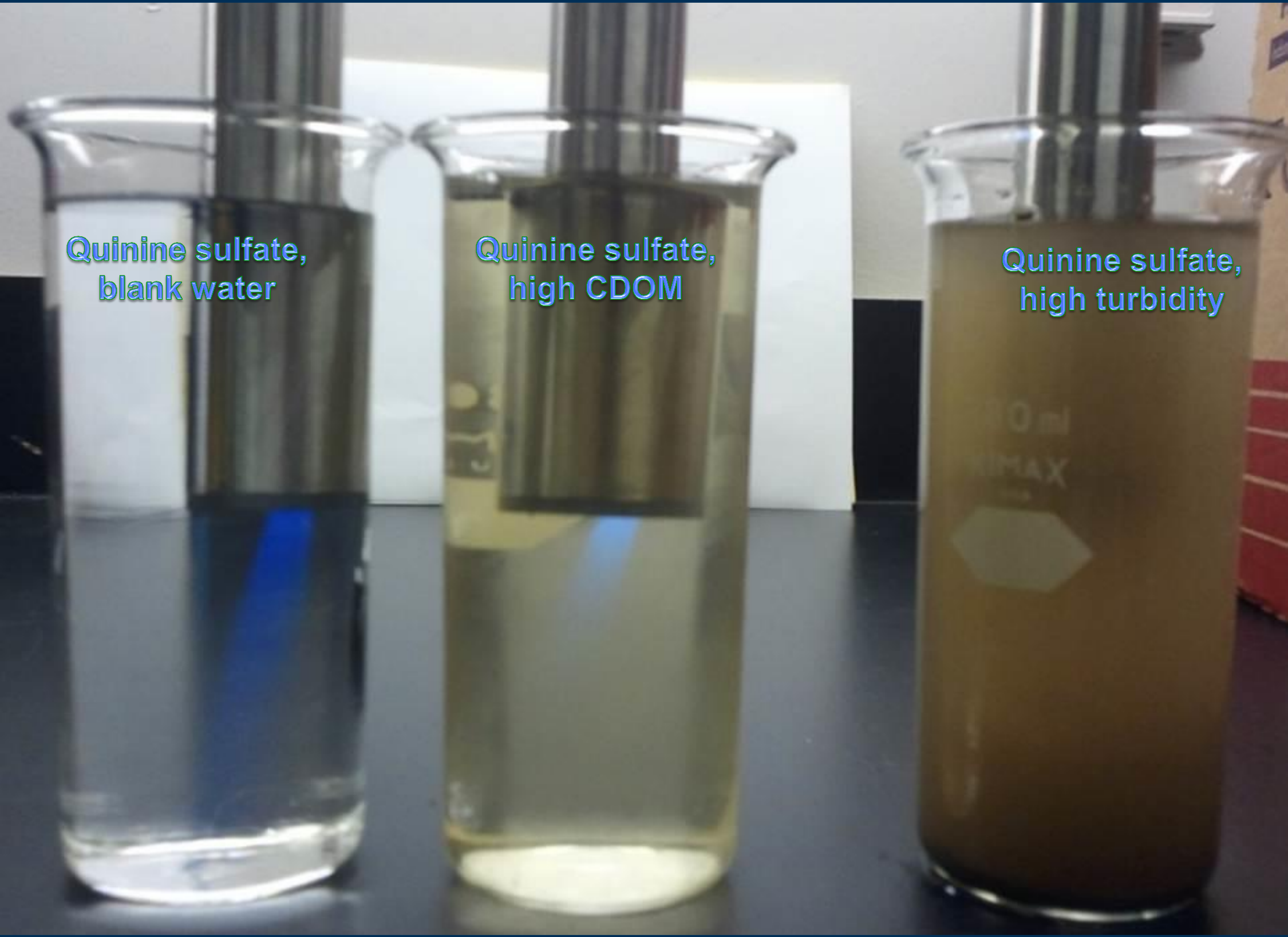
Challenges

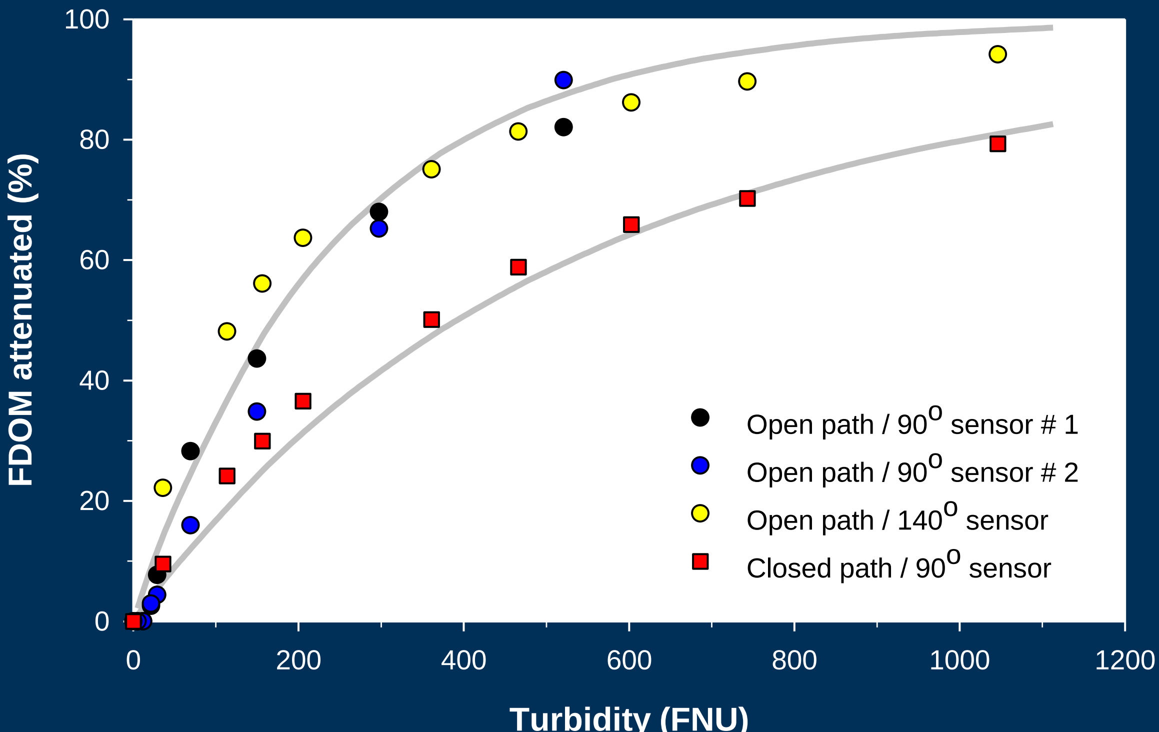
- Fouling
- Drift
- Power
- Communication
- Interferences
- Sensor design
- Units


Quinine sulfate, blank water
Quinine sulfate, high CDOM
Quinine sulfate, high turbidity

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)



Downing et al., 2012

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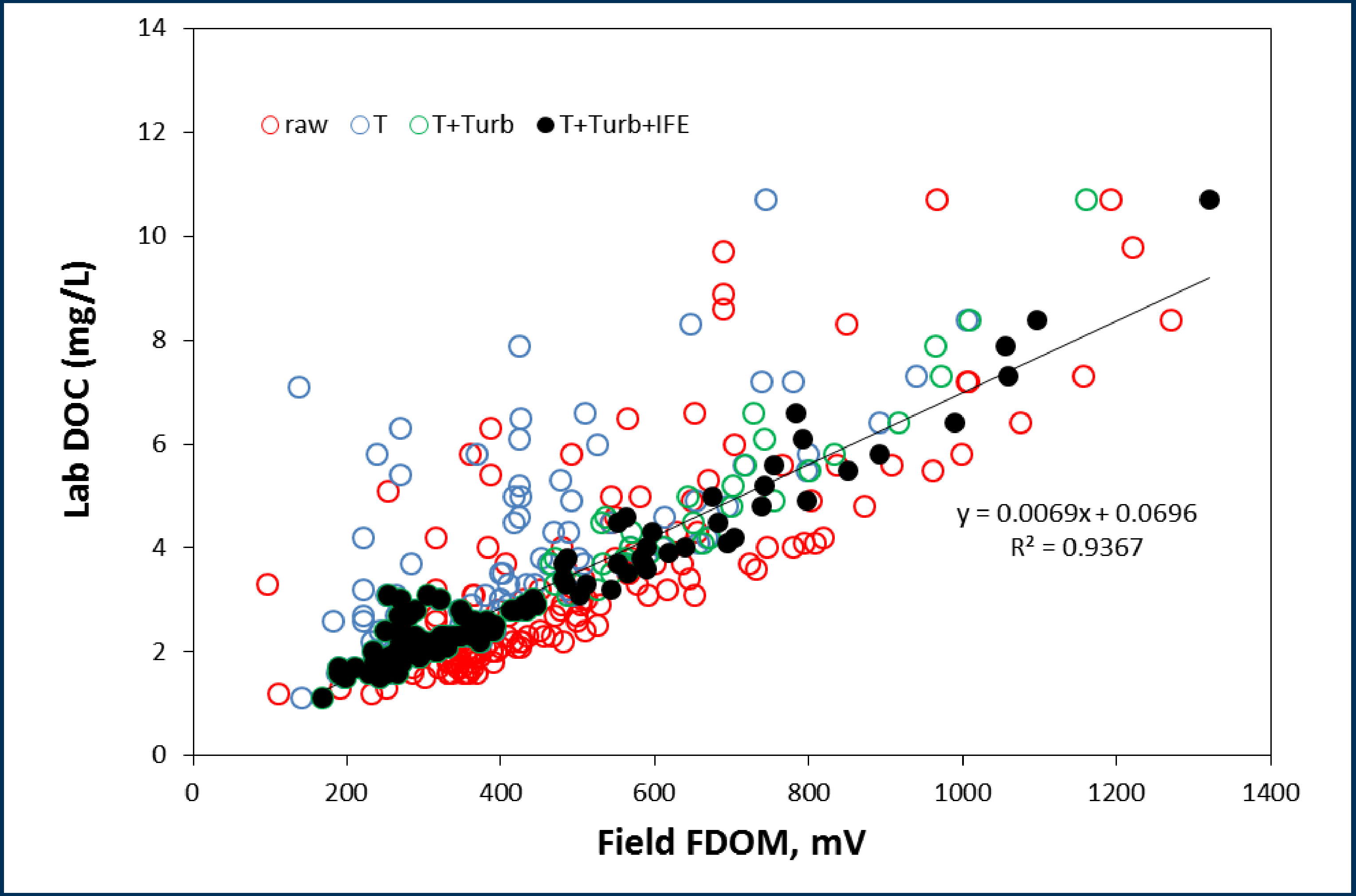
FDOM vs. DOC

Raw and corrected sensor data from Sleepers River, Vermont



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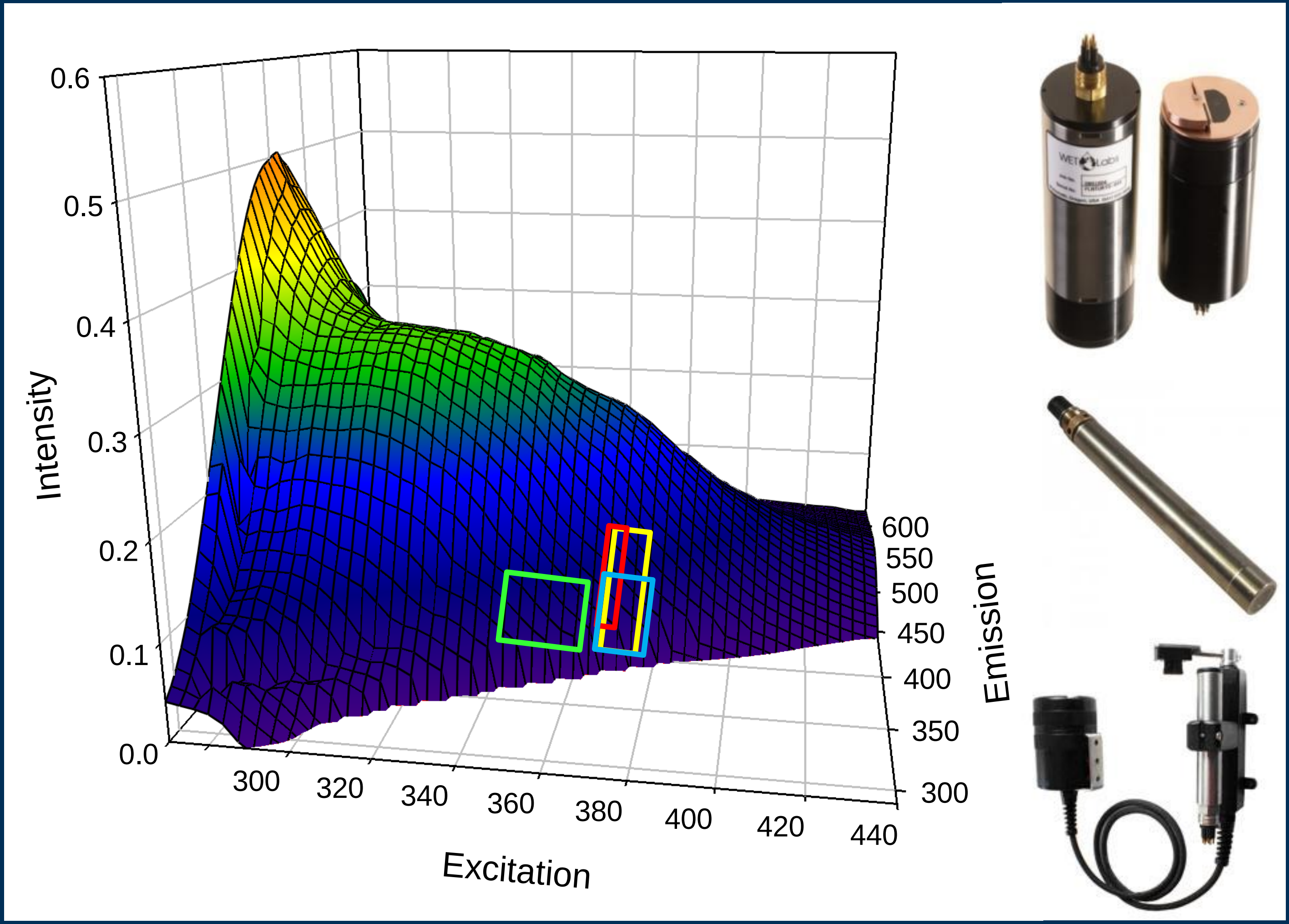
Data comparability

- Differences in ex/em and bandpass between manufacturers
- Field FDOM data in quinine sulfate equivalents (QSE) can differ dramatically



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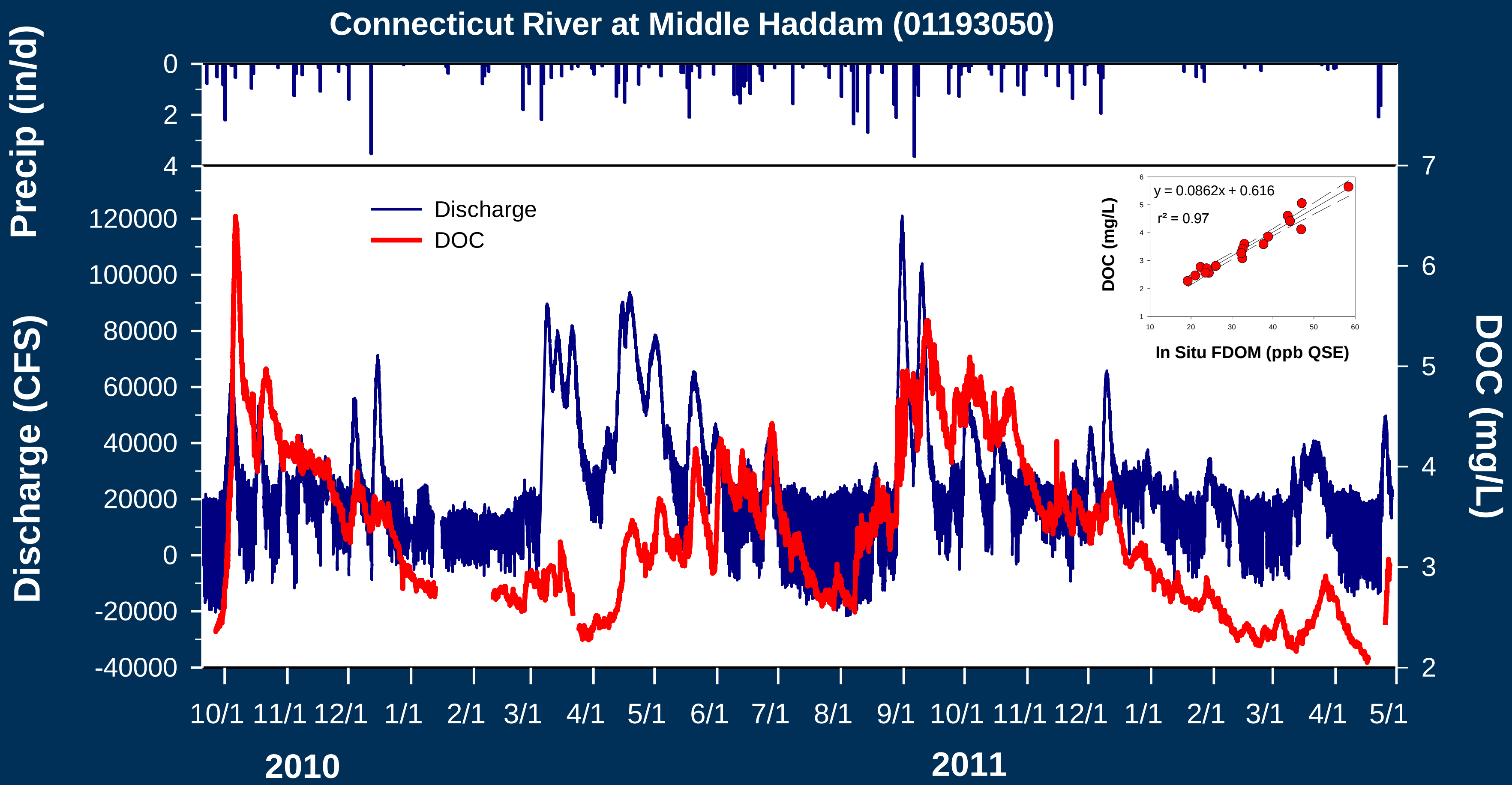
How is DOC transport affected by large events?

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



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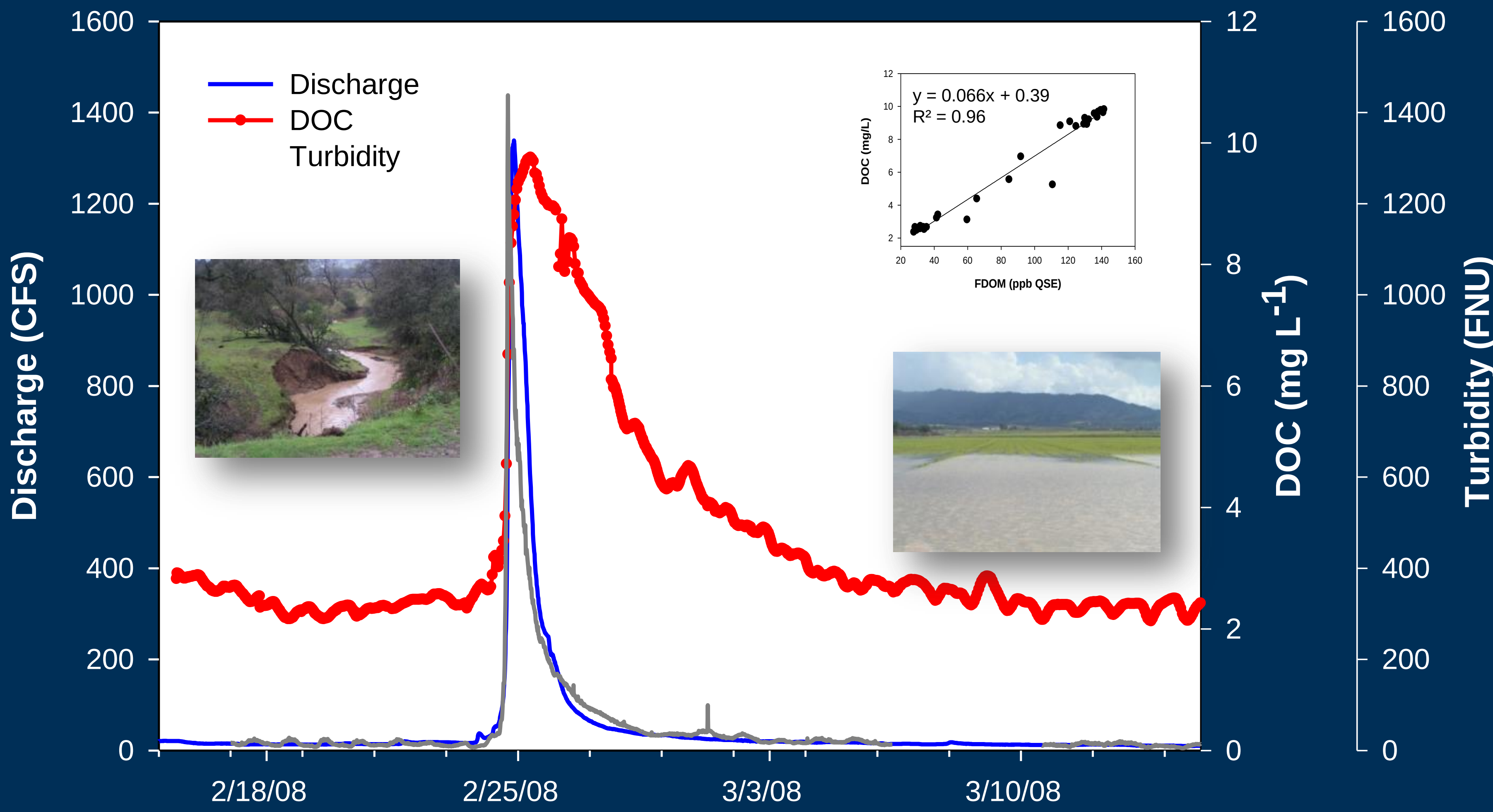
Agricultural watersheds: DOM sources

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)



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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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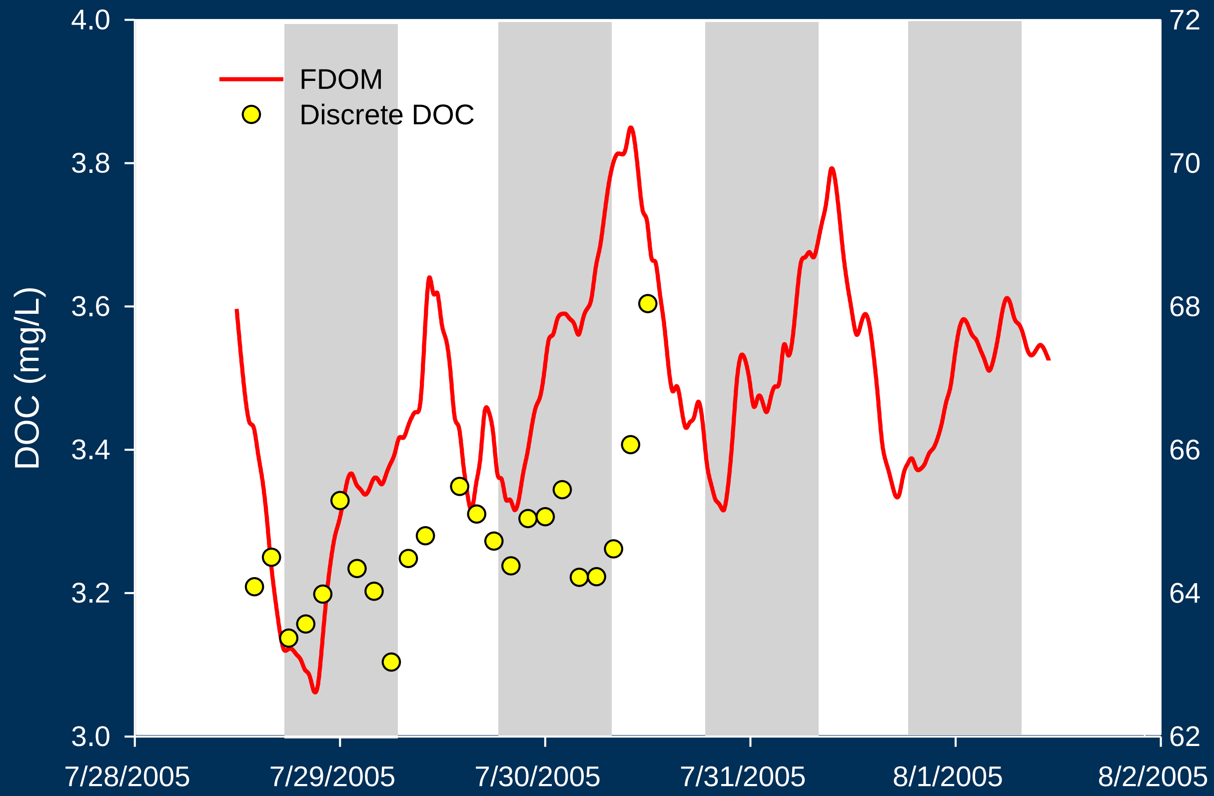

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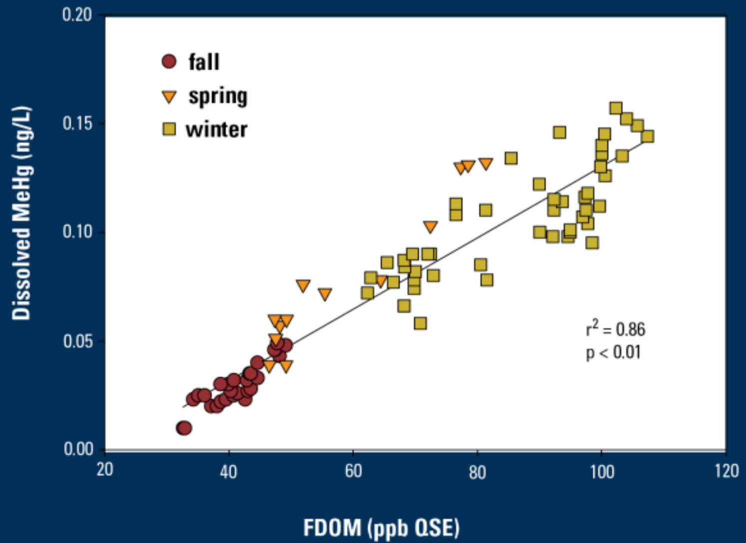
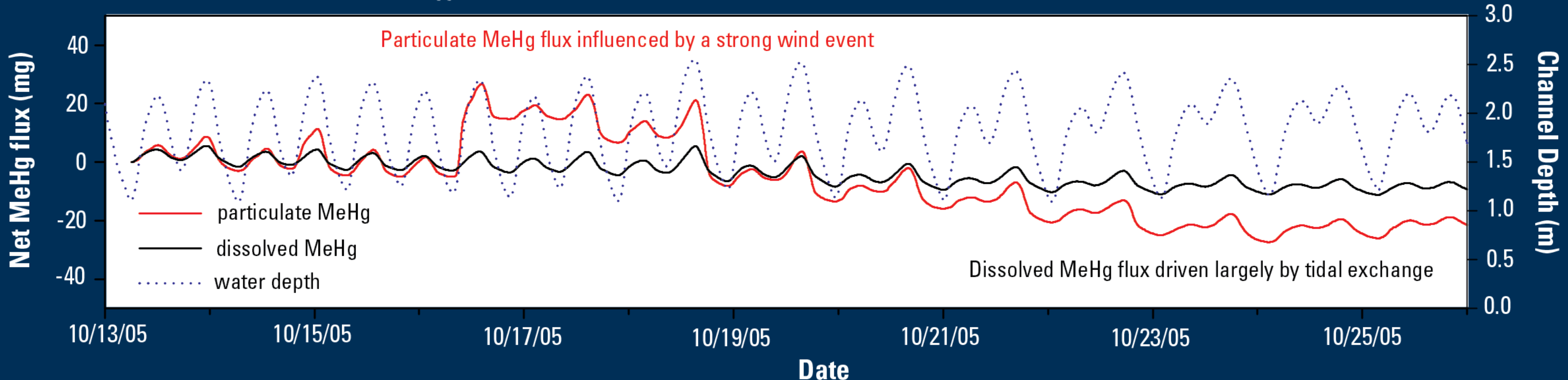
Spencer et al. 2007, Pellerin et al. 2009

Proxies: methylmercury

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





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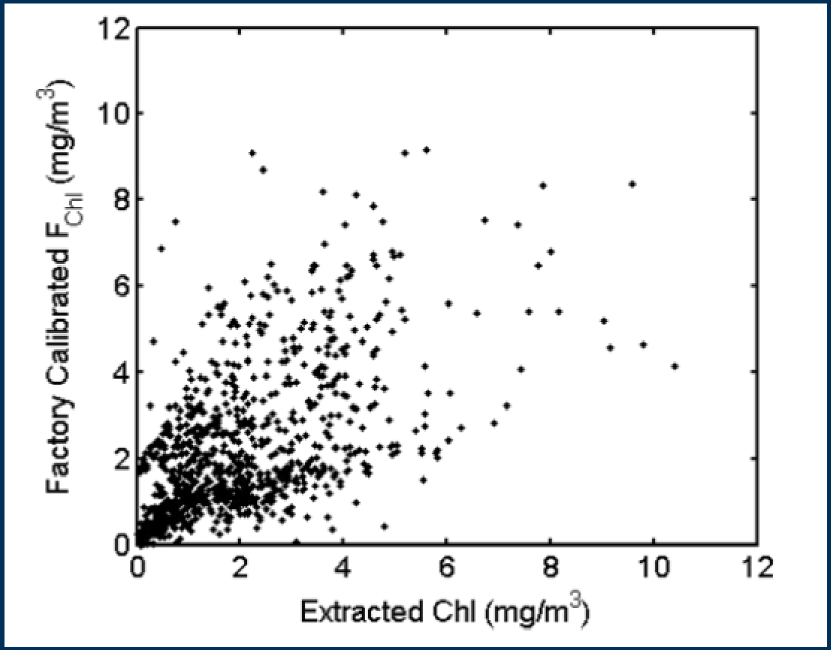
Bergamaschi et al., 2011

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

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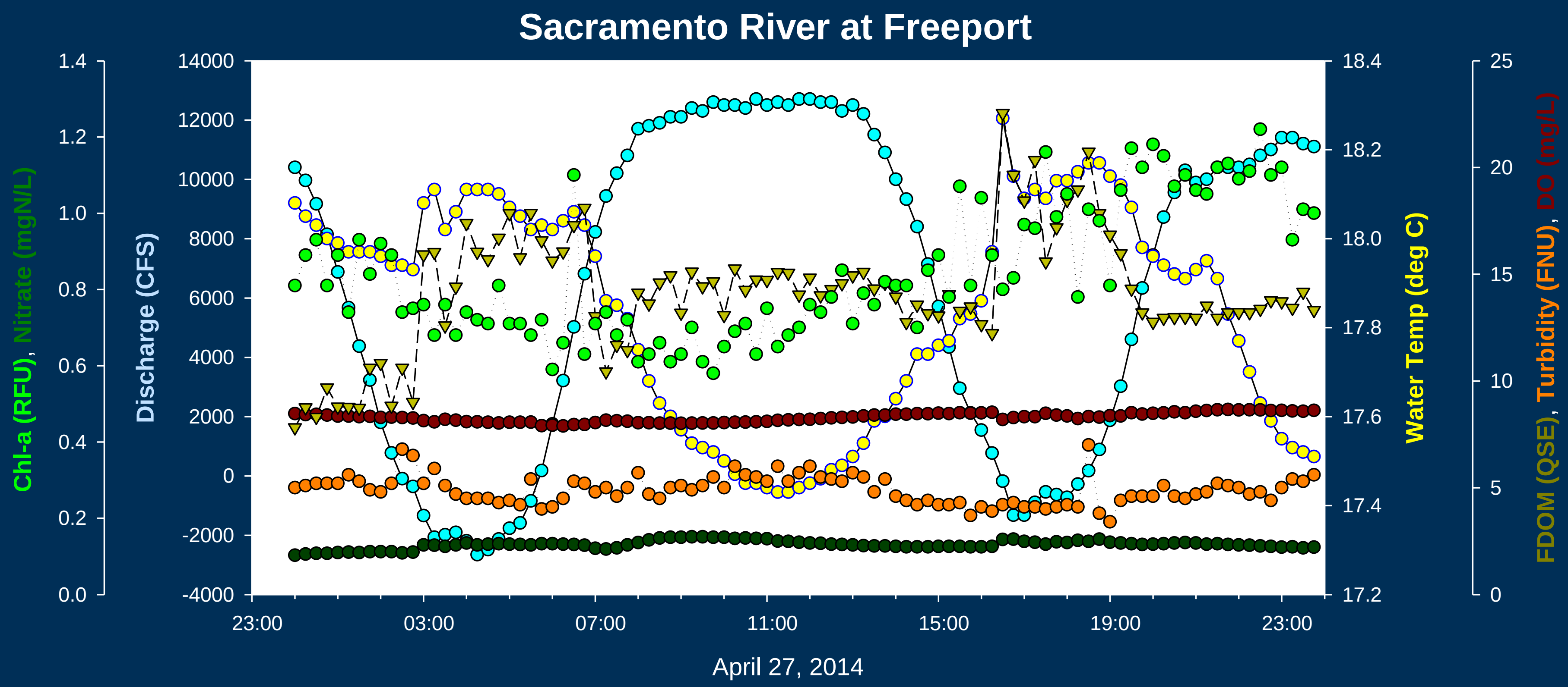
Is continuous water quality data "big data"?

- "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 (PO_4, NH_4, phycocyanin, particle size, …)



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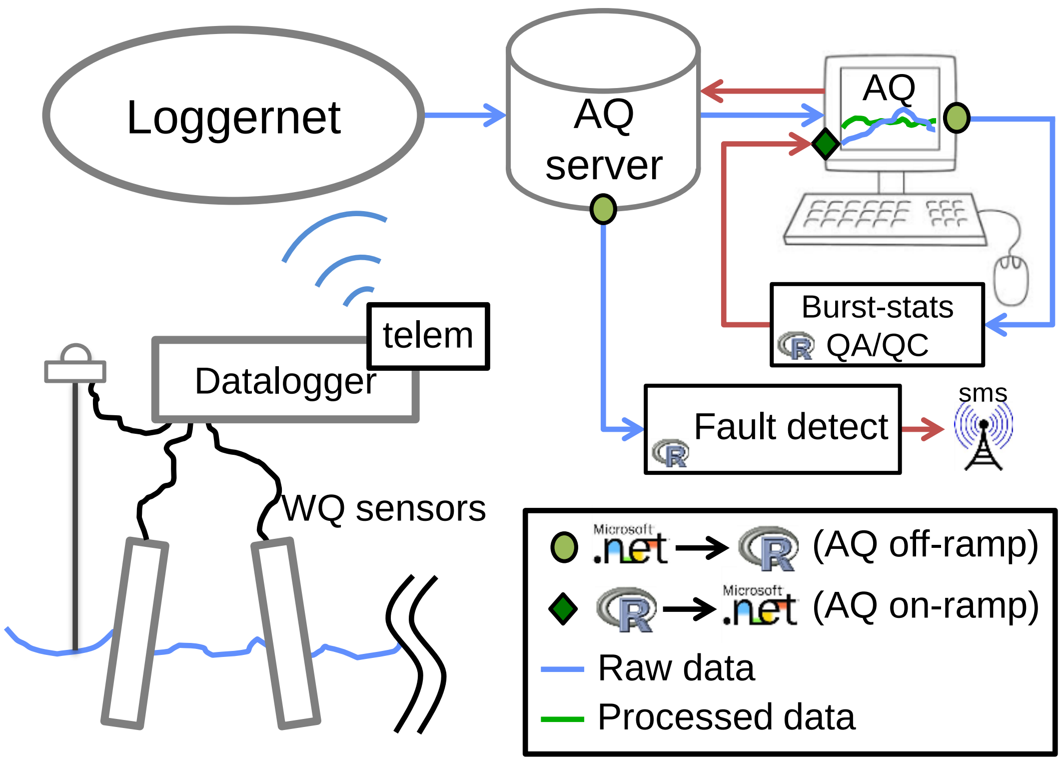
Advancing the QA of WQ Data



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

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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
- …

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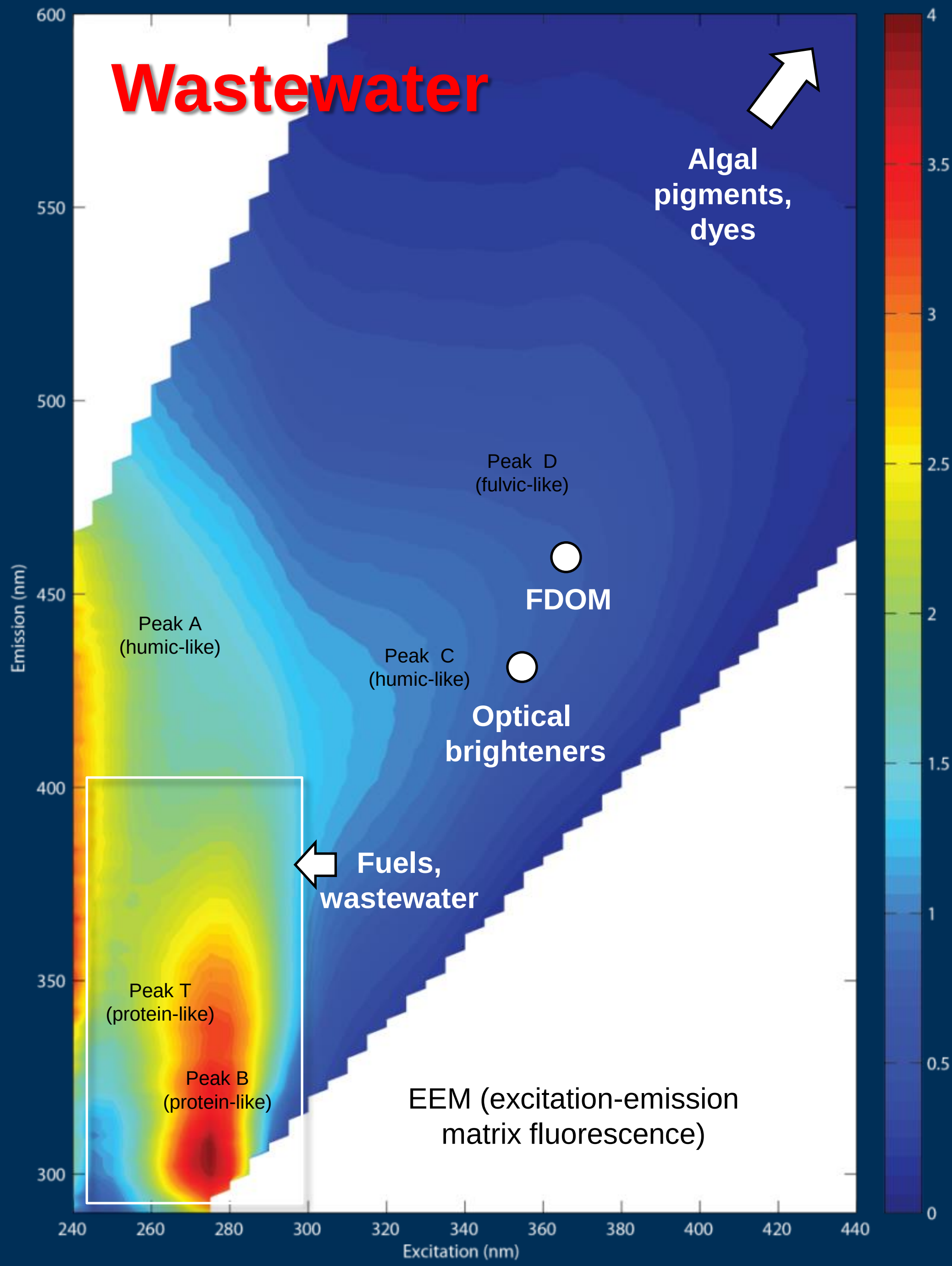
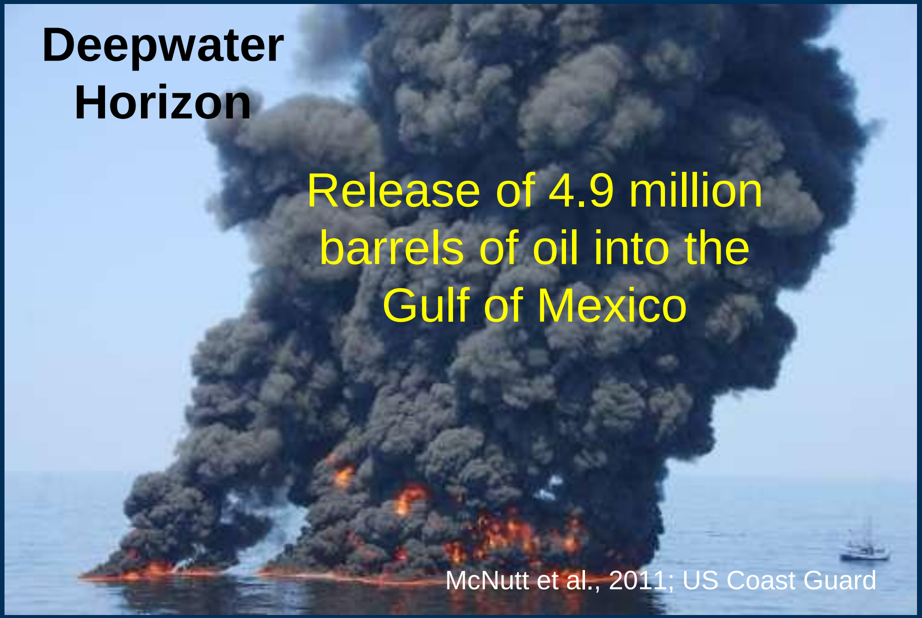


Rapid Deployment Systems

Event response

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



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)?

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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
  - ….

USGS (Andy Zeigler)

Thanks!

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