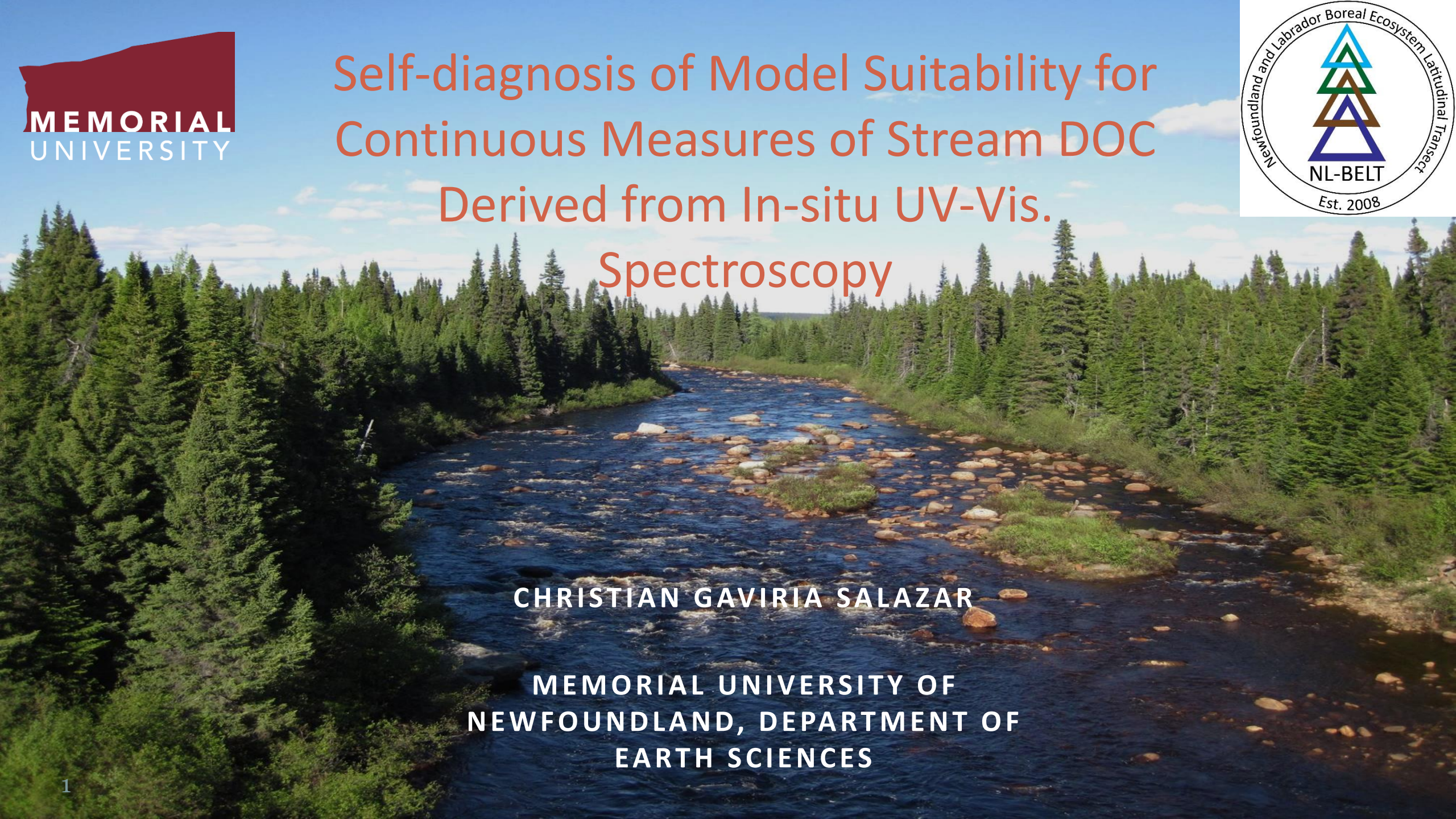
Self-diagnosis of Model Suitability for Continuous Measures of Stream DOC Derived from In-situ UV-Vis. Spectroscopy

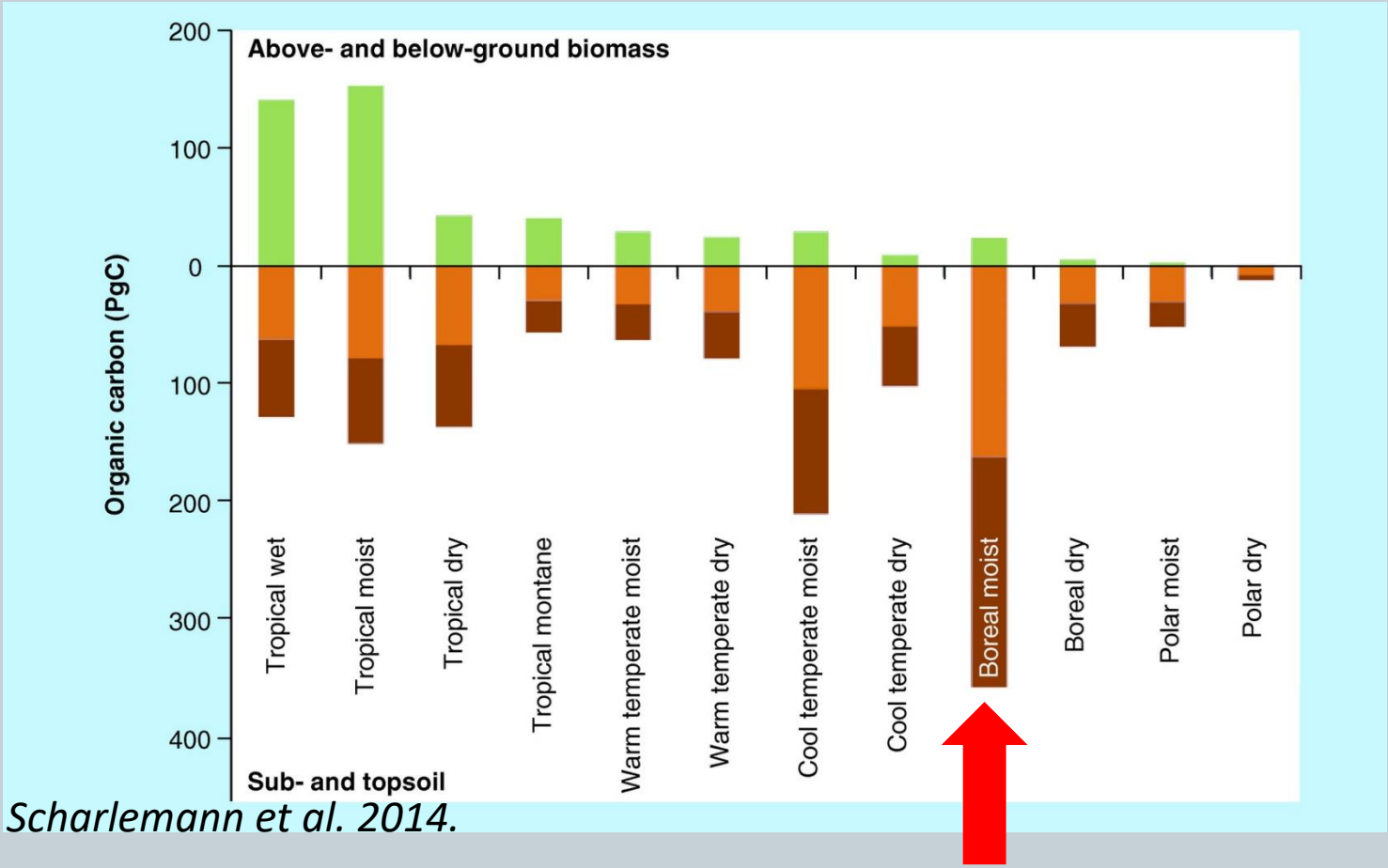


CHRISTIAN GAVIRIA SALAZAR

MEMORIAL UNIVERSITY OF NEWFOUNDLAND, DEPARTMENT OF EARTH SCIENCES

Boreal Forest Soils are a Major Carbon Sink

- Nearly one third of global terrestrial carbon stores
- Vulnerable to climate change



Scharlemann et al. 2014.

Headwater Streams Export a Significant Amount of DOC

- Landscape is responding to climate change
  - C export from the landscape is accelerating
  - Browning of surface waters
- Headwater streams: intimately connected to landscape

Measuring DOC Directly Takes Time

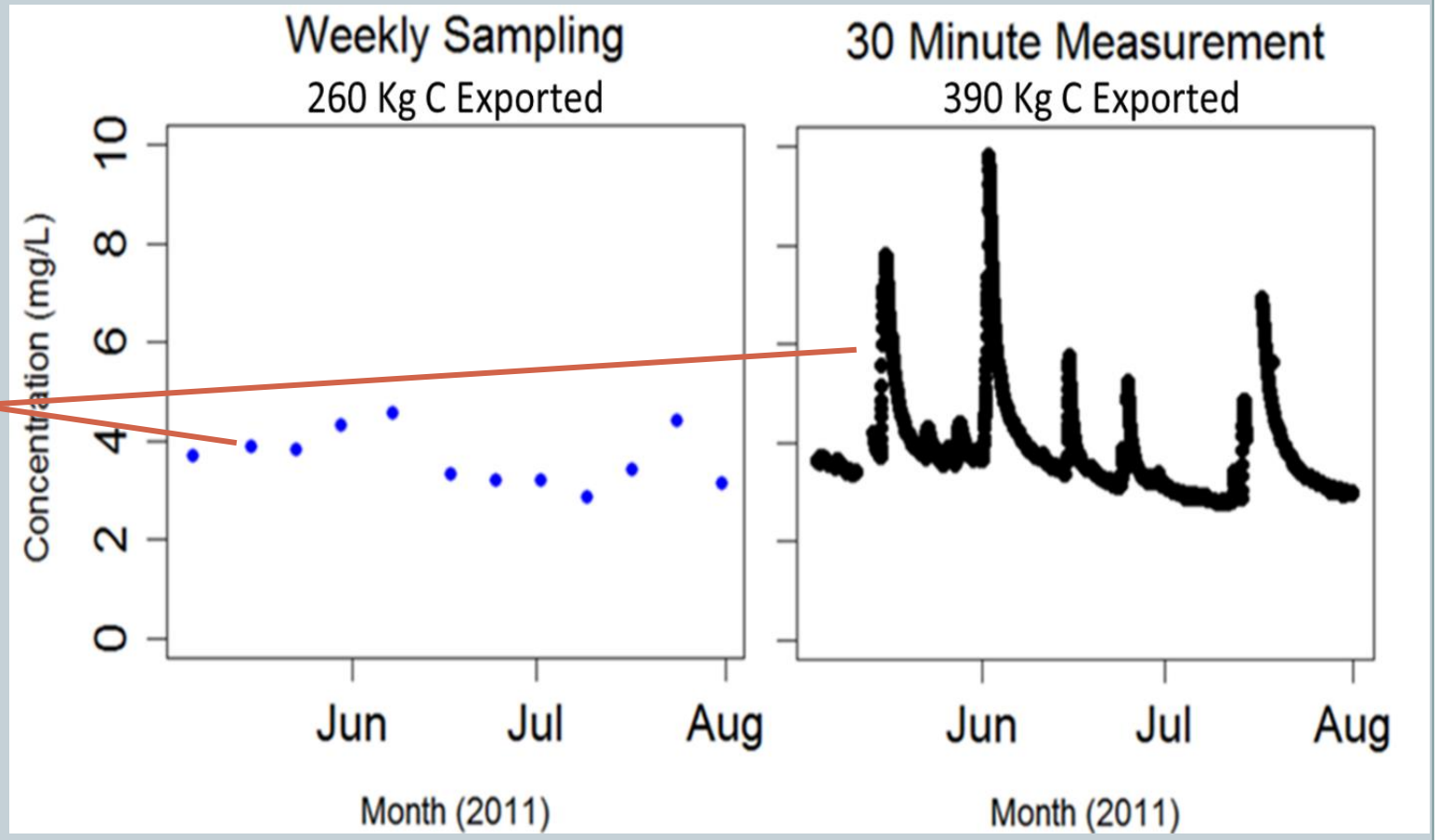
Grab-Sample

Filtration

Analysis

High-Frequency Sampling **is a Requirement** for Accurate Export Estimates

- **High-frequency sampling:** hour-minute scale
- Stream water DOC ***content*** is temporally variable*



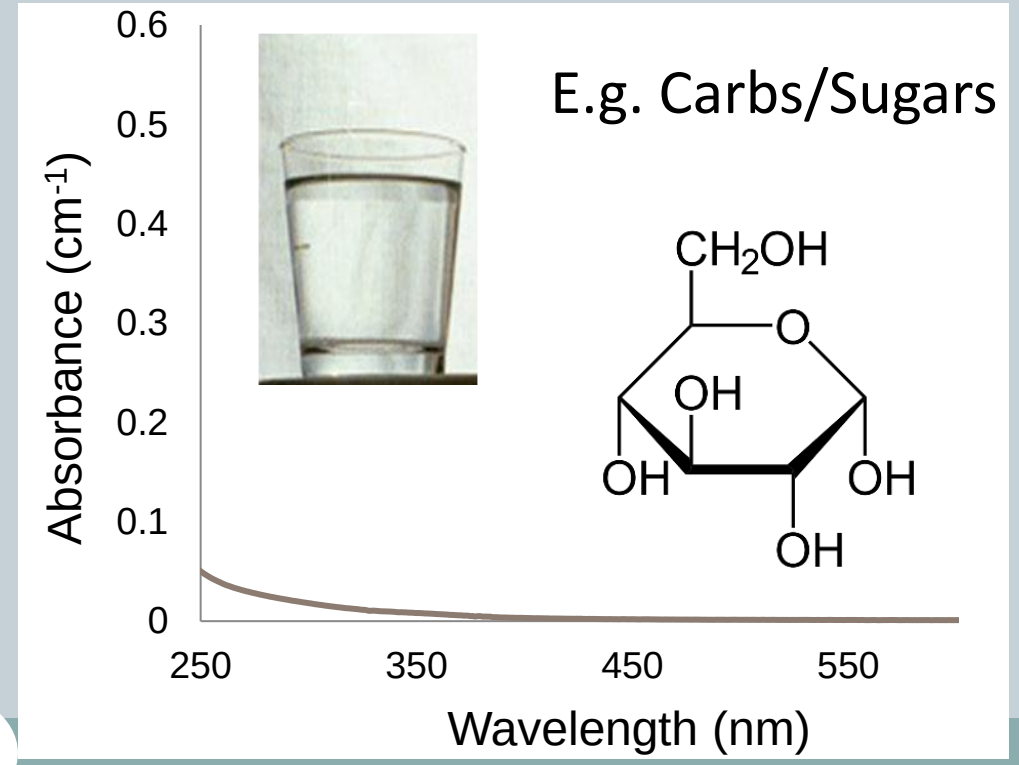
Jollymore et al. 2012.

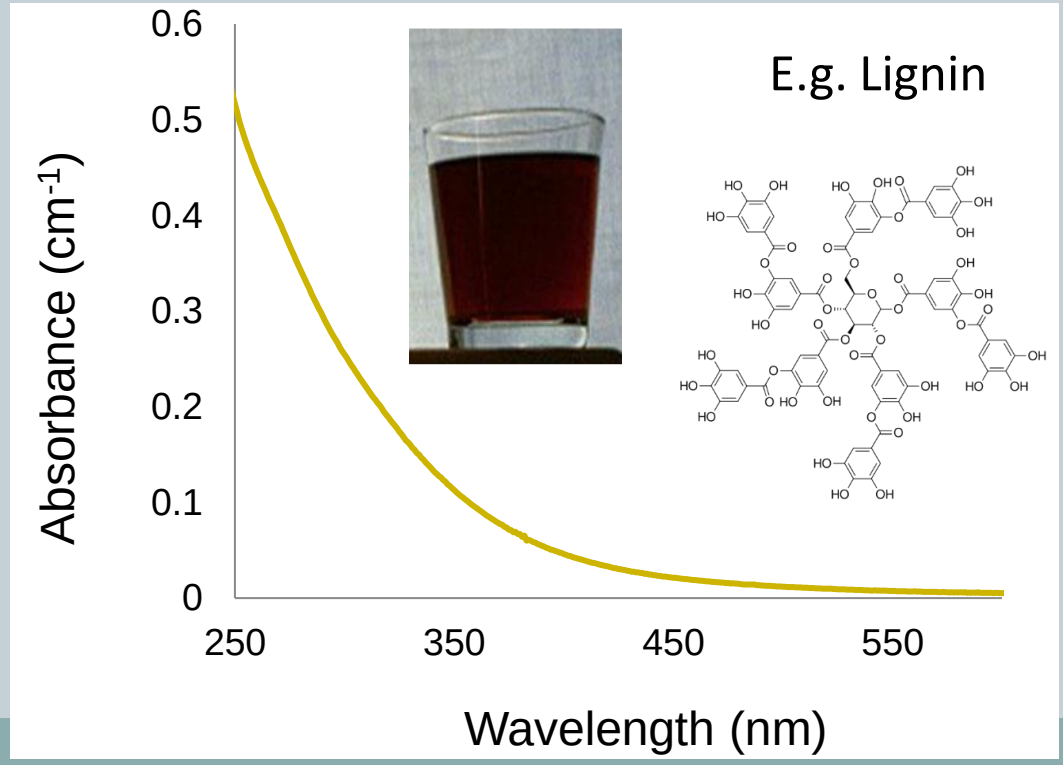
*Dependent on season (baseflow) and weather (storm or melt events)

DOC is a Complex Mixture with Different Behaviours

- Some of it can absorb light and is therefore colored

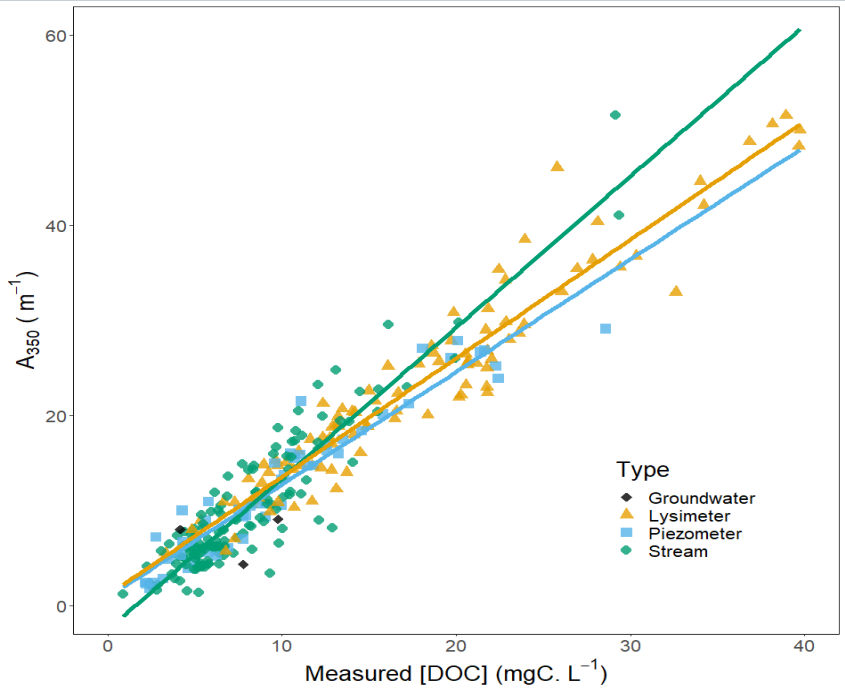
Adapted from Kritzberg et al., 2020

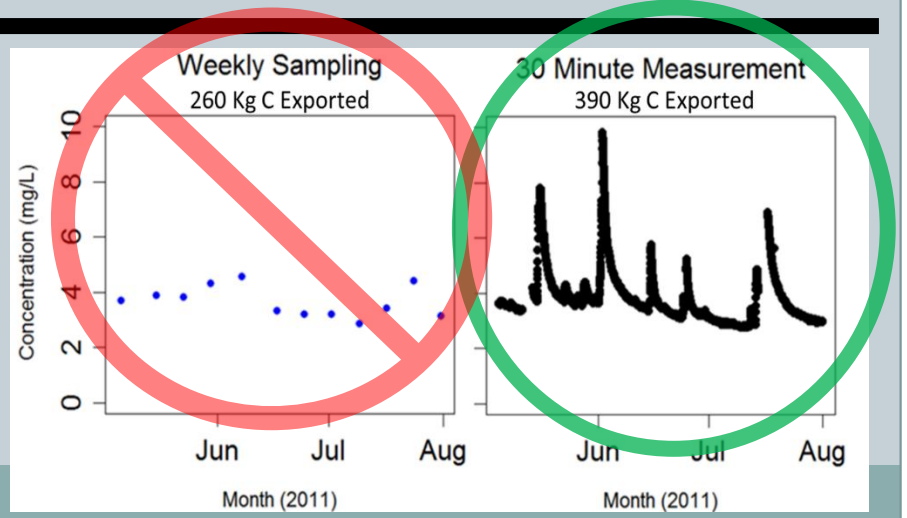




Using Proxy Measurements to Continuously Measure DOC

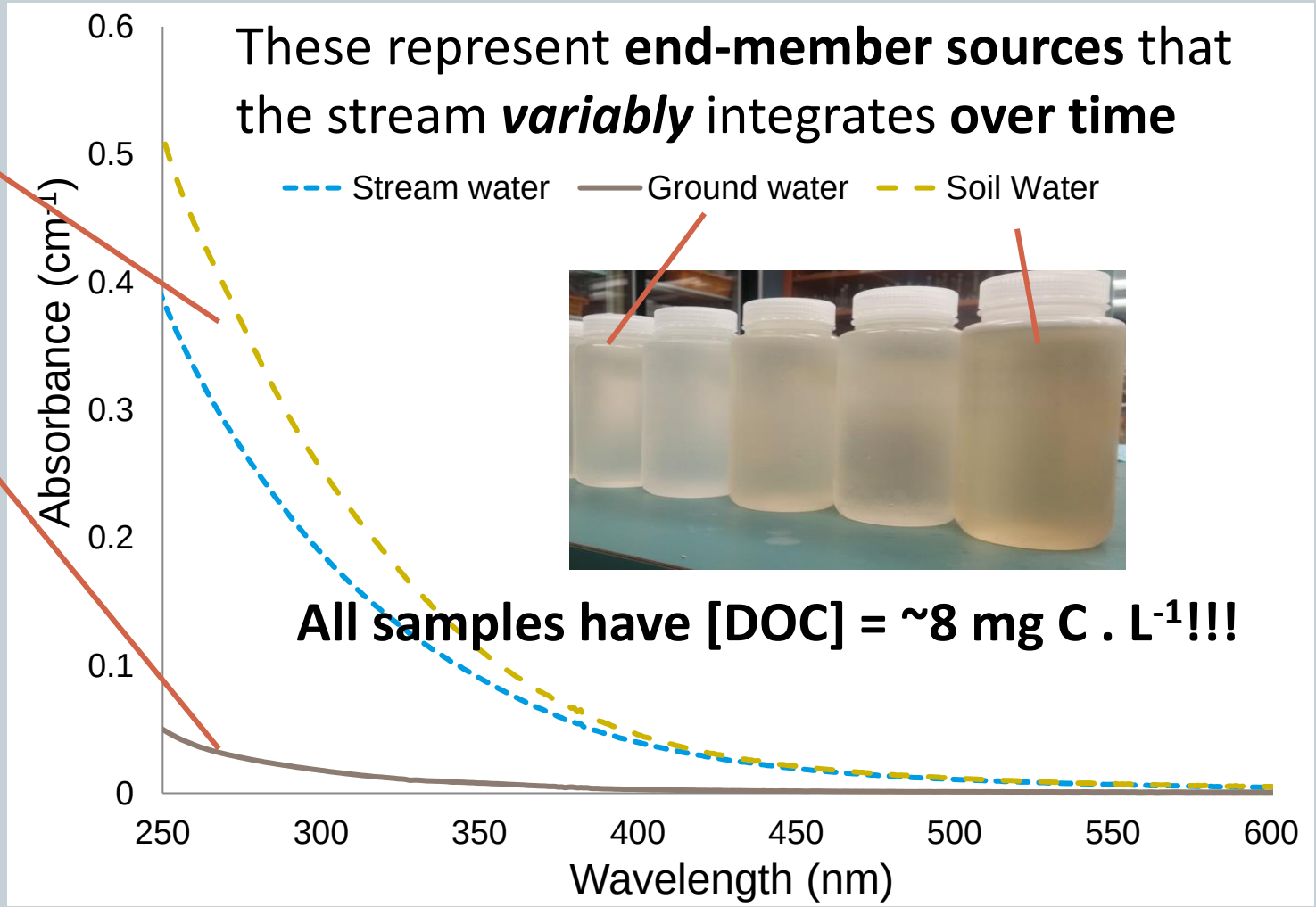
- Strong relationship between **DOC** and **absorbance**





DOC **Sourcing** can Change as a Function of Time

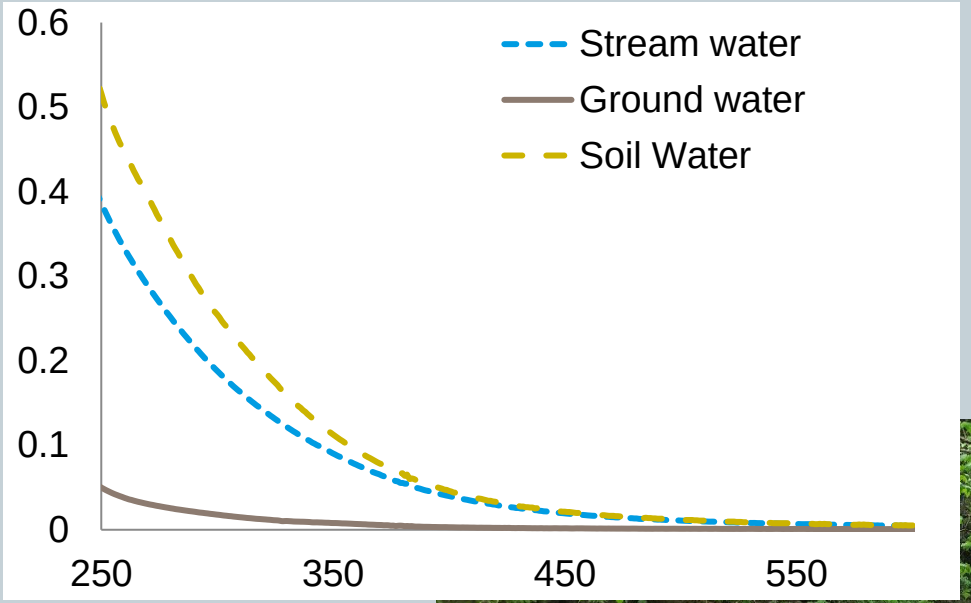
- Stream water DOC ***composition*** is temporally variable*



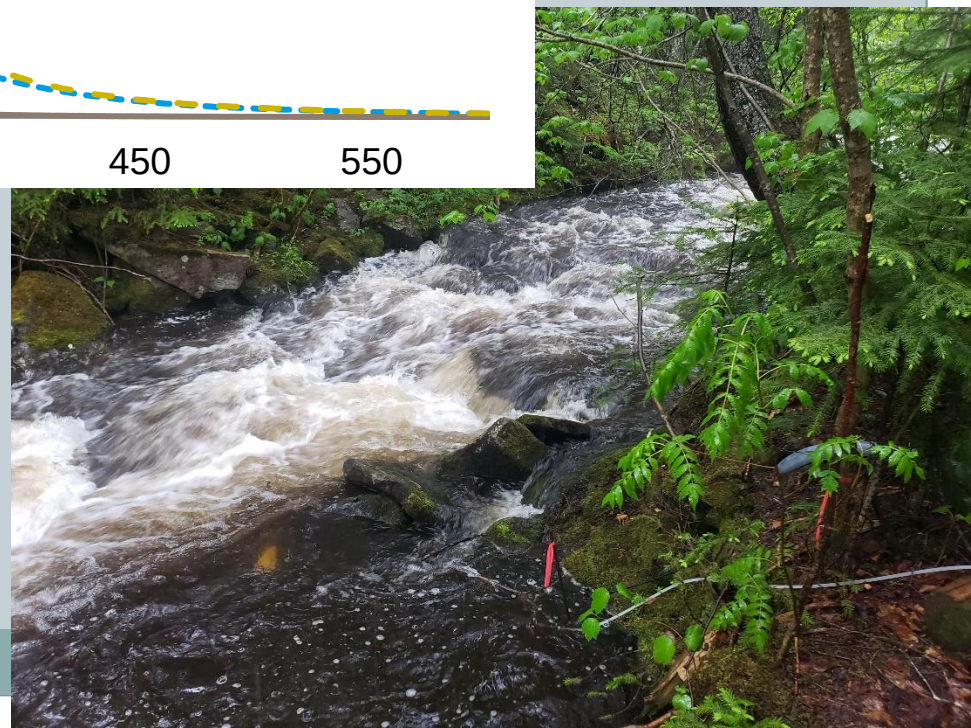
*Dependent on season (baseflow) and weather (storm or melt events)

How to Continuously Monitor Headwater Stream DOC

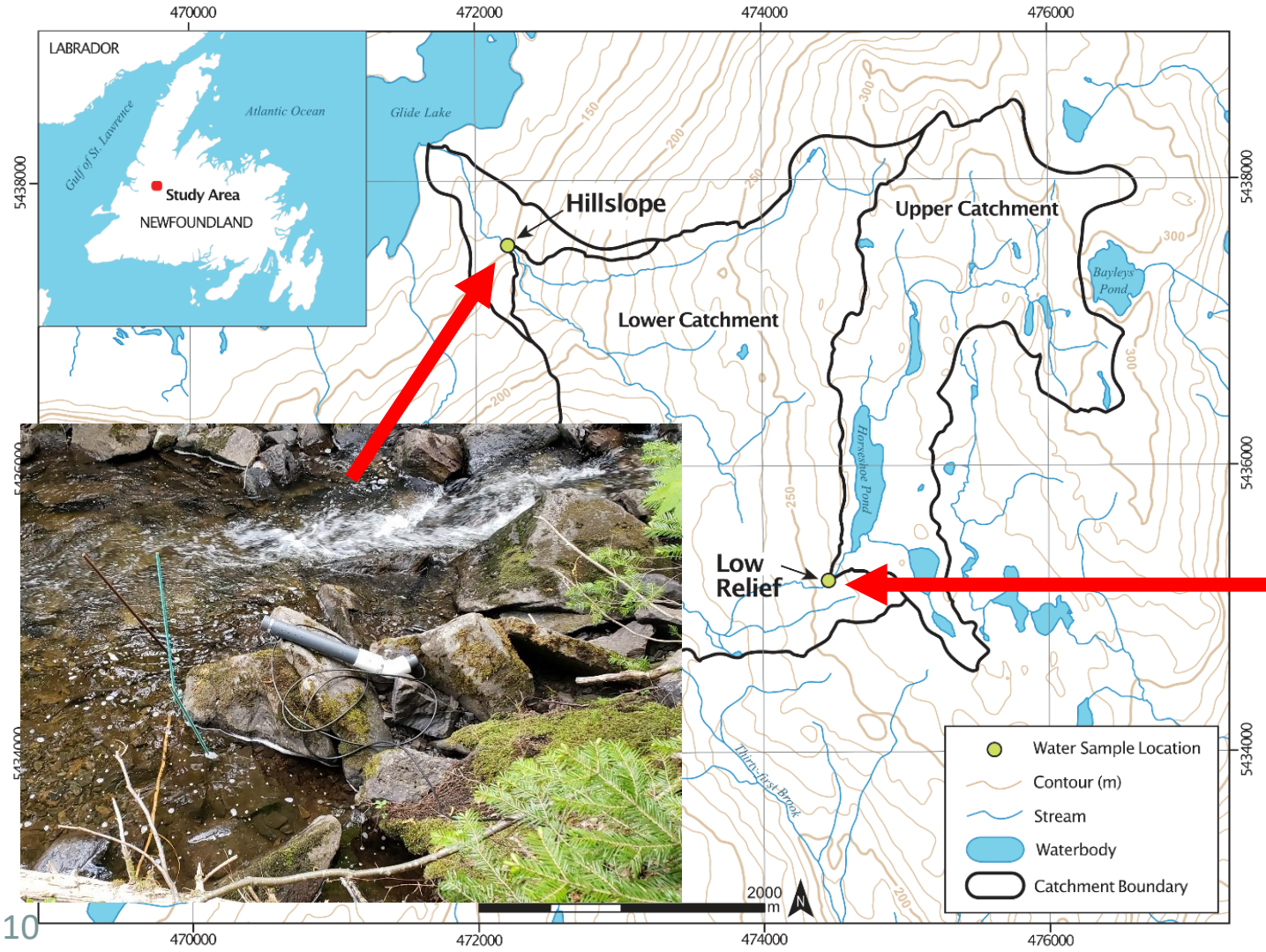
1. Can we develop a model to predict stream DOC that can account for temporal dynamics?



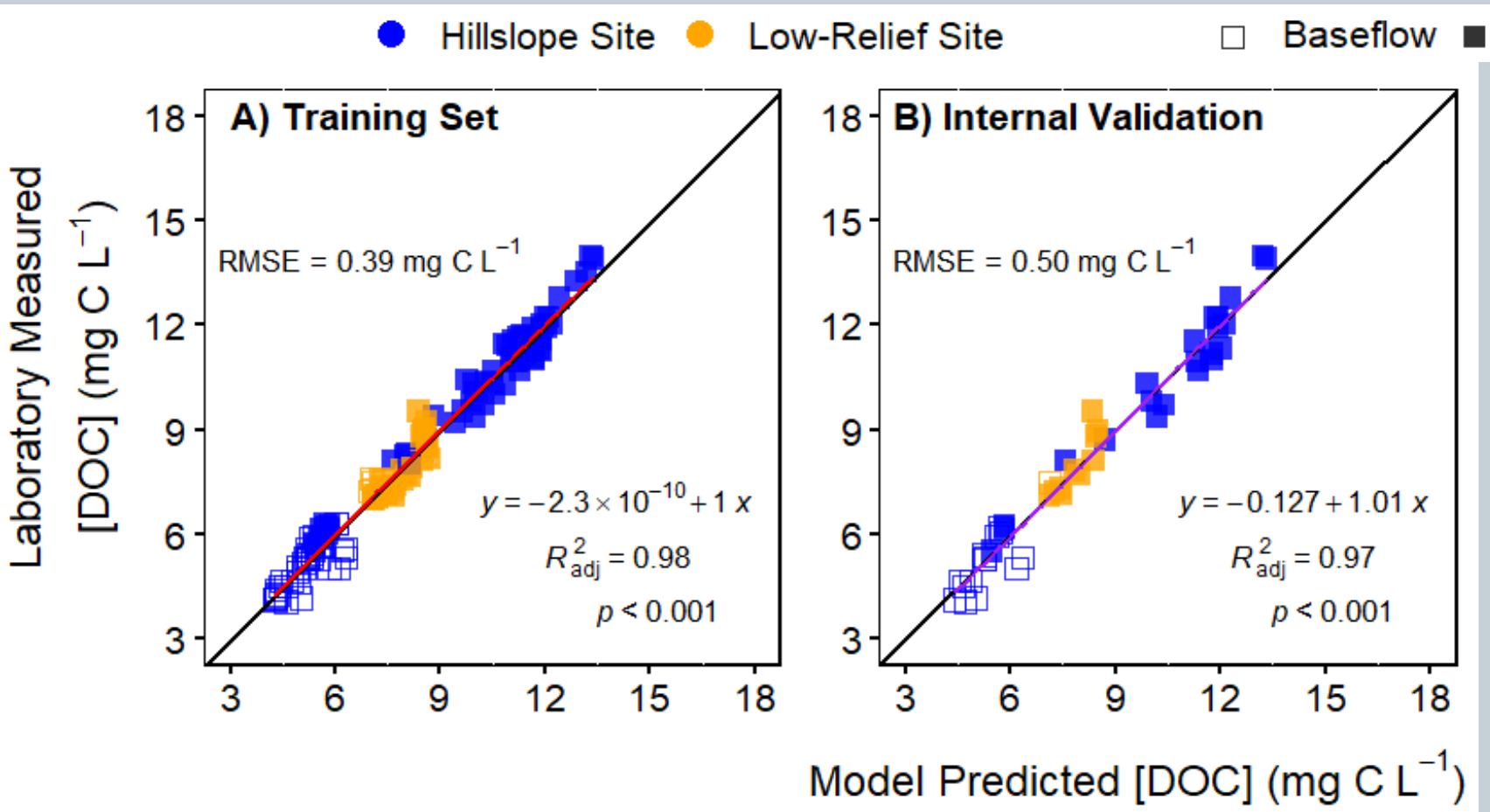
2. How can we monitor the suitability of the model as new data gets collected and used to predict DOC?



Sampling Locations – Pynn's Brook Experimental Watershed

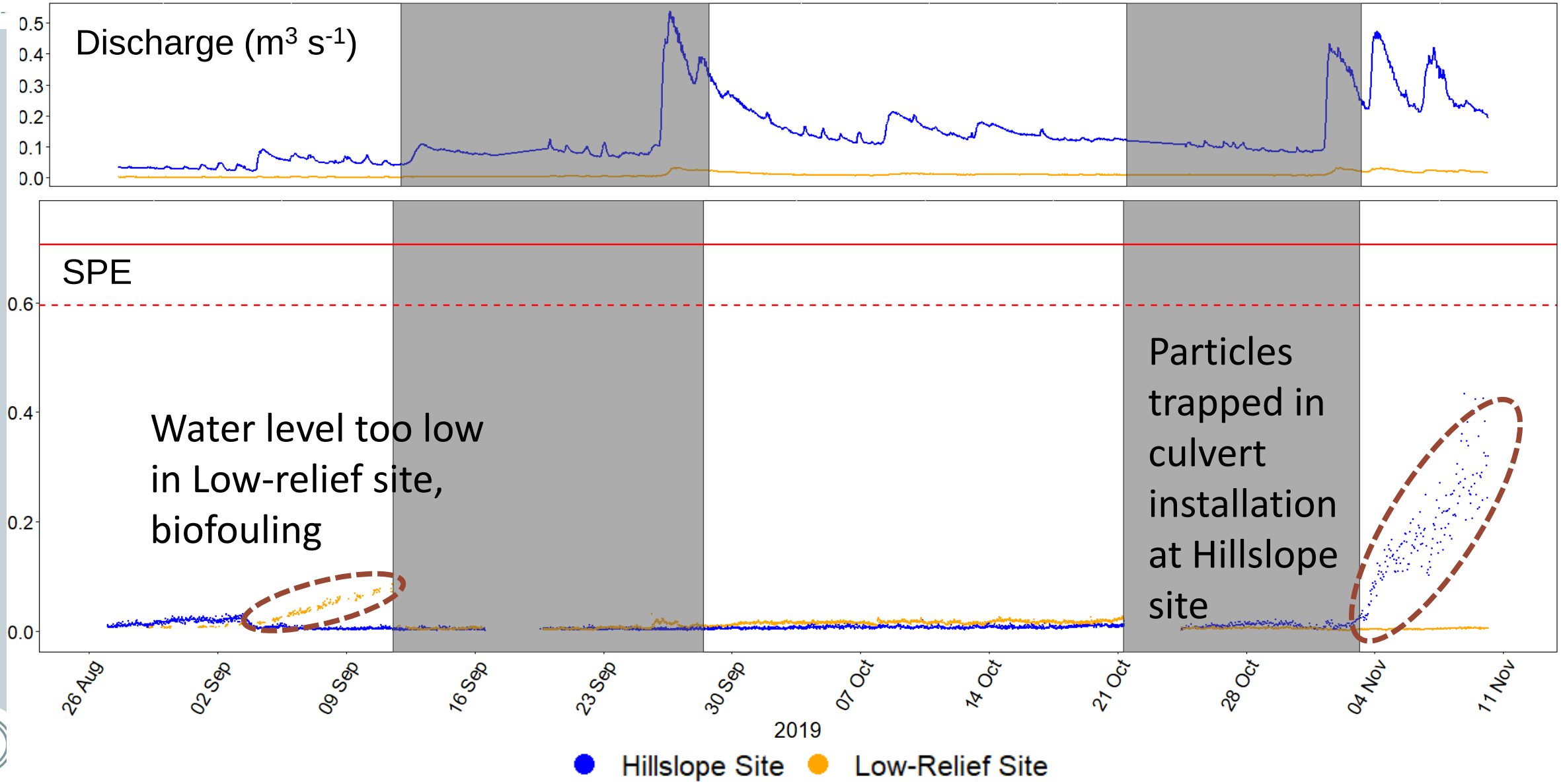


Training a PLS Model using Samples from Both Sites

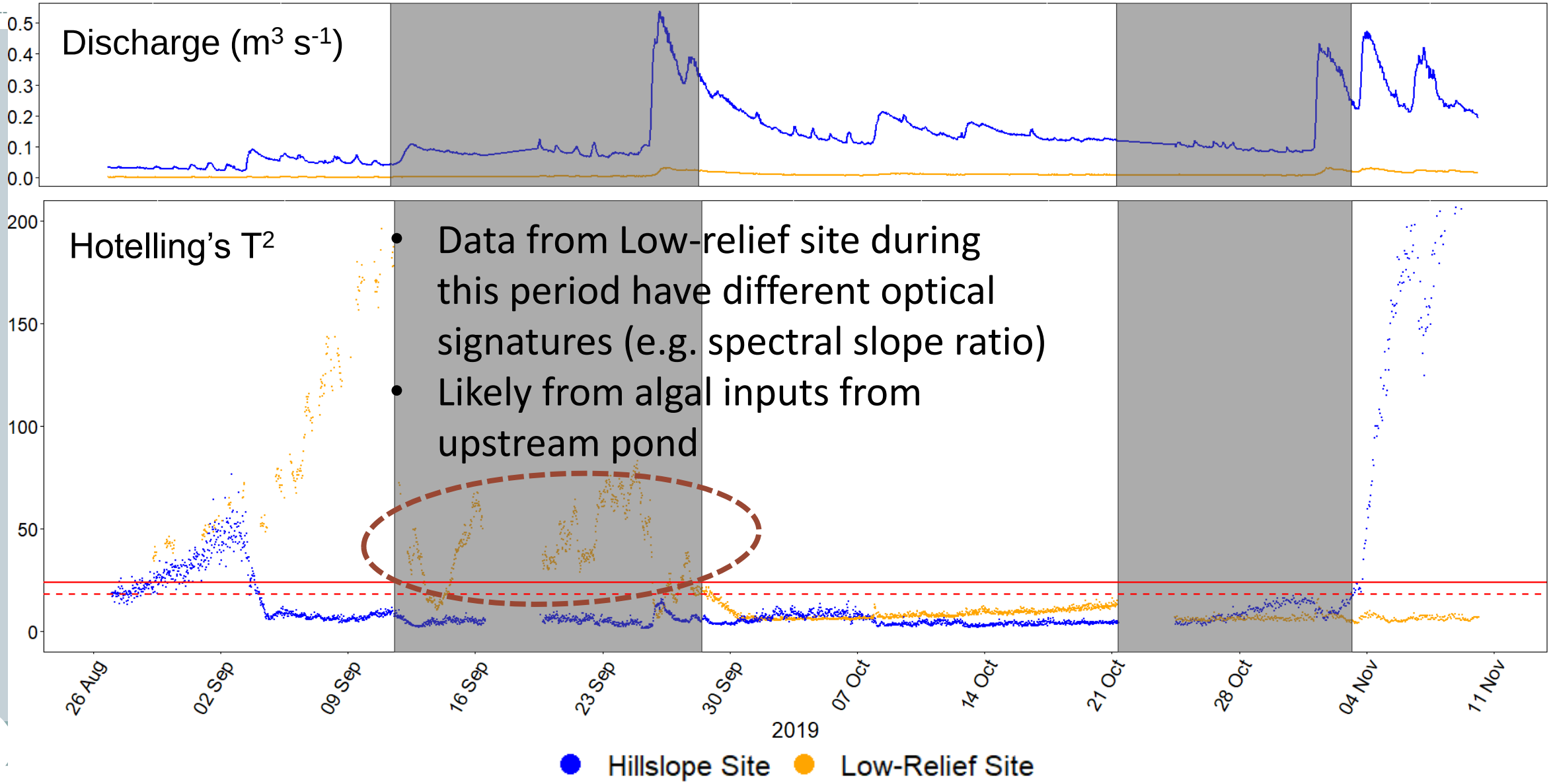


- Samples collected 2019-2020 (*N* = 139)
- Internal validation: a series of randomized 3-fold cross-validations

SPE Highlights Periods for which Data are **Incompatible** with the Model



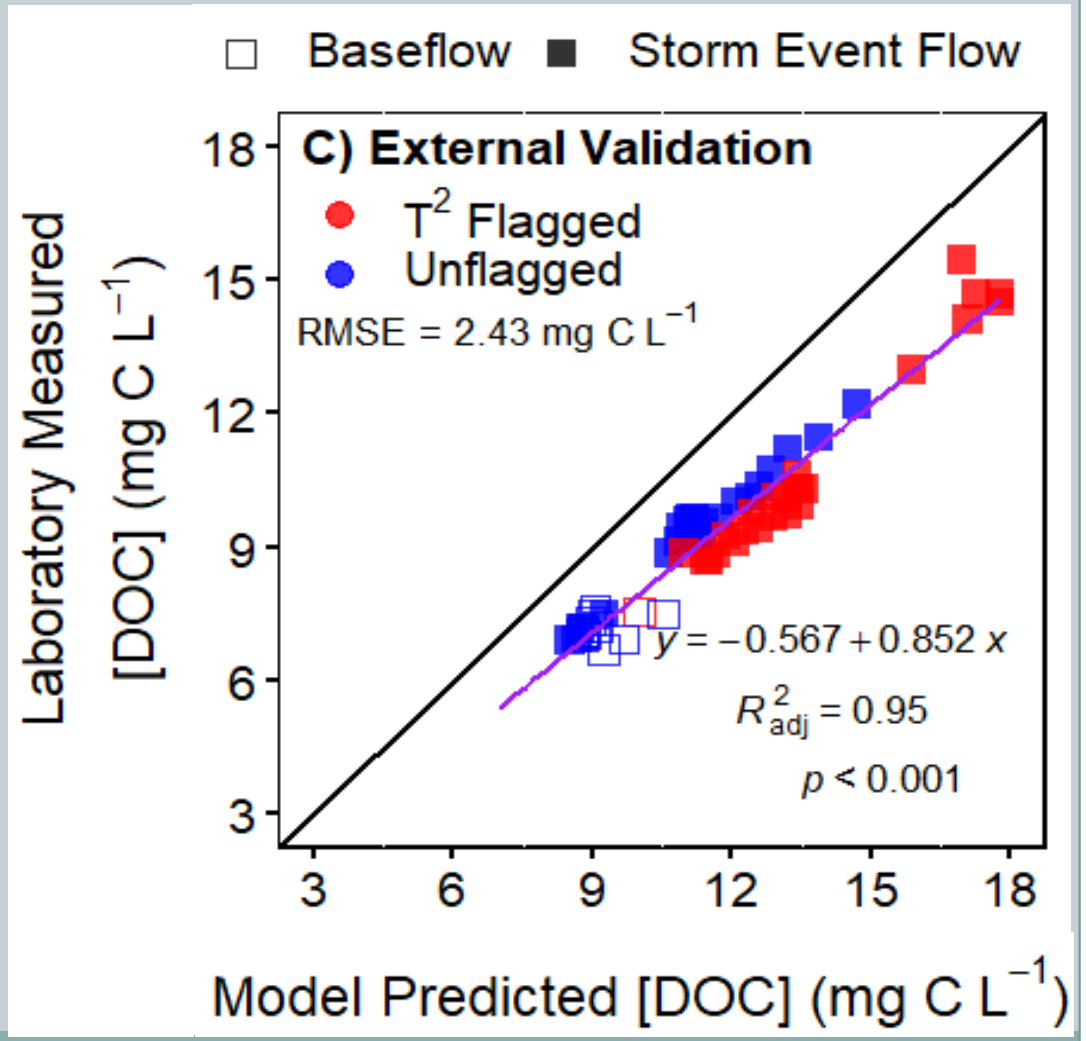
Hotelling's T^2 Highlights **Abnormal** Periods



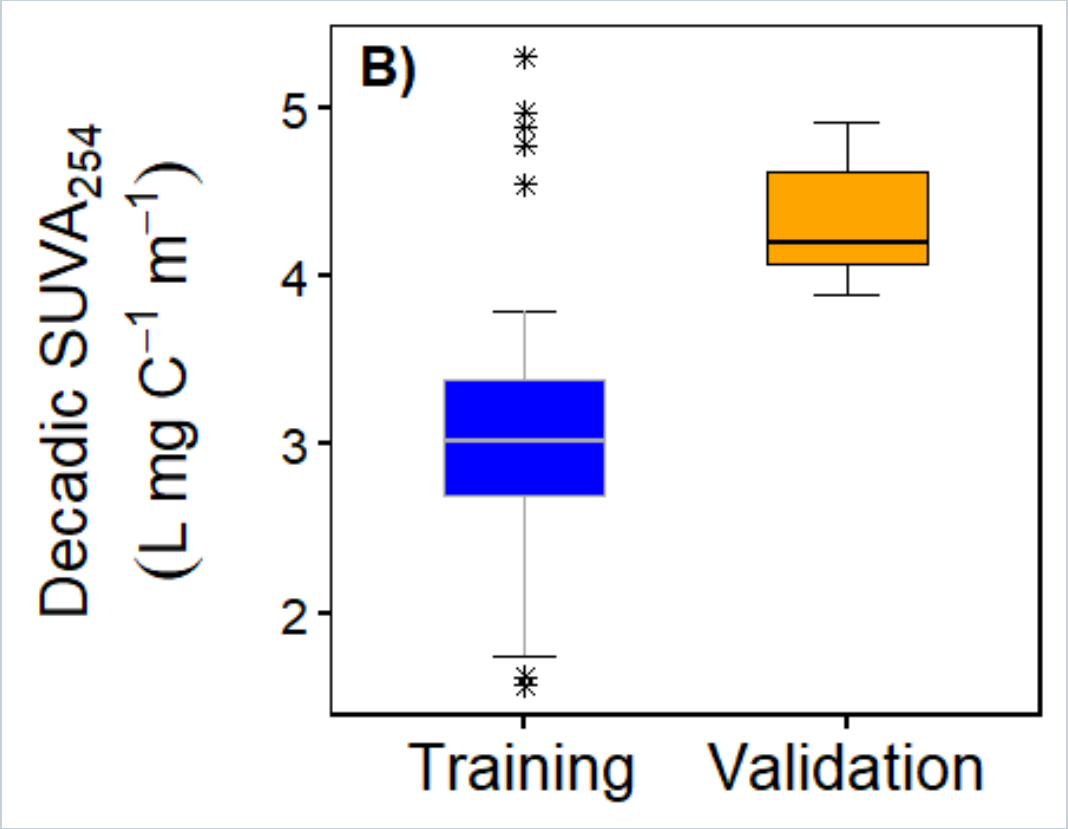
- Data from Low-relief site during this period have different optical signatures (e.g. spectral slope ratio)
- Likely from algal inputs from upstream pond

Bias Present in External Validation

- Samples collected in September 2021 (*N* = 59)
- Model trained using samples from 2019-2020 (*N* = 139)
- None were flagged by SPE
- Some were flagged by T^2

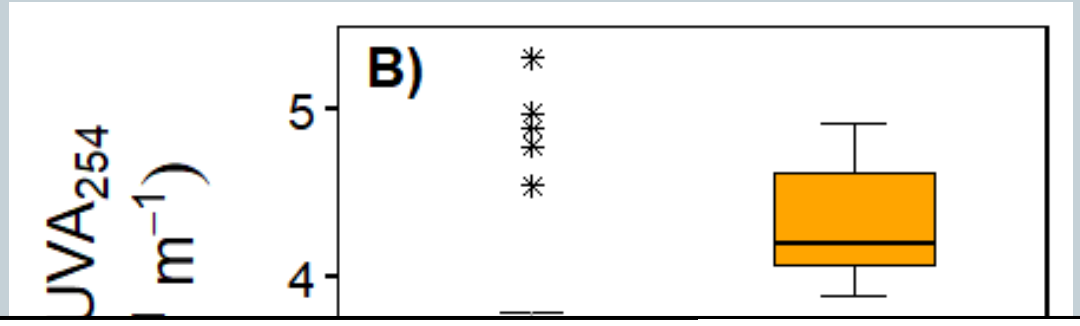


External Validation is More Aromatic than Training Set



Antecedent Conditions Dictate Quantity and Composition of DOC

- More aromatic DOC can be mobilized following wetter antecedent conditions



Water Resources Research

RESEARCH ARTICLE
10.1029/2022WR033358

Key Points:

- Watershed scale responses of dissolved organic matter are heterogeneic and controlled by spatially distinct and moisture dependent hydrobiogeochemical processes
- Antecedent conditions are important for the quality and quantity of dissolved organic matter (DOM) delivered to boreal headwaters
- Differences in water routing between geomorphologically distinct boreal catchments control pathways for delivery of DOM in boreal systems

Hydrobiogeochemical Controls on the Delivery of Dissolved Organic Matter to Boreal Headwater Streams

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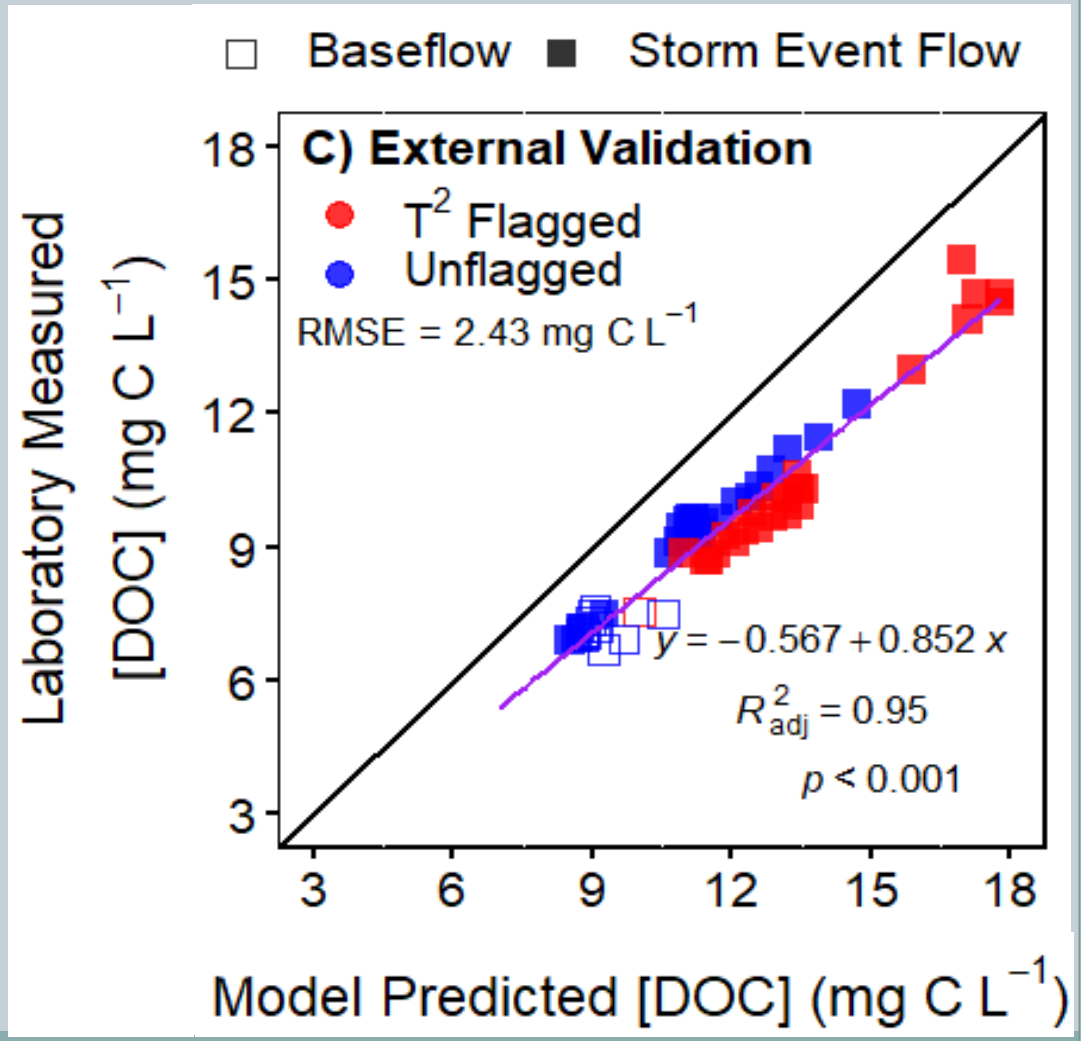
[1]Department of Earth Sciences, Memorial University, St. John's, NL, Canada, [2]Marine and Coastal Research Lab, Pacific Northwest National Laboratory, Sequim, WA, USA, [3]Department of Geology, University of Maryland, College Park, MD, USA

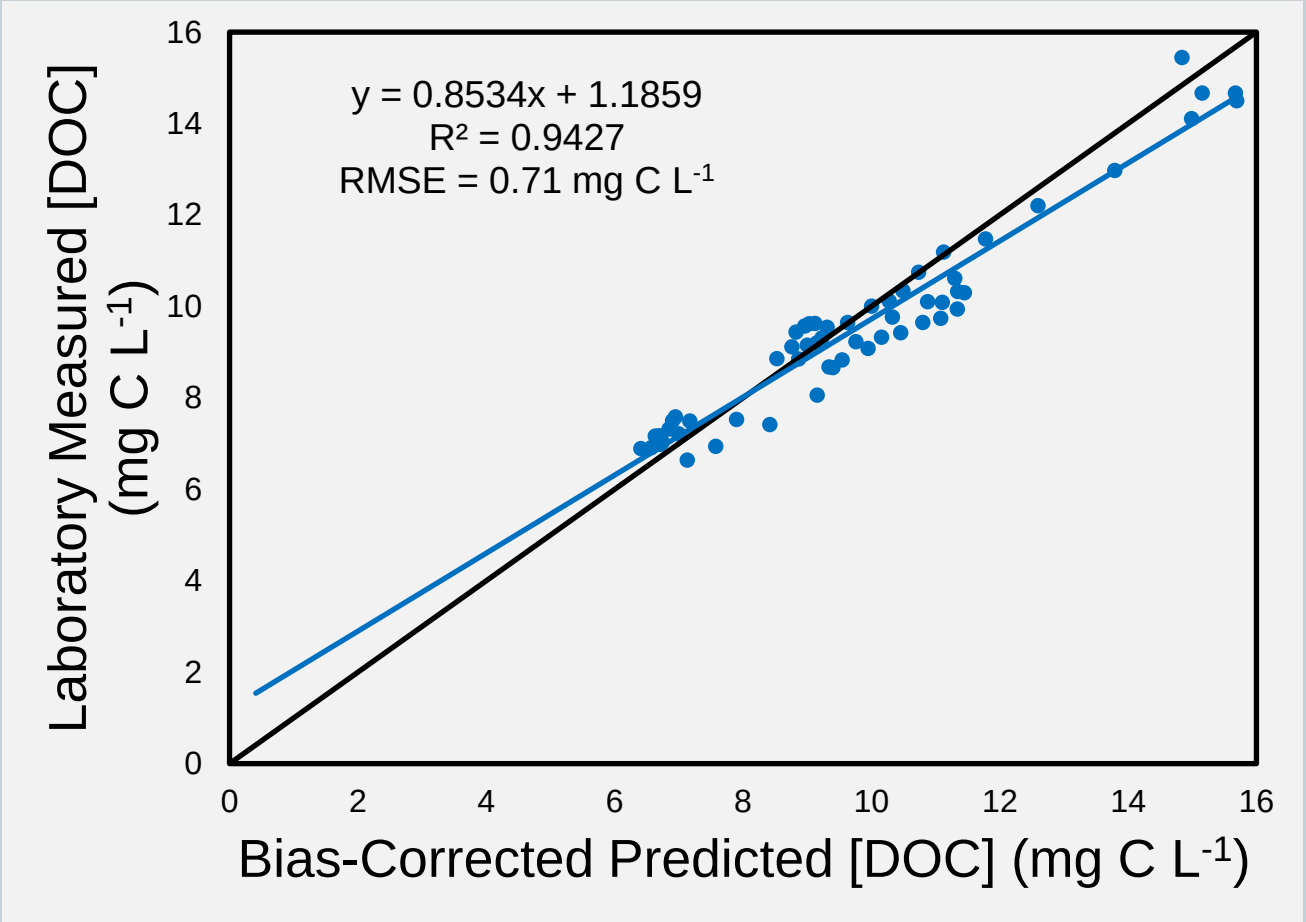
Bias Present in External Validation

- What can we do?



Baseflow Grabs Can Correct Bias

- Baseflow grab-samples are more accessible
- Comparable studies RMSE = 1.3 - 3.8 mg C L^{-1}



Accurate and Precise Modeling of Stream DOC is Feasible and Achievable

- Models are needed and we need to be able to track if they work
- Demonstrated an approach for diagnosing model consistency
  - Indicates when and how a model needs updates
- This approach is being used in ongoing research to monitor carbon stores at the watershed scale

Questions?

LIMNOLOGY and OCEANOGRAPHY: METHODS

ASLO

Limnol. Oceanogr.: Methods 2023

doi: 10.1002/lom3.10559

Self-diagnosis of model suitability for continuous measurements of stream-dissolved organic carbon derived from in situ UV–visible spectroscopy

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