Climate controls on organic carbon flux from northern forest watersheds

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Most important project outcomes:

- In situ fluorescing dissolved organic matter (FDOM) measured at fine time steps provides insight into sources of stream DOC, catchment contributing areas during high flows, and hydrologic flow paths.
- Disproportionately large DOC fluxes from large events suggest DOC fluxes will continue to increase under future higher precipitation regimes.

Completion date: 30 Sept. 2014

Funding support for this project was provided by the Northeastern States Research Cooperative (NSRC), a partnership of Northern Forest states (New Hampshire, Vermont, Maine, and New York), in coordination with the USDA Forest Service.
http://www.nsrcforest.org

Project Summary

Stream losses of DOC are often dismissed as an unimportant part of the global carbon budget. However, stream DOC flux in the temperate and boreal northern hemisphere has been increasing during the past two decades. Because changes in DOC concentrations and yields mirror changes in ecosystem processes that are sensitive to climate forcing, this study was designed to better quantify the stream DOC component of the C balance in watersheds in the northern forest region of the northeastern USA, using natural climatic variation to infer the magnitude and direction of future DOC shifts. This study built on two previous NSRC-funded studies, continuing measurements at three small watersheds: Arbutus Inlet, NY; Sleepers River W-9, VT; and Hubbard Brook WS-3, NH. We used *in situ* fluorometers to measure fluorescent dissolved organic matter (FDOM) as a proxy for DOC to: (1) accurately quantify DOC yields at high temporal resolution at three headwater streams, and (2) improve our understanding of the northern forest carbon cycle and its response to climatic perturbations.

The three sites spanned a gradient of DOC concentrations, which corresponded to the amount of wetlands in the watersheds (Arbutus >Sleepers River > Hubbard Brook). DOC concentrations at all sites showed dynamic increases during high flows, increasing by an order of magnitude at Sleepers River and Hubbard Brook. FDOM closely tracked discharge, but the FDOM response nearly always lagged the hydrograph response. This lag resulted in counterclockwise hysteresis loops. The high-resolution hysteresis loops that can be generated from these data offer possibilities to interpret both DOC sources and water flow paths. DOC flux was disproportionately higher in water year 2011, which was an extremely wet year with several large events, than 2012, which was drier than average.

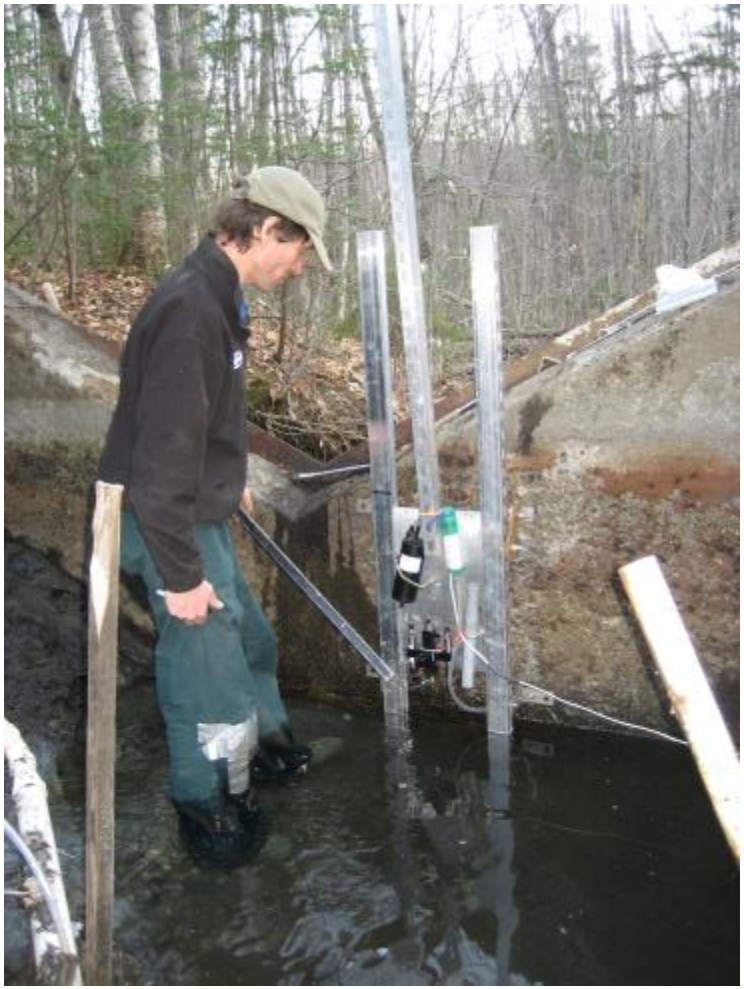
This research has strong implications for the Northern Forest. Regional increases in stream DOC in response to changing atmospheric deposition chemistry and/or climate change has drawn greater attention to the role of DOC in forest nutrient cycles. The use of in-stream fluorometers can greatly enhance the acquisition of DOC and detail its response to the stream hydrograph, which in turn can give clues about what is driving DOC dynamics. An immediate practical reason to monitor DOC is that too much DOC entering public water supply can lead to the formation of Disinfectant Byproducts (DBPs). As this study has shown, high DOC loads during storms make these periods especially challenging for treatment plants with surface water intakes.

Background and Justification 1

Installation work at Hubbard Brook

- DOC concentrations have increased in many temperate forested streams and global change is shifting carbon allocation across the northern forest landscape.
- Shifts in the timing and location of precipitation, temperature-related effects on soil geochemistry, changing vegetation cover, and catastrophic events (fire, insect defoliation) are all key components of global change.
- These phenomena directly affect the character and quantity of organic matter in surface waters, which in turn affect aquatic ecosystem productivity.
- Organic matter in surface waters is also an important regulator of solute transport, particularly metals.
- As part of an earlier NSRC study, our team demonstrated the strong control of organic matter quantity and quality on mercury mobility in northern forest streams (Dittman et al., 2009, 2010).

Background and Justification 2



- Our earlier NSRC-supported studies have demonstrated proof-of-concept for *in situ* optical sensors serving as a proxy for DOC in streams.
- High frequency *in situ* measurements allow for observations of changes at the rate at which they occur during episodic events, seasons, and years.
- Results yield highly accurate DOC flux estimates that are not prone to the pitfalls that arise from reliance on concentration-discharge relationships, such as complex hysteretic responses, unsampled storms, and seasonal shifts like the sudden DOC pulse during leaffall.
- Stream DOC responses vary from storm to storm, season to season, and year to year. The more variability that one can capture, the better one can quantify the relation of DOC export to climate and forecast future change.

Working in the weir pool (drained) at Sleepers River

Background and Justification 3

Results from prior NSRC grant that provided proof-of-concept.

Figure 1. Discrete DOC concentrations versus in situ CDOM (FDOM) at Sleepers River, VT from October 2008 to September 2009.

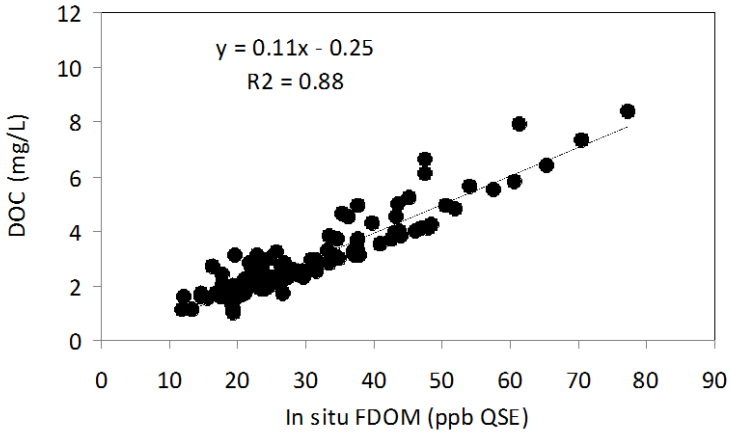
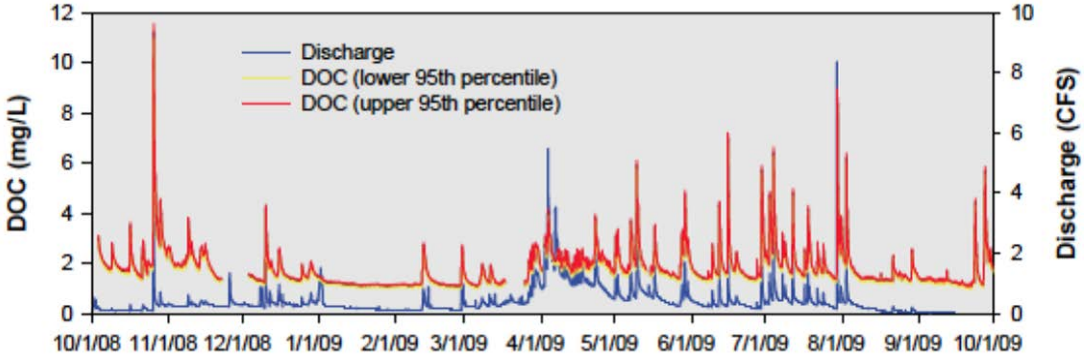


Figure 2. DOC concentration (modeled from CDOM measurements and relation in Figure 1) and discharge for Water Year 2009 at Sleepers River W-9 with 95th percentile confidence intervals.



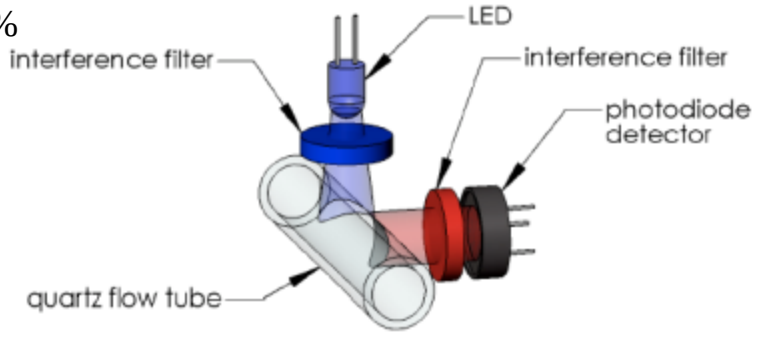
Methods 1

Field and Laboratory

- We built on an earlier NSRC grant by the same team and revisited the same 3 sites – Arbutus Inlet, NY; Sleepers River W-9, VT; and Hubbard Brook WS-3, NH.
- We resumed measurements of Fluorescing Dissolved Organic Matter (FDOM), using in-stream fluorometers, in October 2010 and continued through September 2012 (two full water years).
- The fluorometers were periodically cleaned in the field to minimize fouling.
- All sites measured stream discharge, water temperature and other site-dependent parameters
- At each site we took approximately 30 samples per year to compare to the sensor data.
- Samples were filtered and shipped to the USGS Aiken Organic Matter lab in Boulder, CO.
- The Aiken lab analyzed for dissolved organic carbon (DOC), absorbance at 254 nm (UV254), and FDOM

Pump (left) and fluorometer (right) used in this study.

The fluorometer LED emits ultraviolet light. This excites roughly 2% of the organic carbon molecules in the water, which give off visible (blue) light as they return to their resting state. The detector is tuned to the blue range.



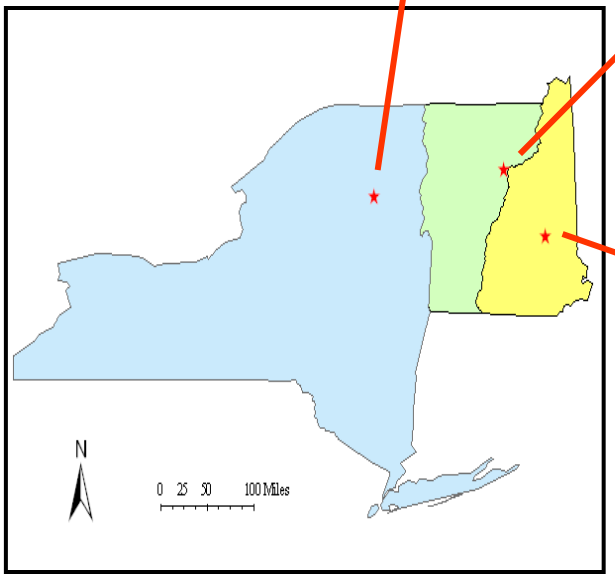
Methods 2

Huntington Forest,
New York

Three study sites along a wetland gradient

Sleepers River,
Vermont

Hubbard Brook,
New Hampshire



<----------Increasing Wetlands

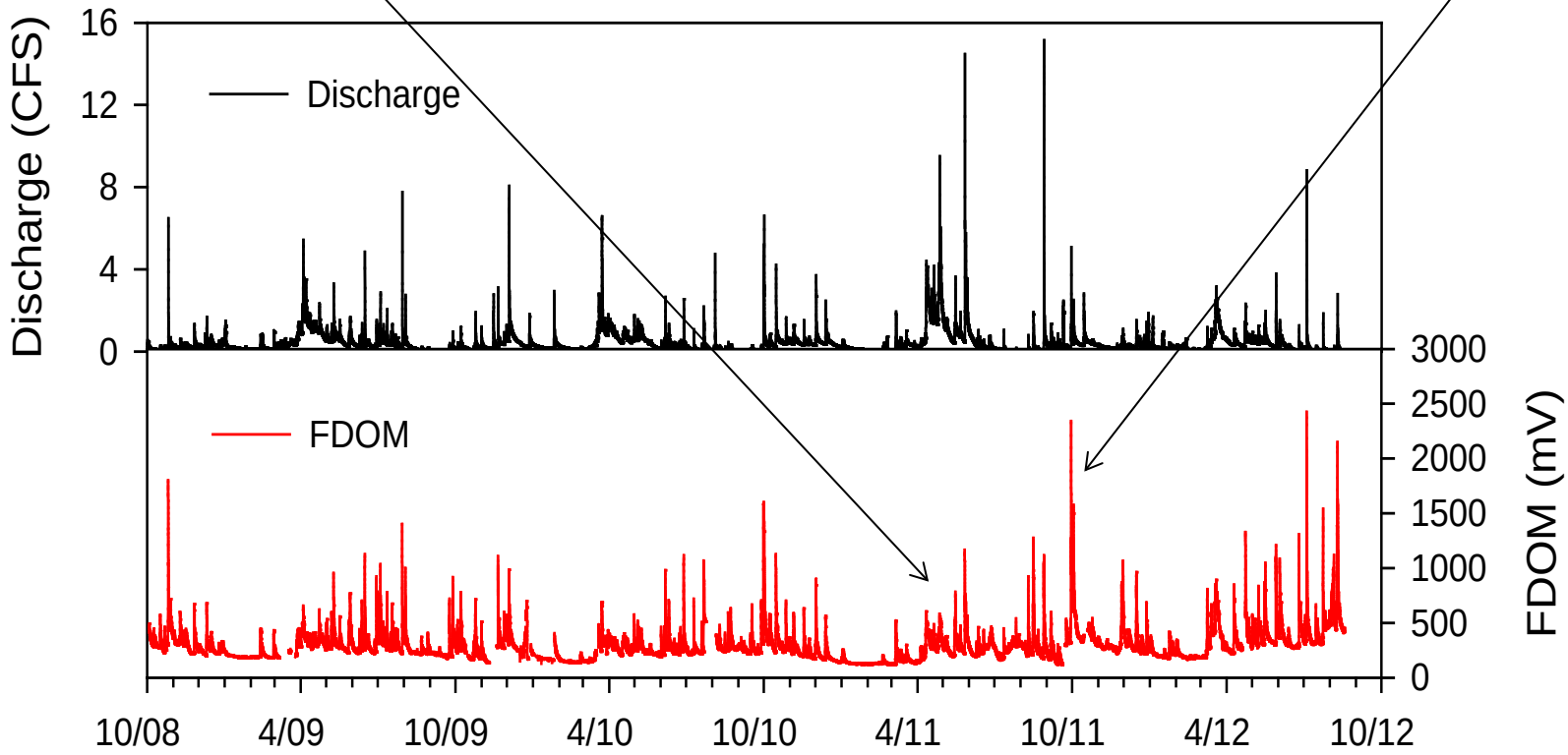
Methods 3

Data analysis

- The FDOM time series (15-min time step) were adjusted for fouling to obtain the adjusted raw time series.
- FDOM values need corrections for water temperature, turbidity, and high DOC (inner filter effect)
- Only Sleepers River had turbidity measurements (as part of a separate project), but we knew from the earlier study that Arbutus and Hubbard Brook rarely needed a turbidity correction.
- Fluorescence decreases with increasing temperature so values must be normalized to a common temperature.
- Turbidity blocks light interfering with the optically measured FDOM. But values can be corrected up to fairly high turbidity levels.
- Corrections are being made in an Aquarius database – one lesson learned from this project is that these time series quickly get too long to work them efficiently in Excel spreadsheets!
- Sample DOC concentrations are regressed against the final corrected FDOM value at the sample time to evaluate the power of FDOM as a DOC proxy.

Results/Project outcomes 1

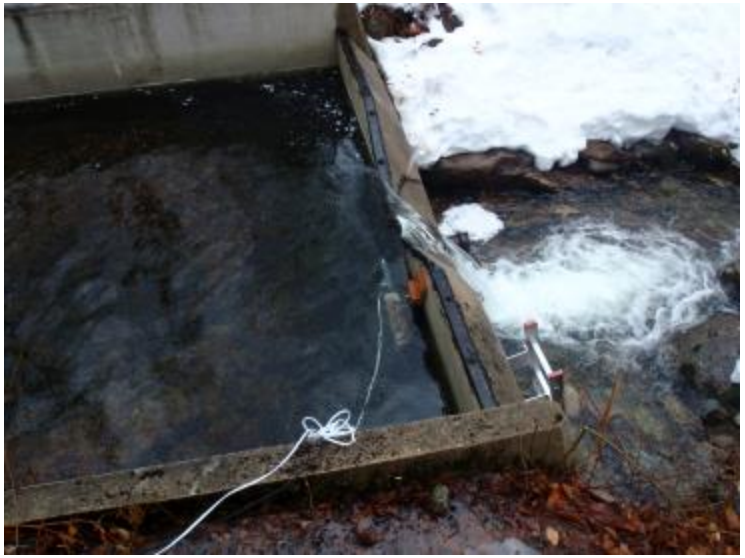
This NSRC project allowed us to continue what may be the world's longest continuous stream FDOM record at Sleepers River. Note that FDOM is very responsive to changes in discharge. Highlighted are two events that had nearly the same discharge, but a greater FDOM response during leaffall, following abundant input of labile carbon, compared to snowmelt.



Results/Project outcomes 2

At all sites, FDOM closely tracked the hydrograph. The general interpretation of the FDOM-discharge correspondence is that rainfall, snowmelt, and associated rising groundwater levels mobilize DOC from organic-rich soils near streams and in the forest floor.

Ann Chalmers of the USGS uses high tech method to check on FDOM at Arbutus.

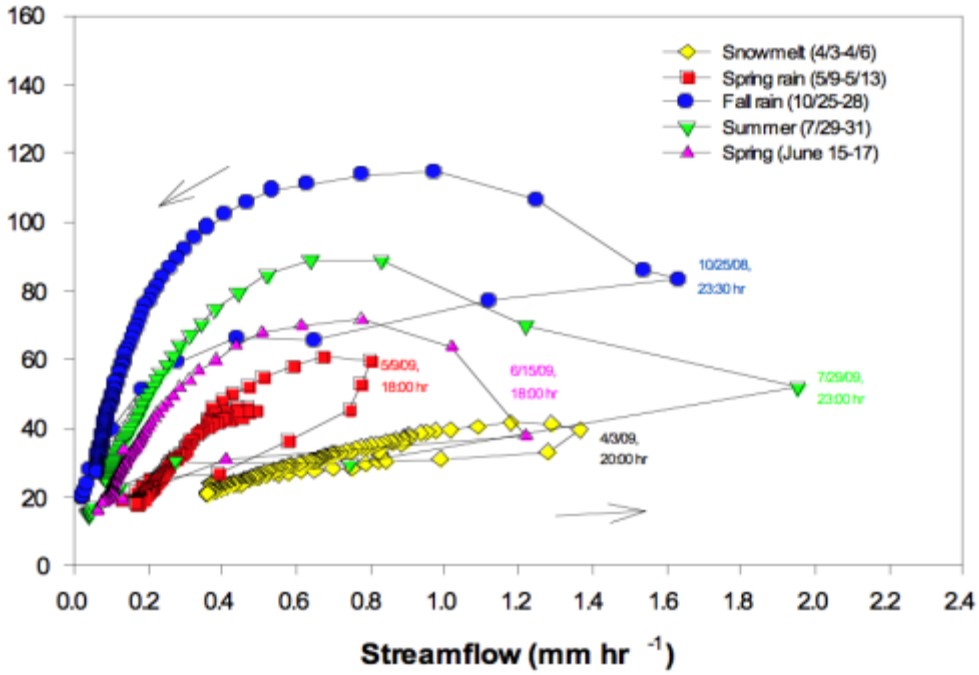


Hubbard Brook installation

Results/Project outcomes 3

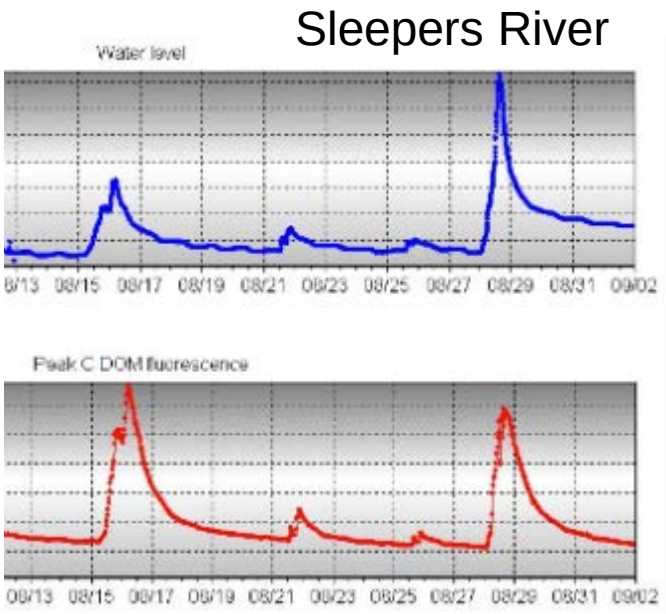
Hysteresis – where concentration is different at the same discharge on the rising and falling limbs of the hydrograph – has long been observed for DOC. The fine-resolution FDOM measurements give sharp definition to these hysteresis “loops”, where the number of points were formerly limited by the number of samples. Most previous studies reported clockwise DOC hysteresis (concentrations higher on the rising limb) while we found consistent counterclockwise hysteresis at all 3 sites, with occasional exceptions at Hubbard Brook. We are working on a manuscript that interprets what these hysteresis loops mean for the source and travel time of DOC sampled at the stream gage.

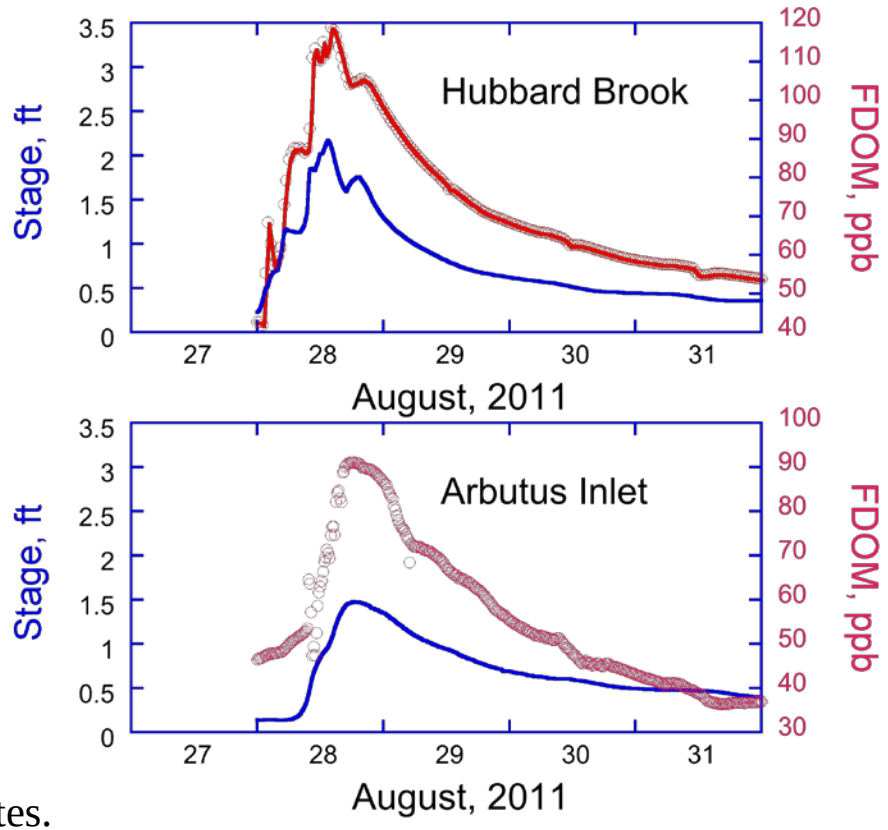
The figure at right depicts hysteresis loops from 5 high-flow events through the seasons at Sleepers River. Hysteresis was minimal at snowmelt, but the size and slope of the loop increased as the seasons progressed, with the largest loop and highest DOC concentrations following leaffall.



Results/Project outcomes 4

Storm of 28 August, 2011 – all 3 sites

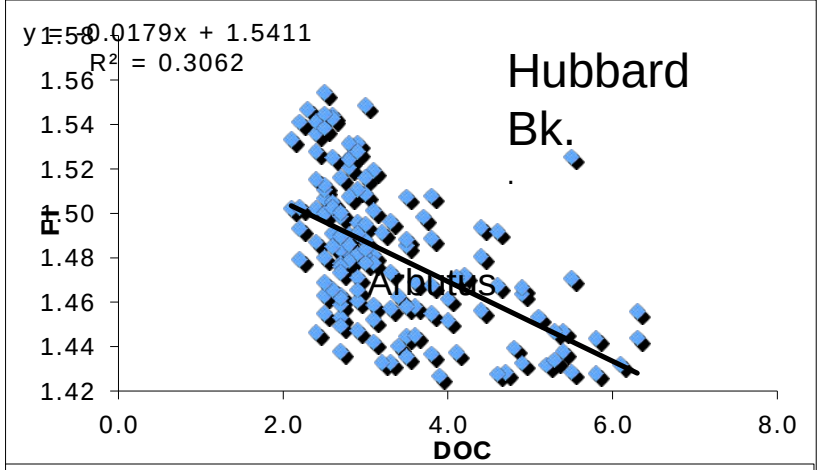


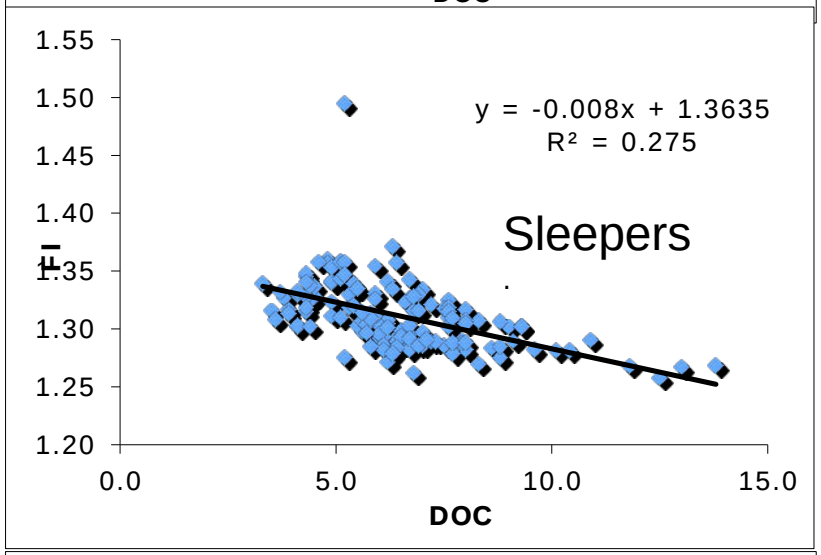


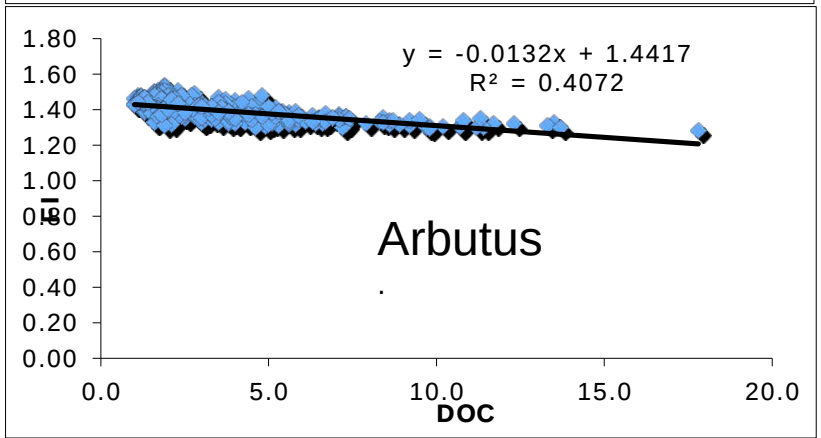
A large storm crossed the region on 28 August, producing very high flow at all 3 sites.

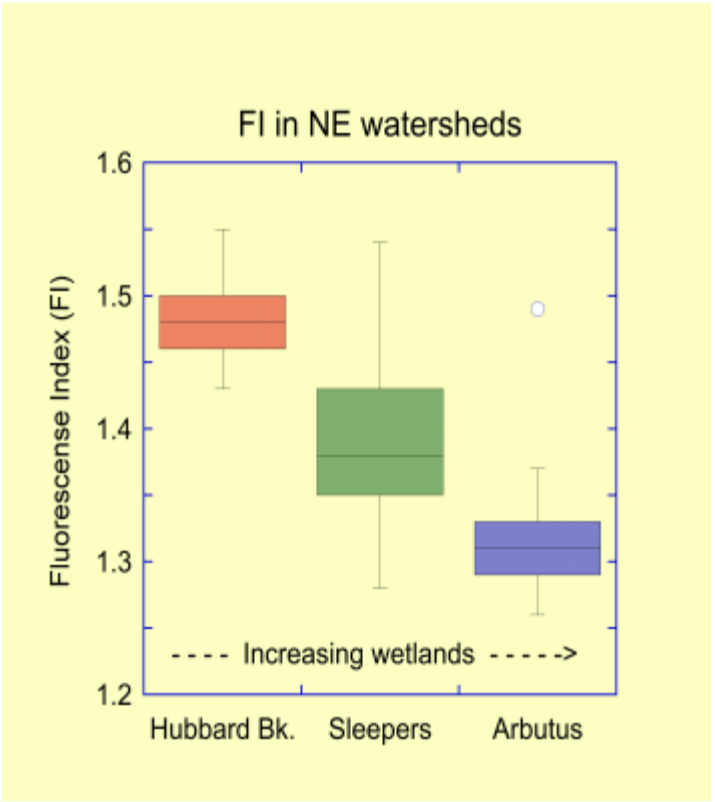
This panel illustrates several points: (1) Large storms generate large DOC peaks; (2) Discharge exerts a very strong control on DOC; (3) Turbidity partially masks the FDOM response. The latter point is noted at Sleepers River, where FDOM had a lower peak in the 28 August storm (on the right) than in a much smaller storm on 15-16 August (on the left). The 28 August peak was affected by turbidity, and becomes much higher after correction.

Fluorescence Index









The Fluorescence index (FI) is the ratio of two fluorescence pairs at different emission and excitation wavelengths:

FI = Ex 370 Em 450 / = Ex 370 Em 500

FI is an indicator of DOC source, with values near 1.2 indicating terrestrially-derived DOC, and values near 1.9 indicating microbially-derived DOC. The values in our study are near the terrestrially-derived end of the spectrum, and even more so at higher DOC (i.e. high flow), indicating that little in-stream production of DOC occurs in these headwater systems.

Results/Project outcomes 6

Outreach activities

- Most of the outreach on this project has been to fellow scientists, with numerous presentations, field trip demonstrations, and general proselytizing about the optical sensors.
- We can point to one public outreach connection associated with the Fairbanks Museum in St. Johnsbury, Vermont, which is just 2 miles from the Sleepers River watershed. The Museum has a strong public outreach mission, and last fall they did a major educational exhibit titled “Where does St. Johnsbury get its water?” CUAHSI hosted a “Let’s talk about water” meeting at the museum last fall, where P.I. Shanley interacted with museum staff, and discussed concerns about DOC in drinking water. The interaction led to Shanley helping with a Fairbanks Museum proposal focused on stream restoration to protect the water supply, which in turn has an outreach component where Shanley will meet with students for hands-on learning about stream organic carbon and how it is measured.

Installation at Hubbard Brook

Implications and applications in the Northern Forest region

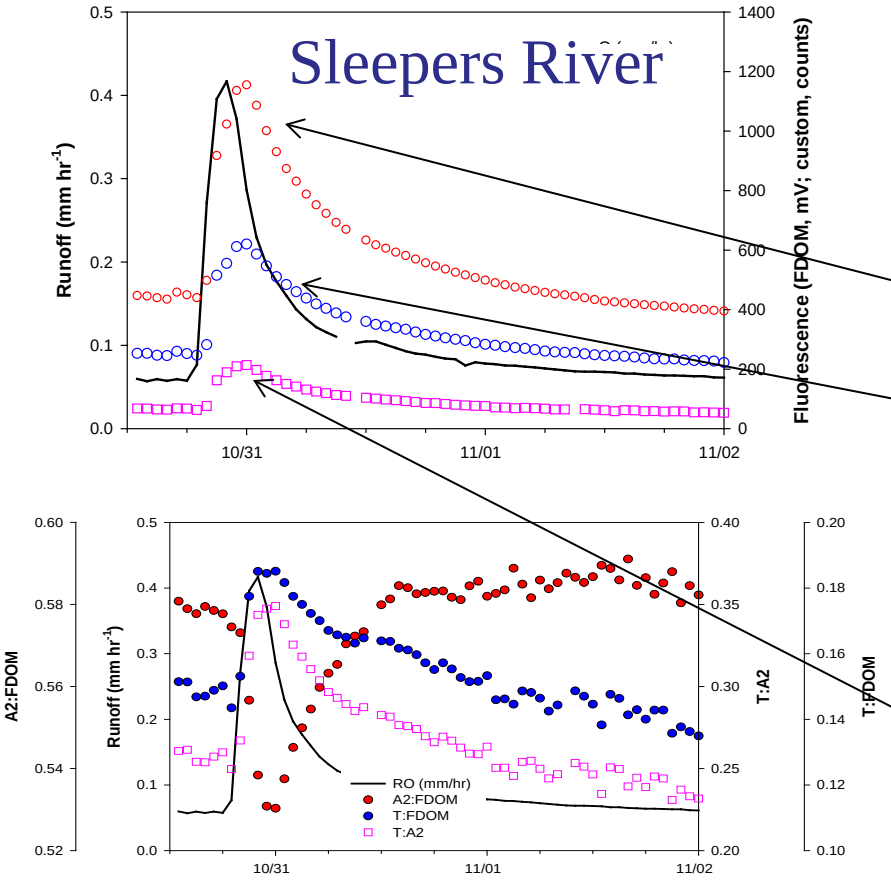
- DOC has received increasing attention lately. Stream DOC increases in response to changing atmospheric deposition chemistry and/or climate change has drawn greater attention to the role of DOC in forest nutrient cycles.
- The use of in-stream fluorometers can greatly enhance the acquisition of DOC and detail its response to the stream hydrograph, which in turn can give clues about what is driving DOC dynamics.
- DOC associates with many trace metals, notably mercury, with which it is highly correlated. Thus in situ fluorometers can provide an inexpensive proxy measurement of mercury.
- A very practical reason to study DOC is that too much DOC entering public water supply can lead to the formation of Disinfectant Byproducts (DBPs).
- The high DOC loads during storms make these periods especially challenging for treatment plants with surface water intakes.

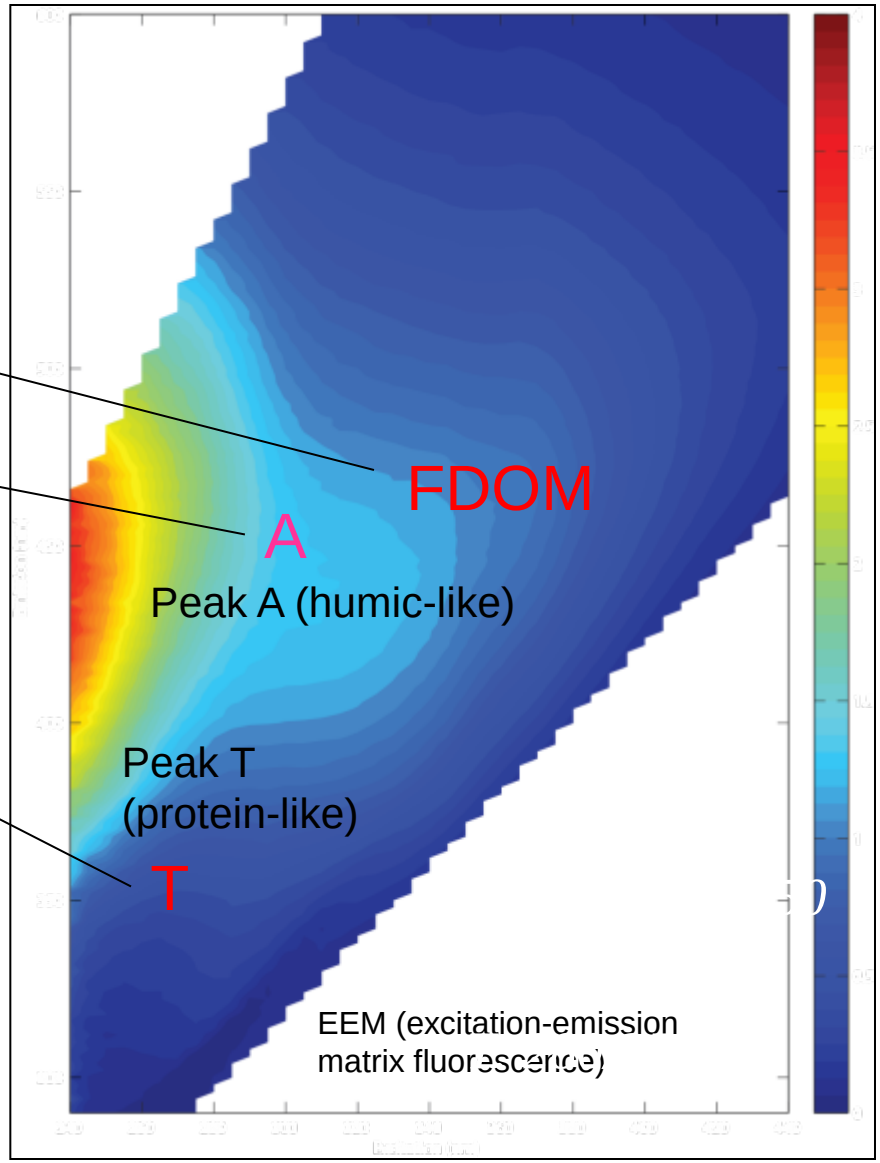
Future directions 1

- The Northern Forest, with its numerous small research catchments and network of collaborating scientists, is an ideal environment for coordinating a regional network of in situ FDOM measurements. This should become more obtainable as the technology continues to advance.
- Analytical advances have rapidly improved our ability to characterize DOC, nearly down to the molecular level. The ability to track how the mix of various classes of organic compounds shifts over storms and across seasons can impart valuable information about DOC sources, and how DOC and water move through a watershed.
- Expect in situ sensors to get more sophisticated and measure more and more parameters. For example, we deployed a fluorometer that measures three different types of dissolved organic matter – two humic-like classes and one protein-like class. We had this fluorometer at Sleepers River for Superstorm Sandy, one month after the present study ended. See result next page.

Future directions 2

Super Storm Sandy, 31 Oct. 2012





All 3 DOC fractions responded similarly during Sandy (top panel), but plots of ratios (bottom panel) indicate a relatively stronger response of the protein-like DOC over the hydrograph peak. Sandy preferentially mobilized more labile organic matter at the peak.

List of products 1

Peer-reviewed publications

- Pellerin, B.A., J.F. Saraceno, J.B. Shanley, S.D. Sebestyen, G.R. Aiken, W.M. Wollheim, and B.A. Bergamashi, 2012. Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. Biogeochemistry, 2012. 108(1-3), 183-198, DOI: 10.1007/s10533-011-9589-8.
-
- Campbell, John L., Rustad, Lindsey E., Porter, John H., Taylor, Jeffrey R., Dereszynski, Ethan W., Shanley, James B., Gries, Corinna, Henshaw, Donald L., Martin, Mary E., Sheldon, Wade. M., Boose, Emery R. 2013. Quantity is nothing without quality: Automated QA/QC for streaming environmental sensor data. BioScience 63(7): 574-585.
-
- Creed, IF, DM McKnight, BA Pellerin, MB Green, BA Bergamaschi, GR Aiken, SEG Findlay, DA Burns, JB Shanley, RG Striegl, BT Aulenbach, DW Clow, H Laudon, BL McGlynn, KJ McGuire, RA Smith, SM Stackpoole, in press. The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. Canadian Journal of Fisheries and Aquatic Sciences.

In preparation for peer-reviewed publications

- Shanley, J.B., Pellerin, B., Saraceno, J., Green, M., Aiken, G.R., and Sebestyen, S.D., in preparation. Climate controls on organic carbon flux from northern forest watersheds. Target Jounal: Hyrological Processes. Expected completion date: September 2015
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- Shanley, J.B., Pellerin, B., McGlynn, B.M., McGuire, K., Laudon, H., and Aulenbach, B.T., in preparation. Interpreting Concentration – Discharge Hysteresis in DOC Target Journal: Biogeochemistry (Synthesis and Emerging Ideas). Expected completion date: July 2015.
-
- Saraceno, J. and Shannley, J.B. Deep UV fluorescence as a clue to aqueous organic matter sources in a headwater stream during superstorm Sandy, October 2012. Target Jounal: Hyrological Processes. Expected completion date: April 2015.

List of products 2

Conference and workshop presentations

- Pellerin, B.A., B.A. Bergamaschi, B.D. Downing, J. Saraceno, J.A. Fleck, T.E. Kraus, J.B. Shanley, G.Aiken, 2010. In situ CDOM fluorescence measurements: A continuous proxy for dissolved organic carbon concentration in rivers and streams? 2010 AGU Fall Meeting.
- Shanley, J.B., 2011. Application of optical sensors to small watershed research. USGS optical sensor workshop, Shepherdstown, WV, June 2011. *Presented.*
- Pellerin, B.A., B.A. Bergamaschi, B.D. Downing, J. Saraceno, J.B. Shanley, G. Aiken, P.S. Murdoch, 2011. The coupling of runoff and dissolved organic matter transport: Insights from in situ fluorescence measurements in small streams and large rivers. 2011 AGU Fall Meeting. ***Invited***.
- Shanley, J.B., S.D. Sebestyen, G. Aiken, B.A. Pellerin, 2011. DOC quantity and quality in northeastern USA catchments. 2011 AGU Fall Meeting. *Presented*.
- Shanley, J.B., Pellerin, B.A., Sebestyen, S.D., McGuire, K., 2012. Hysteria over hysteresis -- what does it tell us about solute sources? Hubbard Brook Cooperators' meeting, July 2012. *Presented.*
- Pellerin, B.A., J.B. Shanley, J. Saraceno, G. Aiken, S.D. Sebestyen, B.A. Bergamaschi , 2012. Relationships between dissolved organic matter and discharge: New insights from in-situ measurements in a northern forested watershed. 2012 AGU Fall Meeting. ***Invited***.
- Shanley, J.B., 2013. DOC and DOC quality in Northern Forest streams: what are we learning from optical measurements? NorthEast Research Cooperative (NERC) biennial meeting, March 2013. *Presented.*
- Shanley, J.B. DOC and DOC Quality research at Sleepers River, VT. Presented at Yale Connecticut River workshop, Mar 3, 2014.
- Shanley, J.B. Sources and travel times for DOC at Sleepers River, VT. Presented at Yale Connecticut River workshop, Feb 5, 2015.

Leveraged grants

- There have been no directly leveraged grants, but our work in this project brought about our participation in Peter Raymond's NSF project at Yale, "The Pulse-Shunt Concept: A conceptual framework for quantifying and forecasting watershed DOM fluxes and transformations at the MacroSystem scale." funded for 5 years beginning 2014. This project uses sensors and sampling to evaluate DOC dynamics in the entire Connecticut River watershed. Similarly, through our sensor work on this project and presenting it at AGU, Shanley was invited to participate as a co-P.I. on two national competition NIWR proposals submitted February 2015.