

### Abstract

The landscapes of Vermont are changing due to the warming climate, urbanization, farm practices, and far more pollution than before. **The overarching question is how these changes in landscape are influencing the composition, abundance, and bioavailability of nutrients in Vermont waterways.**

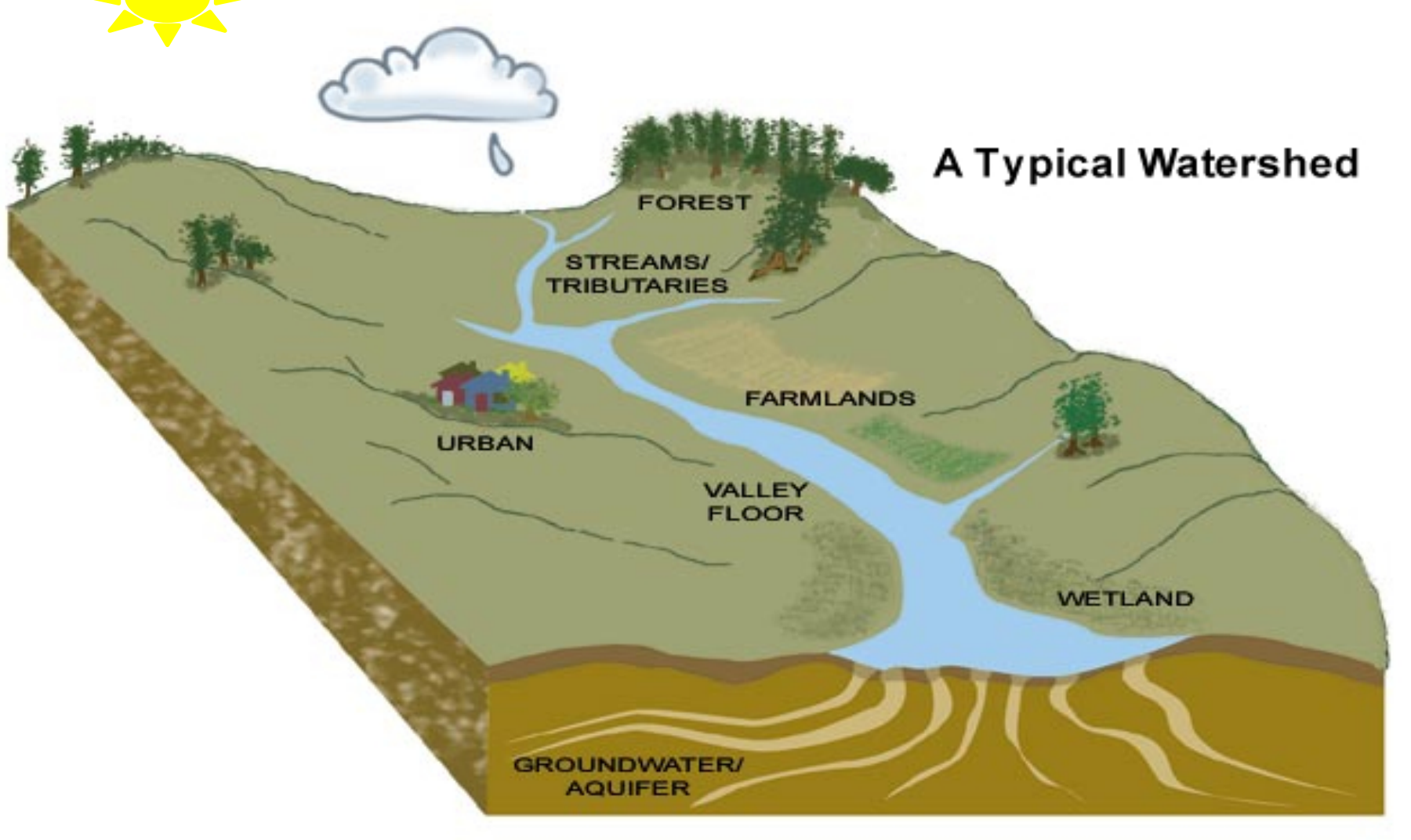
Continuous monitoring of water quality parameters was undertaken to get an understanding of how nutrients change over the course of the season, and during large events (i.e. storms). Locations in Northern Vermont include forested, suburban, agricultural and mixed land use. Using a s::can spectrolyser in situ water quality sensor allowed for nitrate and many other physical parameters to be monitored continuously. **There is a need to obtain continuous nutrient data because discrete, infrequent sampling is insufficient in providing information on small timescales.**

To determine a local calibration, grab samples were taken as a comparison to in situ sensor measurements.

In tandem, experiments were conducted to look at how sunlight will affect the protein (the more bioavailable fraction) and humic components of DOM, characterized by excitation-emission matrices. Sunlight may increase or decrease the bioavailability of these components to microorganisms via photochemical reactions.

**Together, this data can be used to predict changes in organic and inorganic nutrients as the land use in our watersheds evolve.**

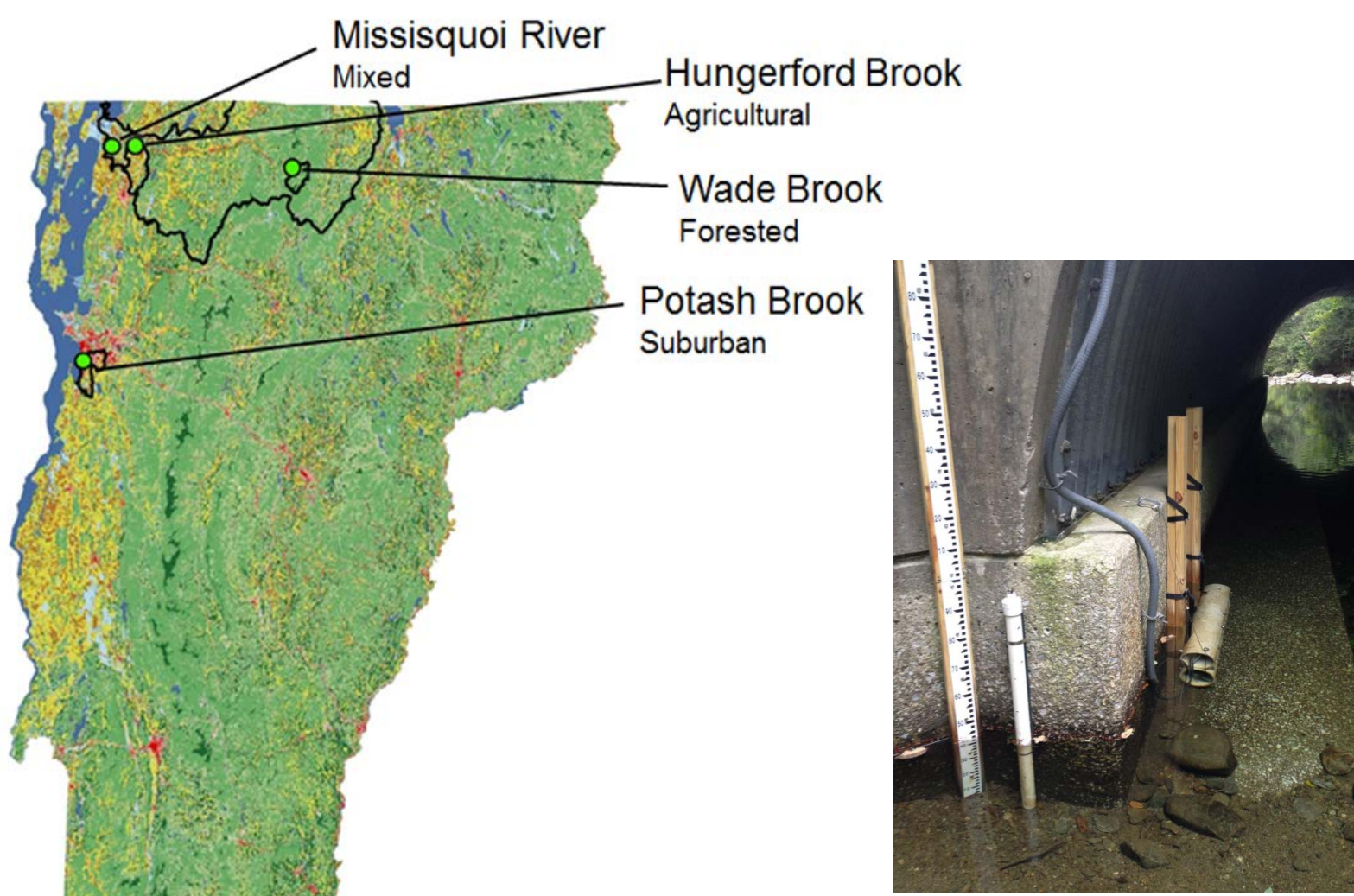
### Introduction



How do different watersheds impact nutrients?

How does sunlight transform carbon nutrients during transport downstream?

### Site Locations and Equipment



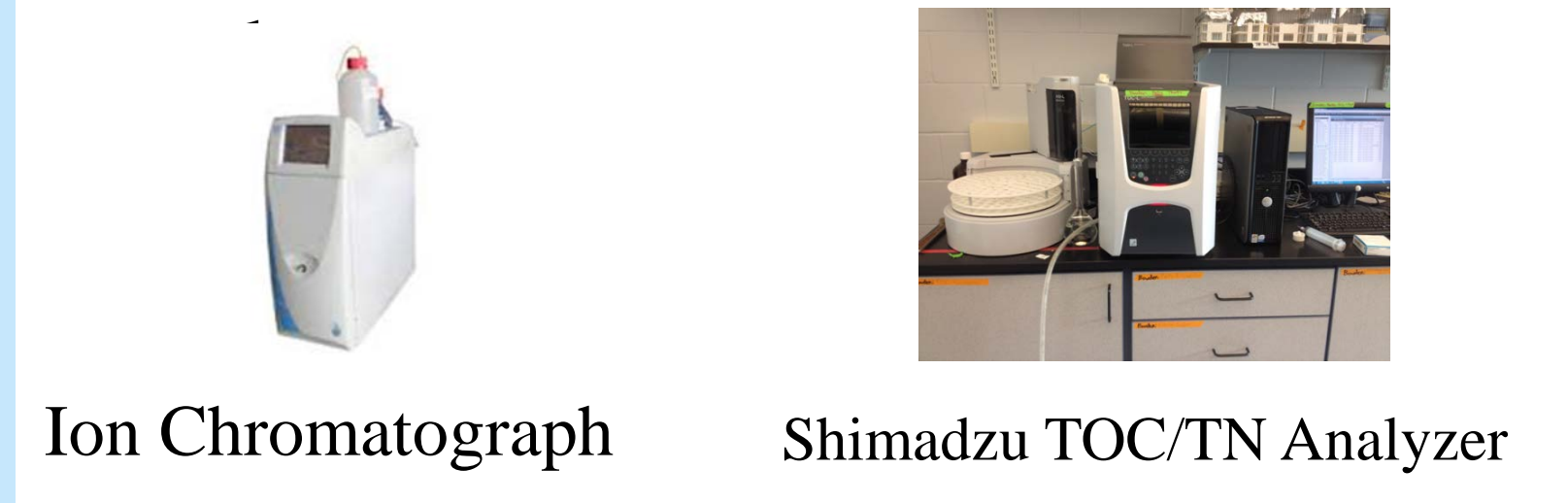
- YSI EXO2
- Conductivity
  - Dissolved Oxygen
  - pH
  - Turbidity
  - Fluorescent Dissolved Organic Matter
  - BGA/Chlorophyll
- S::can Spectrolyser
- Nitrate-N
  - Dissolved Organic Carbon
  - Total Organic Carbon
  - Turbidity
  - Full UV/Visible 'Fingerprint' scan

- Wade Brook- Forested
- Hungerford Brook- Agricultural
- Potash Brook- Suburban
- Missisquoi River- Mixed land use

### Methods

#### Nitrate and Carbon

- 250 mL filtered water collected (Whatman glass microfiber filter, 0.45 μm)
- Samples were frozen until analyzed for nitrate using Ion Chromatograph (ICS 200, Dionex)
- DOC analyzed using a Shimadzu TOC/TN



#### Photochemical

- Experiment lasted between 48 to 96 hours
- DOC samples taken for initial and final
- Changes in carbon quality were measured by both changes in protein-like component from EEMs and Bioavailability experiments



### Results

#### Sensor

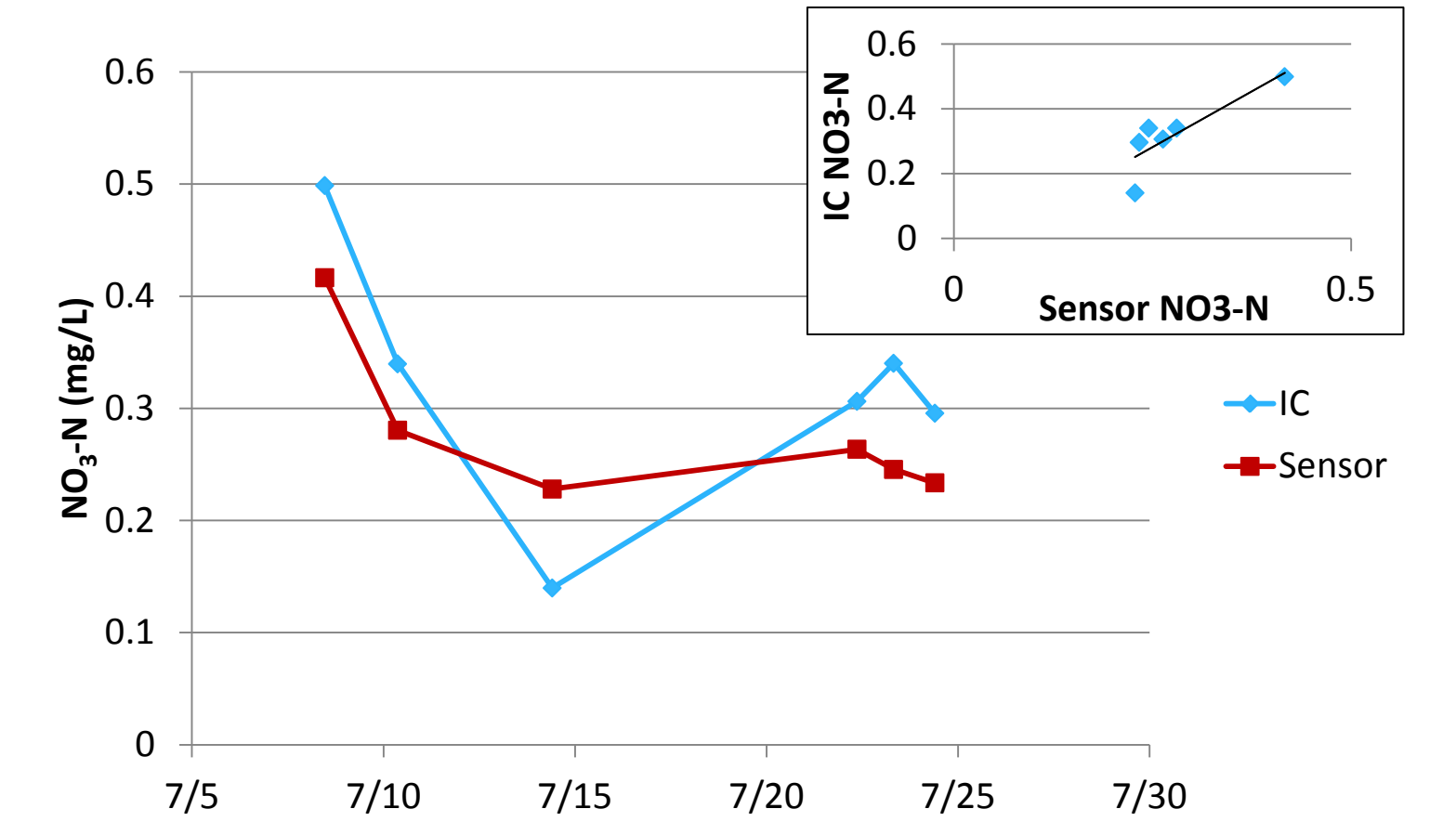


Figure 1. Sensor vs. IC comparison of NO<sub>3</sub>-N for the **Missisquoi River**  
R<sup>2</sup>=0.7201

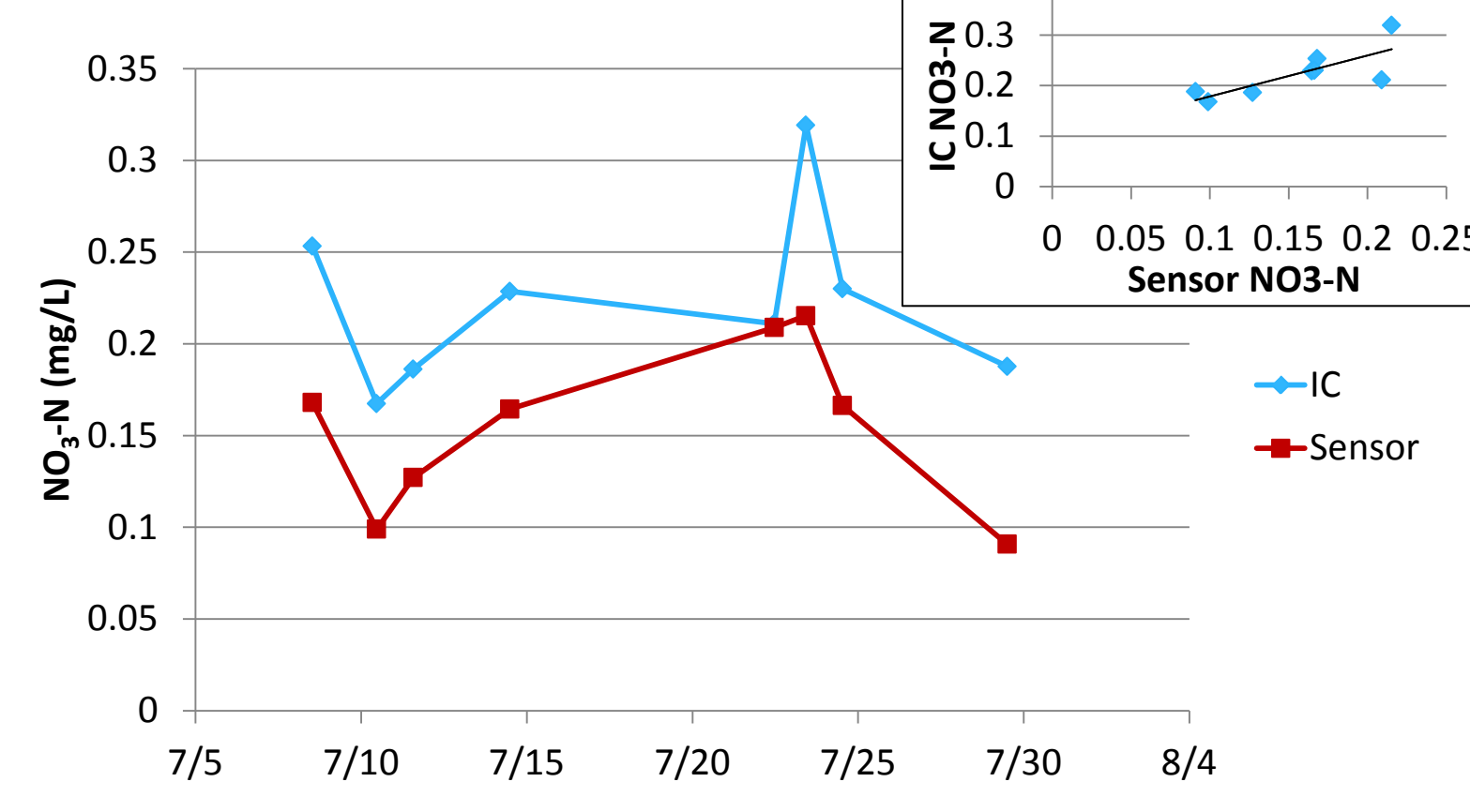


Figure 2. Sensor vs. IC comparison for NO<sub>3</sub>-N for **Wade Brook**  
R<sup>2</sup>=0.6072

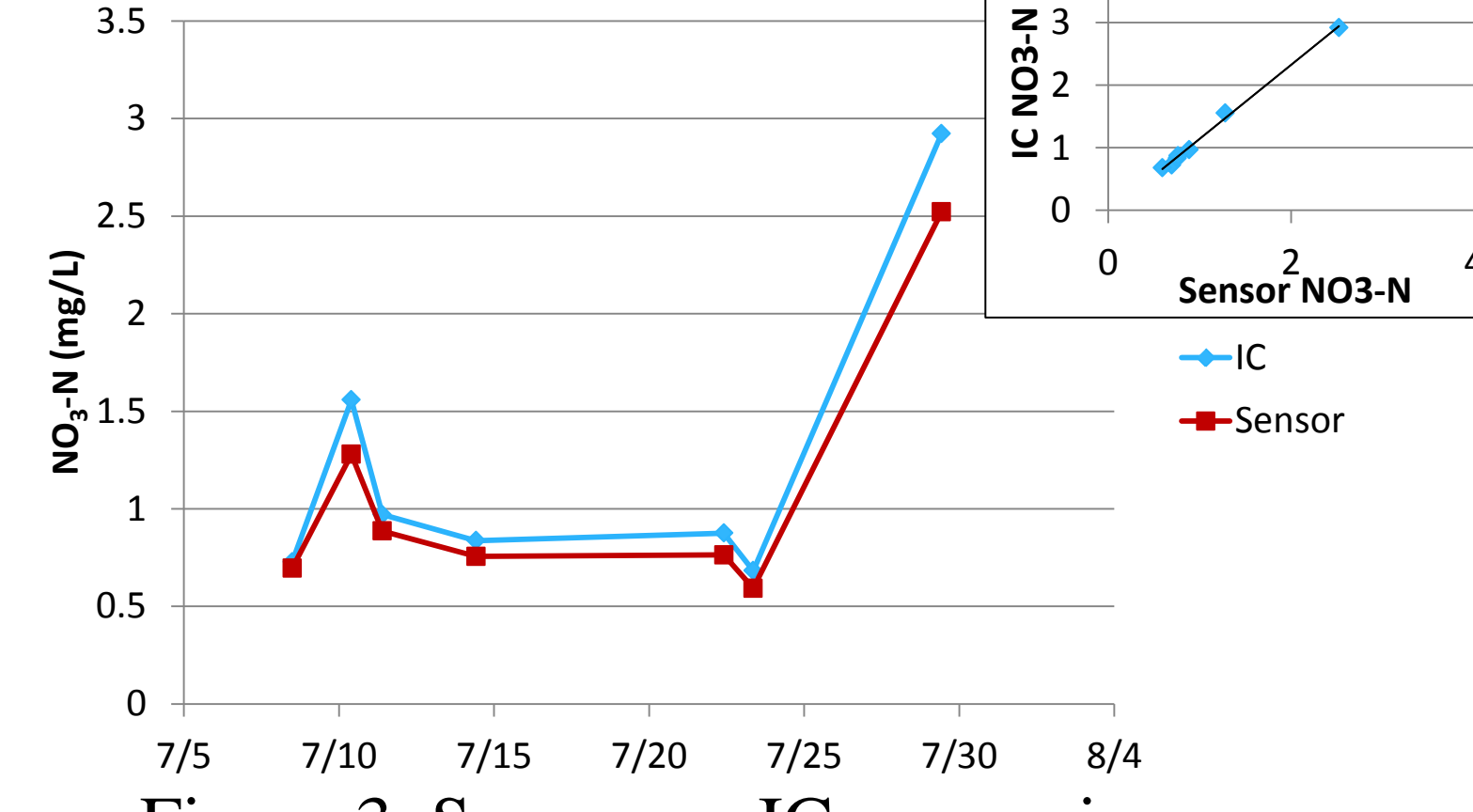


Figure 3. Sensor vs. IC comparison of NO<sub>3</sub>-N for **Hungerford**  
R<sup>2</sup>=0.9966

\* All concentrations are in mg/L

#### Photochemical

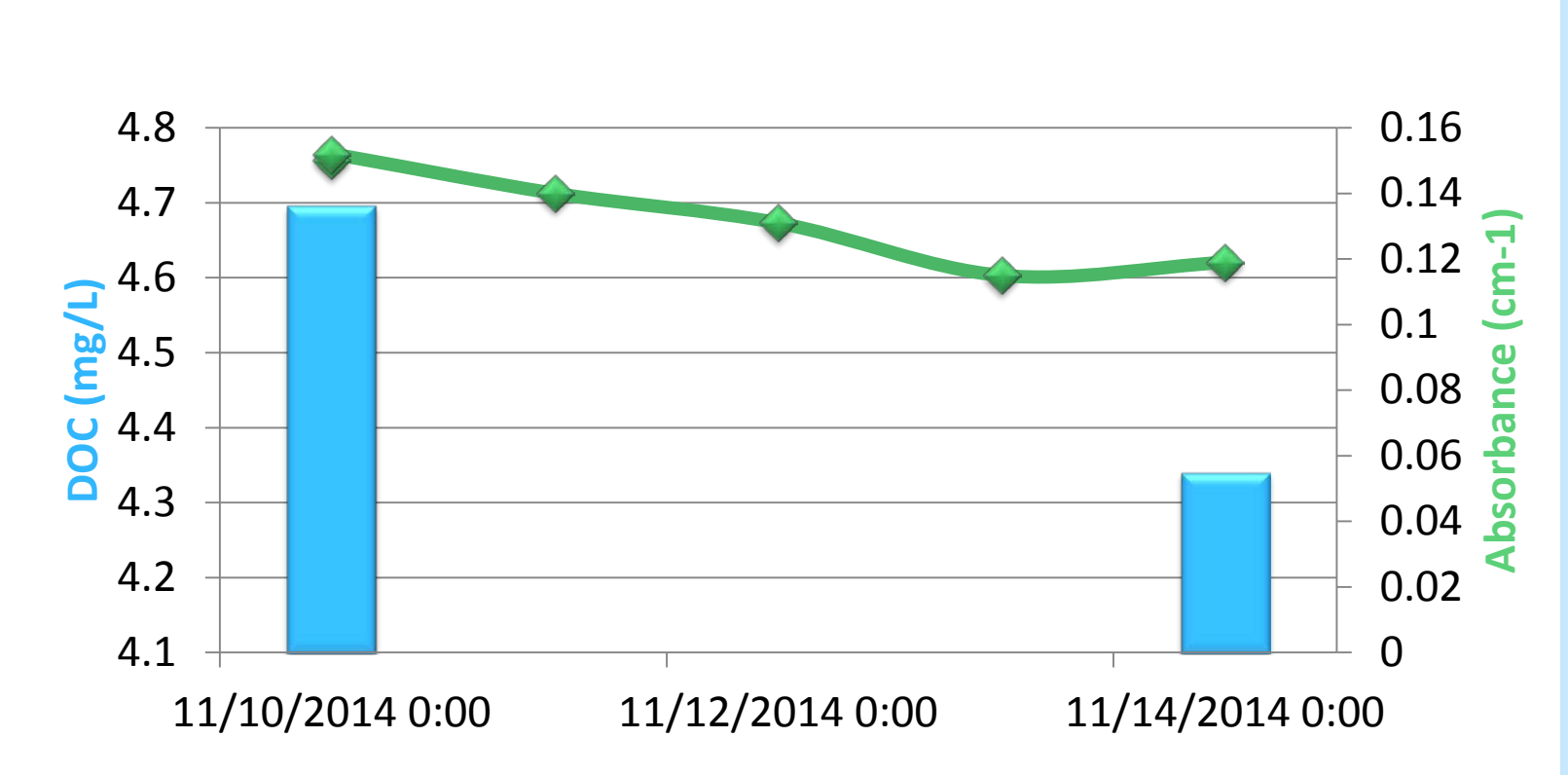


Figure 4. Change in DOC and absorbance after 96 hours for **Missisquoi River**  
DOC Change= 7.6% decrease

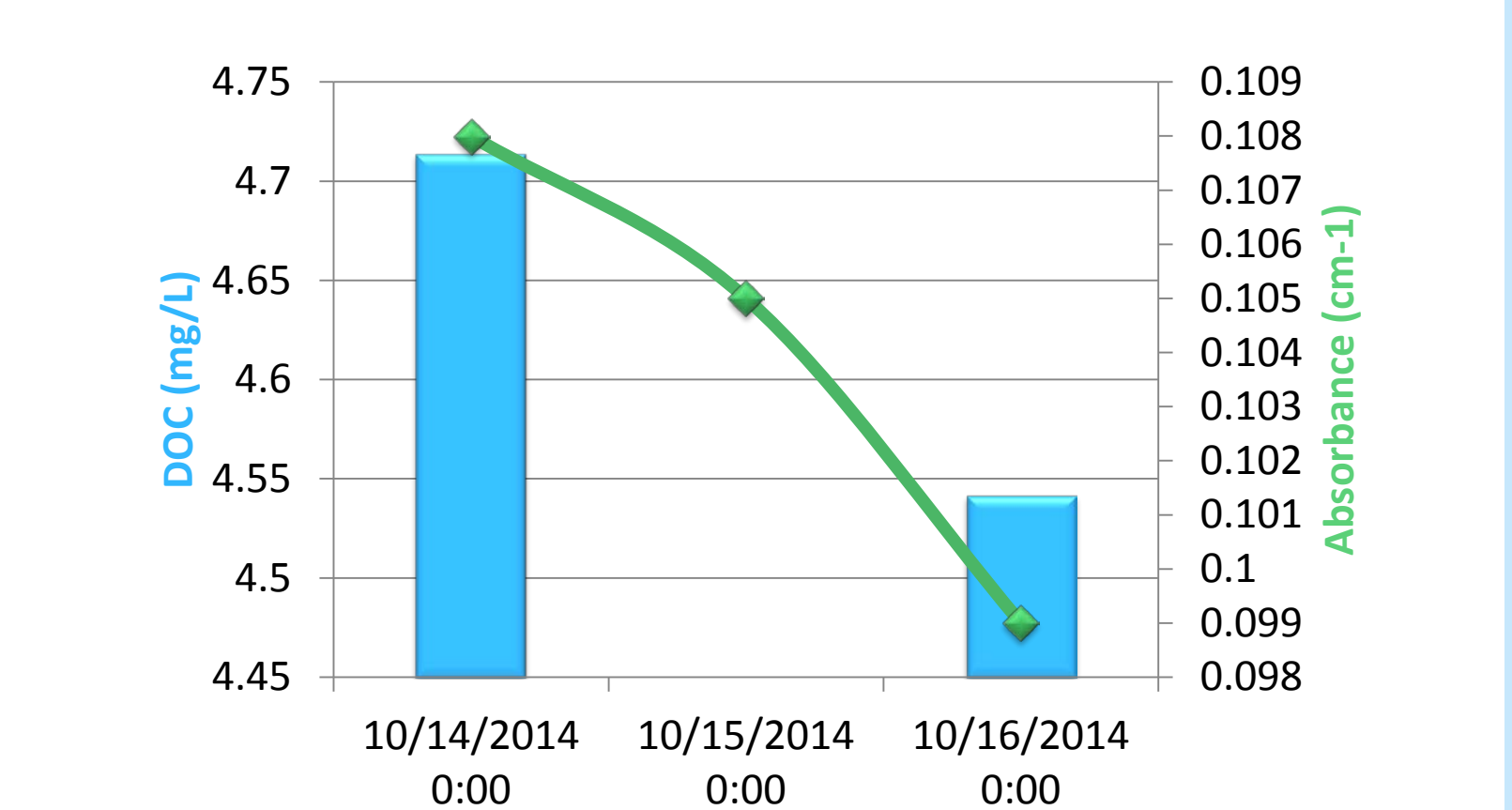


Figure 5. Change in DOC and absorbance after 48 hours for **Potash Brook**  
DOC Change= 3.6% decrease

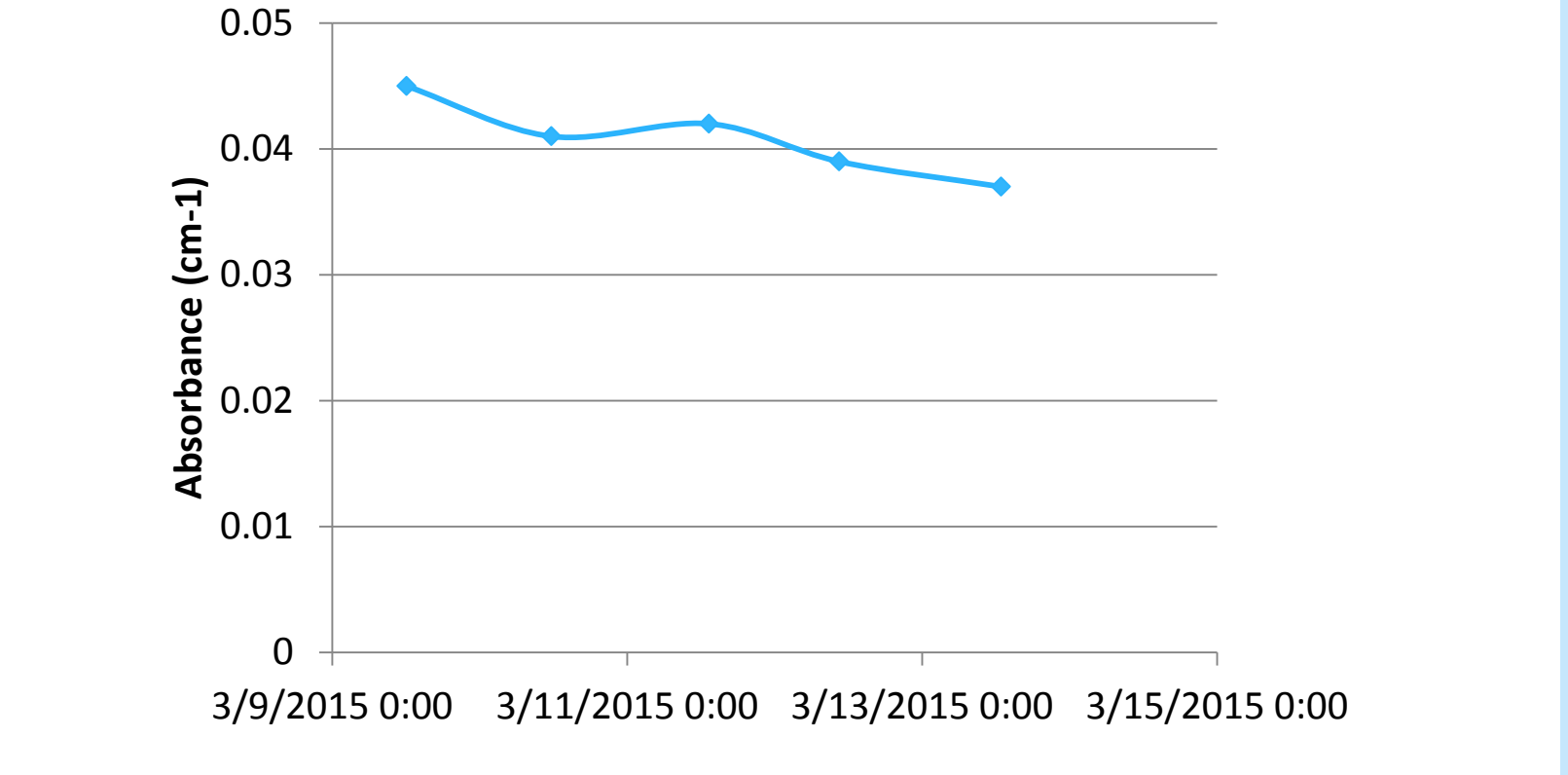
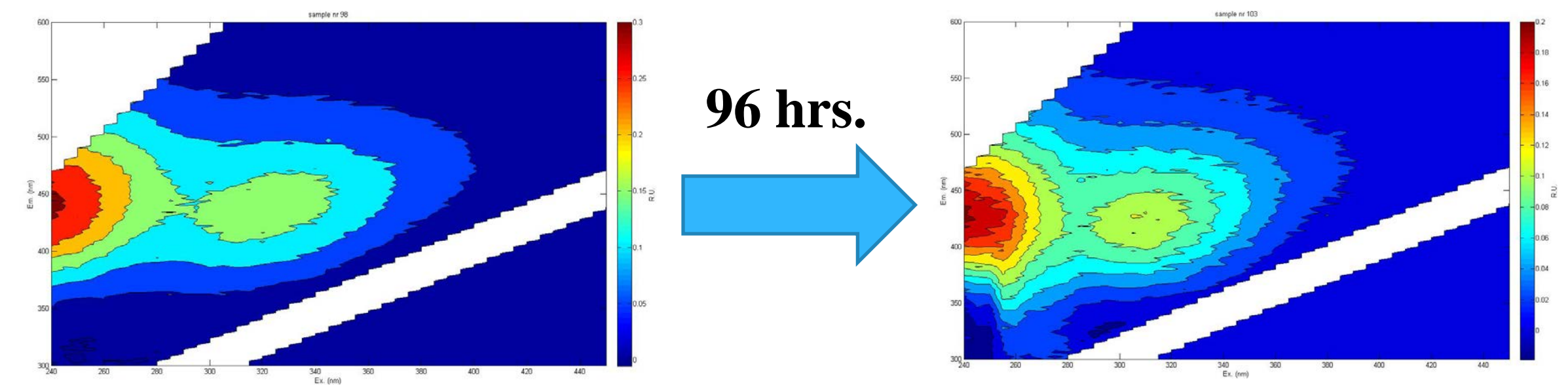


Figure 6. Change in absorbance over 96 hours for **Wade Brook**  
(DOC to be analyzed)

### Excitation-Emission Matrix



Protein component increased by 9.7% as determined by PARAFAC modeling for Missisquoi River indicating increase in bioavailability.

### Sensor Discussion

- Hungerford had the best R<sup>2</sup> value comparing sensor to grab samples.
- Wade had the lowest R<sup>2</sup> value with potential cause being NO<sub>3</sub>-N concentrations close to IC detection limit
- All sensor samples except one underestimated NO<sub>3</sub>-N compared to IC values

Possible explanations

- Detection limit: Wade NO<sub>3</sub>-N concentrations were close to detection limit of IC, therefore possible error and interference could explain greater differences between sensor and IC NO<sub>3</sub>-N results.
- Algorithm for NO<sub>3</sub>-N is offset for our system, therefore needs to be corrected to accurately reflect NO<sub>3</sub>-N concentration.

### Photochemical Discussion

- Both the mixed land use site and the suburban site had a decrease in DOC after exposure to the solar simulator.
- Absorbance decreased gradually for the Missisquoi River over the course of 96 hours.
- The Missisquoi River and Potash Brook increased bioavailability by 9.6% and 2.7%, respectively.
- Hungerford and Wade Brook decreased bioavailability by 6.0% and 2.7% respectively.
- Solar simulator has 1/5 the strength of the sun, indicating that natural reactions occur faster than the changes reported in this study.

### Acknowledgements

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- Mentors: Andrew Schroth, Andrew Vermilyea, Matthew Vaughan and Allison Jerram

### References

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- Pellerin, B. A., Bergamaschi, B. A., Downing, B. D., Saraceno, J. F., Garrett, J. D., & Olsen, L. D. (2013). Optical Techniques for the Determination of Nitrate in Environmental Waters: Guidelines for Instrument Selection, Operation, Deployment, Maintenance, Quality Assurance, and Data Reporting. *U.S. Geological Survey Techniques and Methods*, 1-38.