Continuous *in situ* measurement of carbon quality as a tool for understanding stream mercury dynamics in northern forests

Principal Investigator:
James B Shanley (jshanley@usgs.gov)
US Geological Survey
P.O. Box 628
Montpelier, VT 05601
Tel: 802-828-4466 / Fax: 802-828-4465

Co-Principal Investigators:

Charles T. Driscoll (ctdrisco@syr.edu)
Syracuse University, 151 Link Hall
Syracuse, NY 13244
Tel: 315-443-3434 / Fax: 315-443-1243

George R. Aiken (graiken@usgs.gov)
US Geological Survey, 3215 Marine Street
Boulder, CO 80303-1066
Tel: 303-541-3036 / Fax: 303-447-2505

Brian Pellerin (bpeller@usgs.gov)
US Geological Survey, CA Water Science Center
6000 J Street, Placer Hall
Sacramento, CA 95819
Tel: 916-278-3167 / Fax: 916-278-2071

Kevin J. McGuire (kevin.mcguire@vt.edu) (Formerly at Plymouth State University)
Virginia Tech, 210-B Cheatham Hall (0444)
Blacksburg, VA 24061
Tel: 540-231-6017/ Fax: 540-231-6673

Stephen D. Sebestyen (ssebestyen@fs.fed.us)
USDA Forest Service, Northern Research Station, 1831 HWY 169 E
Grand Rapids, MN 55744-3399
Tel: 218-326-7108 / Fax: 218-326-7123

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Main outcomes:

- We successfully demonstrated the ability to make frequent (every 15 minutes) in-stream optical measurement of organic matter(OM) fluorescence through a full year of Northern Forest climate, even under ice.
- OM fluorescence proved to be a robust proxy for dissolved organic carbon (DOC) and dissolved mercury, showing great promise as a tool for more accurate and less expensive monitoring in near real-time.

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http://www.nsrcforest.org

Project Summary

Like acid rain, mercury pollution enters the Northern Forest landscape via the atmosphere in rain, snow, and dry deposition. Mercury is a neurotoxin that affects wildlife and humans who eat a lot of fish, where mercury bioaccumulates and poses a risk to consumers. Most of the incoming mercury is retained in forest soils, but we conducted this study to better understand the magnitude, timing, and processes that lead to mercury leaving the forest headwaters in streamflow, toward its ultimate uptake by fish downstream. It takes many stream samples to observe mercury behavior, and each sample is expensive to analyze, so we sought a cheaper alternative. Our previous work demonstrated that stream mercury was transported in association with certain components of dissolved organic carbon (DOC), the breakdown product of decaying plant and animal matter. Our approach was to use an in-stream fluorometer, an optical sensor that measures fluorescing dissolved organic matter (FDOM), which represents the Ņreactive DOCÓthought to carry the mercury. We measured FDOM continuously at 15-minute intervals and conducted periodic sampling to test whether the FDOM was a valid proxy for mercury. We conducted the study at three established long-term research watersheds in the Northern Forest that spanned a range of DOC and mercury: Hubbard Brook, NH (low DOC); Sleepers River, VT (intermediate DOC); and Arbutus, NY (high DOC). Despite the inevitable glitches inherent in a novel application, we acquired mostly high-quality data for the one year of measurements, even during the harsh northern winter.

The relation between our measured FDOM and sampled DOC concentration was quite strong, meaning that we could use our ŅcontinuousÓFDOM values to calculate a DOC concentration at any point in time. The relation between FDOM and mercury was not as strong, but the FDOM was nonetheless a reasonable analog for mercury. The continuous measurements showed that DOC and mercury concentrations closely followed changes in streamflow, increasing with storms and snowmelt, and decreasing during dry periods. This pattern makes sense with respect to our understanding of the sources of water feeding the stream. As conditions get wetter, groundwater levels rise into the shallow soil zone rich in organic matter, mobilizing the reactive DOC that carries mercury to the stream. Fluorescence is a promising tool that allows inexpensive assessment of how much DOC and mercury are released from Northern Forest mountains and headwaters, and insight into how the mercury problem may change in a changing climate.

Background and Justification

- Atmospheric mercury deposition has tripled during the past century.
- Mercury is a potent neurotoxin; children and women of childbearing age are particularly vulnerable to its effects.
- The main pathway of human exposure in developed countries is through fish consumption; all 50 states have at least one advisory to limit fish consumption due to mercury.
- Northern Forest lands are prone to mercury contamination for these reasons:
  - Relatively high regional atmospheric input of mercury in rain, snow, and dry deposition
  - Forests receive enhanced mercury deposition because the forest canopy effectively scavenges mercury from the air
  - The region has numerous wetlands and lakes, which foster the conditions that convert mercury to its organic form (methylmercury), which is taken up by organisms.
  - Fishing is a popular activity.
  - Pressure on the land and forest biomass; land disturbance tends to release mercury stored in forest soils.
- The study of mercury is closely linked to two other environmental issues:
  - Acid rain -- mercury and acid rain have a common source in coal combustion, and reductions in acid rain (especially sulfur) have been accompanied by reductions in mercury, but both also have some legacy effects, whereby past deposition has remained in the soil and persists. Also, sulfur is tighly linked tot the methylation of mercury, so reductions in sulfur alone could lead to lower mercury accumulation in fish.
  - Climate change. Mercury is intimately coupled to the carbon cycle. Mercury is associated with soil organic carbon, and it moves in streamwater with both particulate and dissolved organic carbon (POC and DOC). Warmer temperatures and increased atmospheric CO_2 could both intensify carbon cycling, with associated effects on mercury.

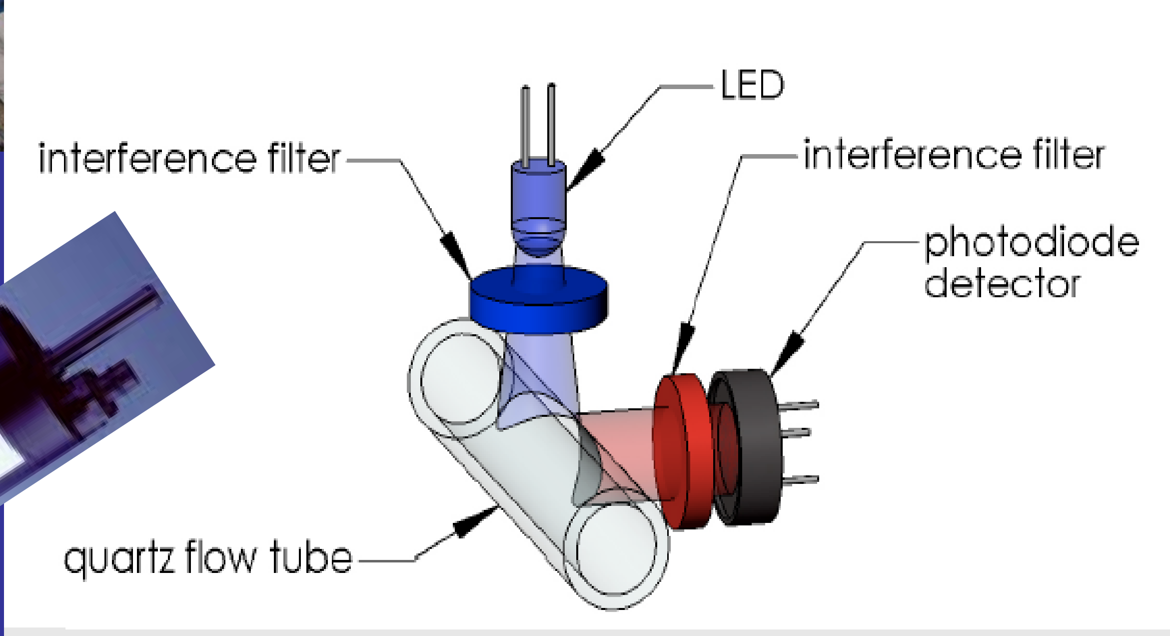
Methods

• In-stream fluorometers were installed to measure and log FDOM every 15 minutes for one year at 3 sites. FDOM tested as proxy for DOC and dissolved mercury.
• At each site, 96 samples for DOC and 32 samples for mercury. Some low flow but mostly high flow. DOC samples sometimes collected by automatic sampler but human presence required for mercury sampling.
• In-stream sonde logging temperature, specific conductance, and turbidity at 15 minute intervals also deployed at each site. Turbidity teted as proxy for total suspended solids (TSS) and particulate mercury.
• The 96 DOC samples at each sites were analyzed at George Aiken's USGS lab in Boulder, CO for DOC, UV absorbance at 254 nm (UV_{254}), and fluorescence (as a check against the in-stream measurement).
• The 32 mercury samples at each site were analyzed for TSS, dissolved and particulate total mercury, and dissolved methylmercury at Charley Driscoll's lab, Syracuse University.
• The fluorometers need no calibration; they were regularly cleaned to limit suppression of the signal due to fouling.
• The sondes were regularly cleaned to limit fouling; turbidity and conductance were periodically tested and recalibrated as necessary.
• All data time series were quality controlled and values adjusted for fouling and turbidity drift, using linear drift corrections.
• At Hubbard Brook, FDOM dynamics were interpreted in light of ongoing hydrologic measurements on hillslope and riparian zone directed by Kevin McGuire.

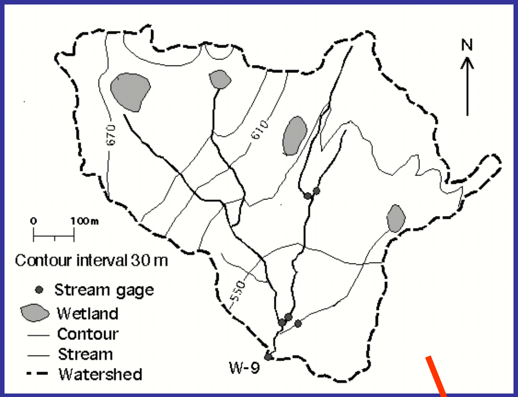
Logging Fluorometers

Fluorescence

Installation at Hubbard Brook



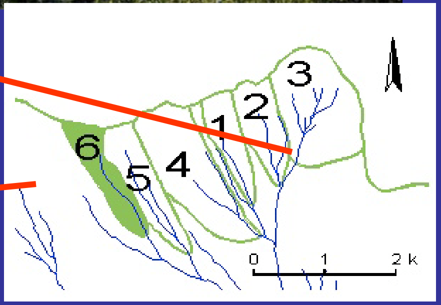
Sleepers River, Vermont

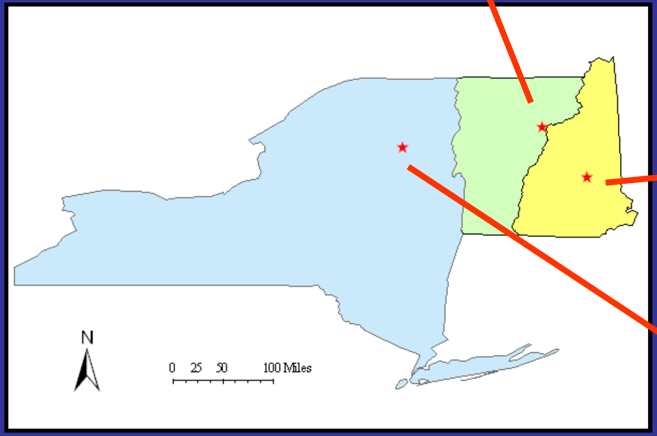


Sampling site
W-9

Hubbard Brook, New Hampshire

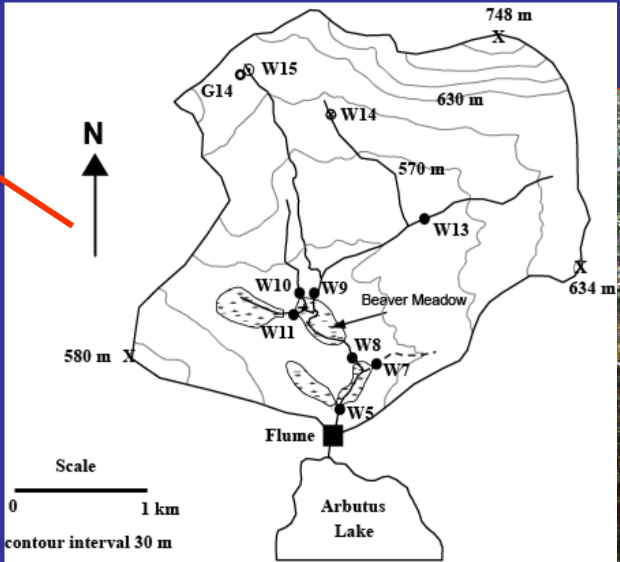
Sampling site
WS-3





Huntington Forest, New York

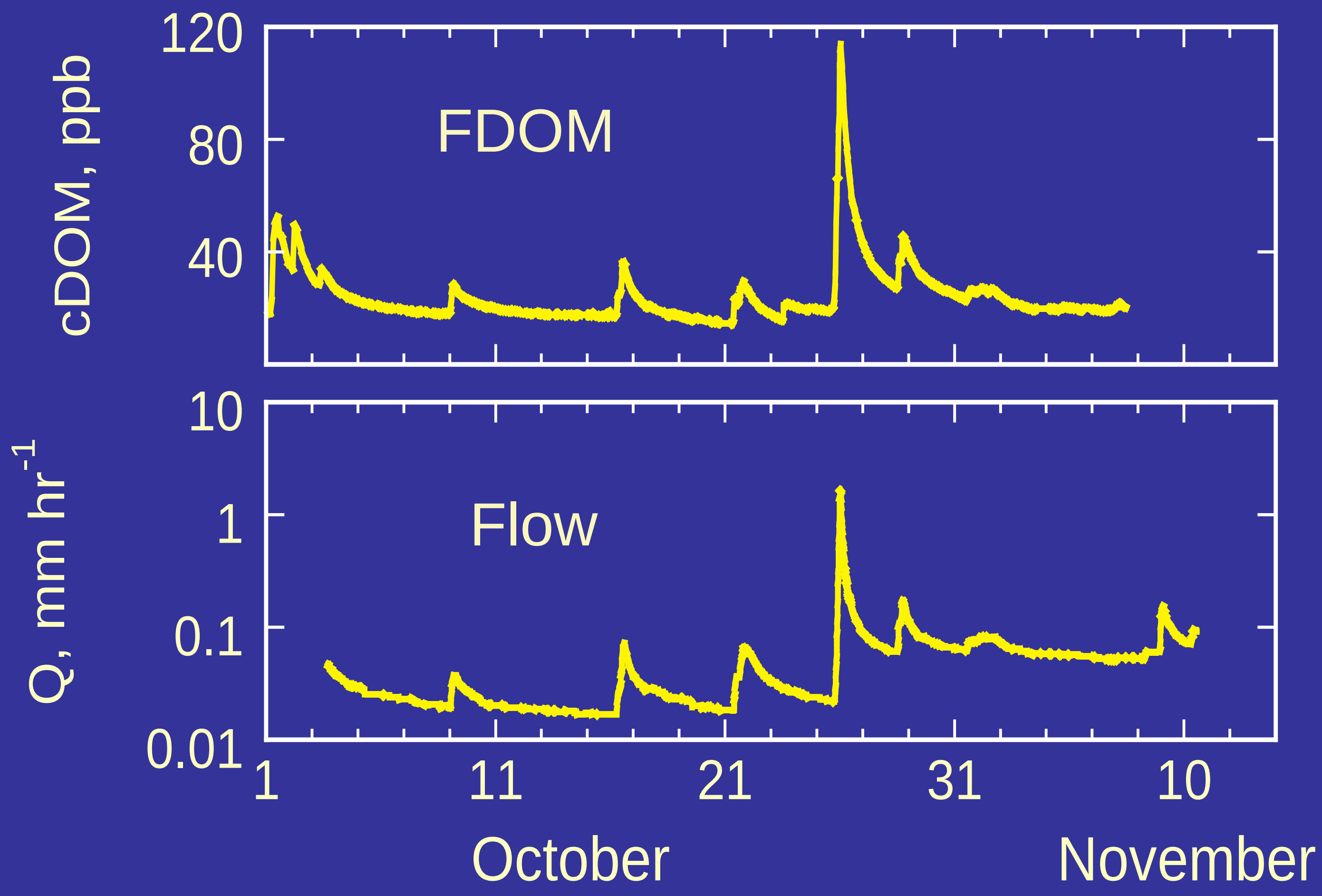
2 sites, above and below Wetlands (W9 and Flume)



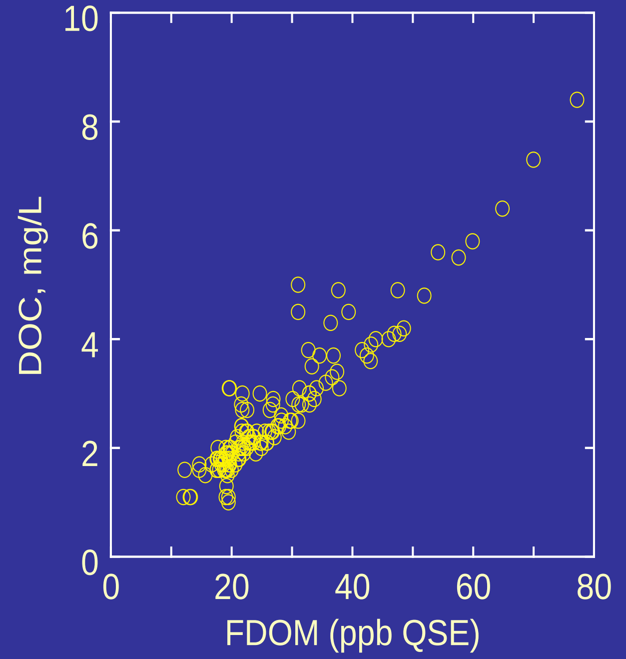
Results/Project outcomes

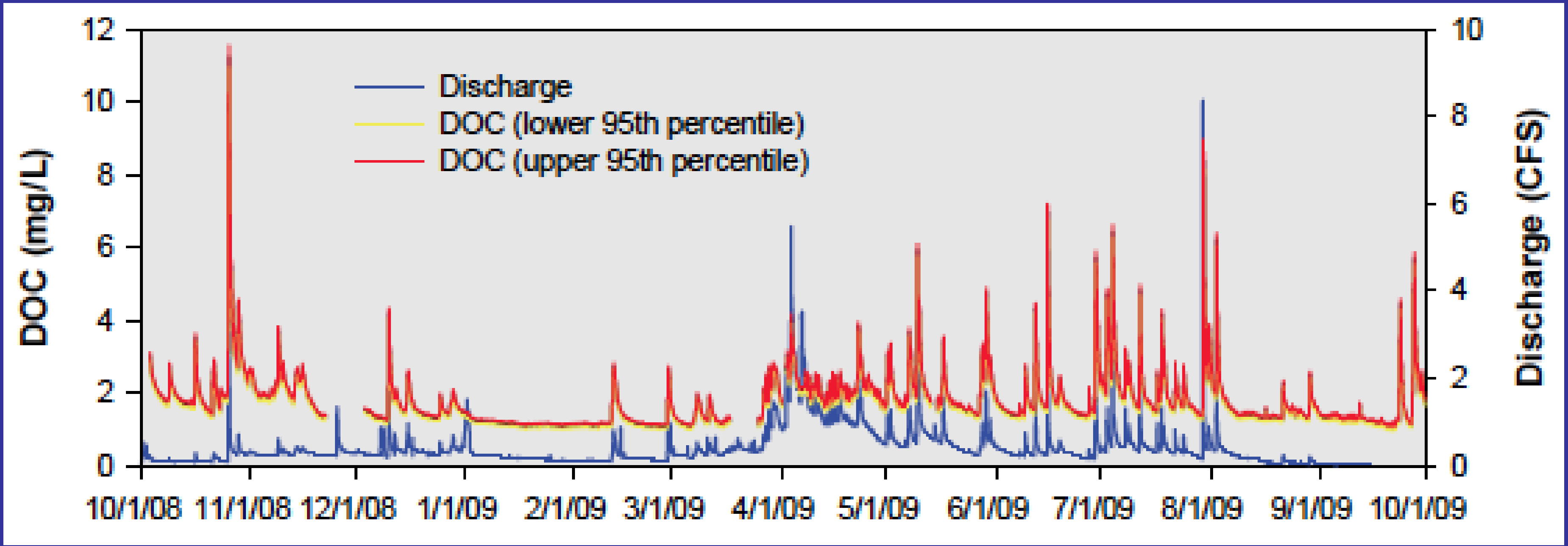
- DOC was highly correlated with FDOM, so FDOM was a reliable proxy for DOC.
- FDOM tracked stream discharge very closely.
- However there were seasonal differences (higher FDOM for a given discharge in fall, due to leaffall) and within-storm variation (clockwise hysteresis; higher FDOM for a given discharge on the falling limb relative to the rising limb). These patterns allow insight into processes, and the continuous logging combined with the strong proxy allow for accurate stream DOC flux calculations.
- FDOM was a less robust proxy for mercury, yet there was a significant relation so that Hg fluxes could also be calculated with greater confidence than from sampling, albeit with greater uncertainty than for DOC.
- Nitrate exhibited a previously unknown diurnal snowmelt late in the melt period, and continuing after daily melt pulses ceased. We attributed this to stream biological uptake in response to sunlight on the channel.
- DOC and mercury concentrations clearly increased as conditions became wetter, but at Hubbard Brook we attributed this to hillslope contributions rather than riparian or channel contributions, as riparian groundwater levels remained below stream grade (losing stream).

Sleepers River
Fall Storms

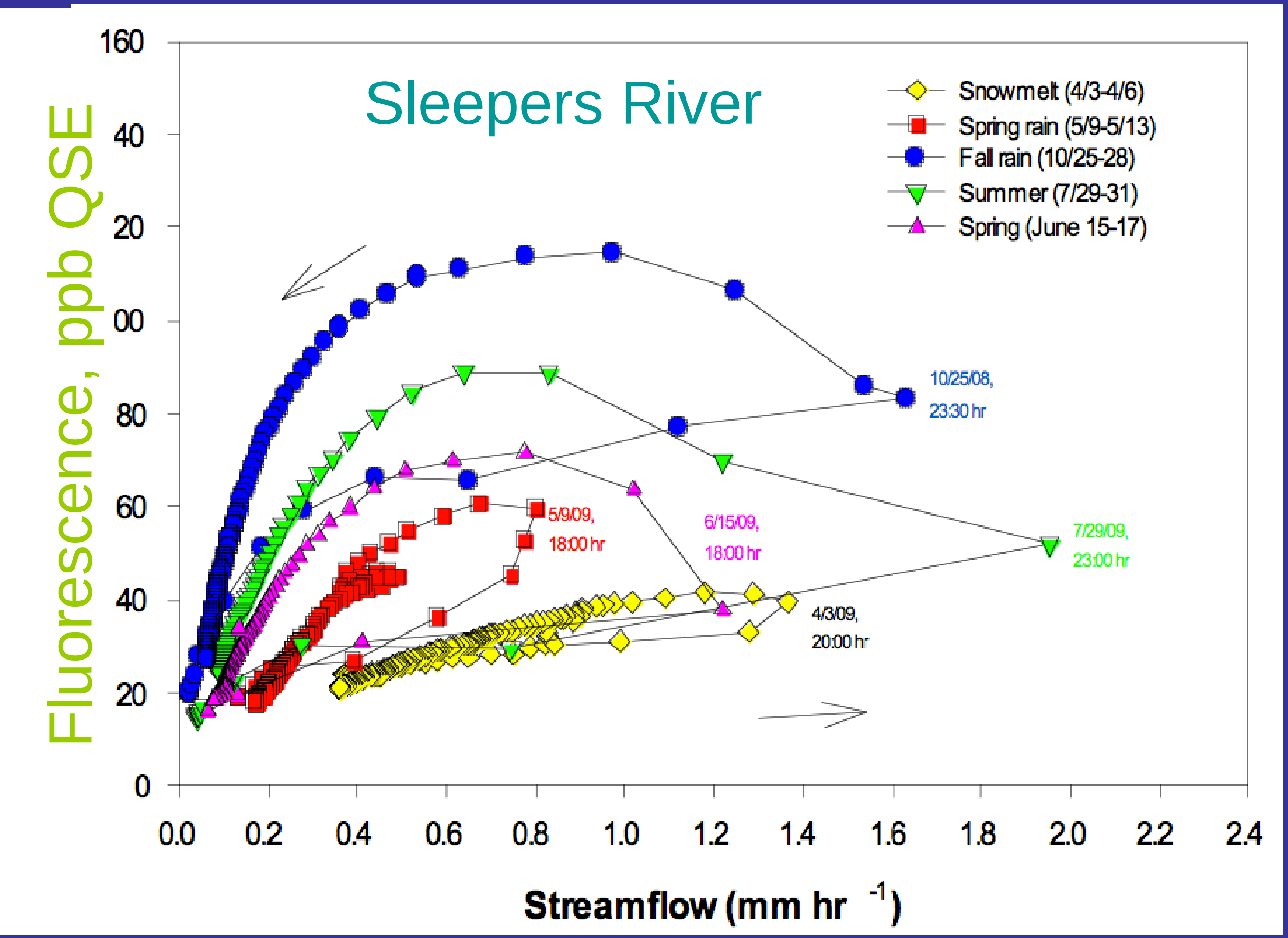


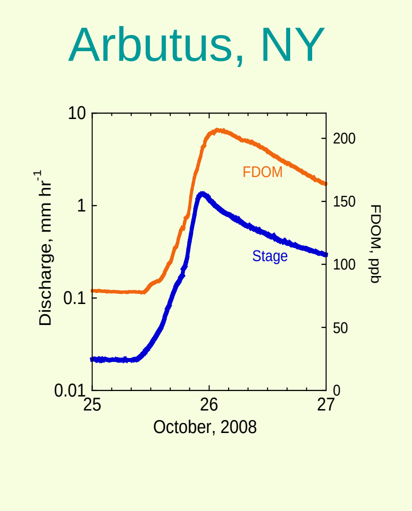
Sleepers River Water Year 2009 DOC computed from FDOM

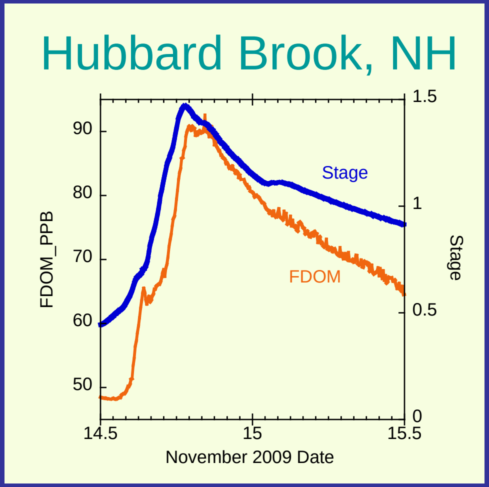




FDOM Hysteresis Loops

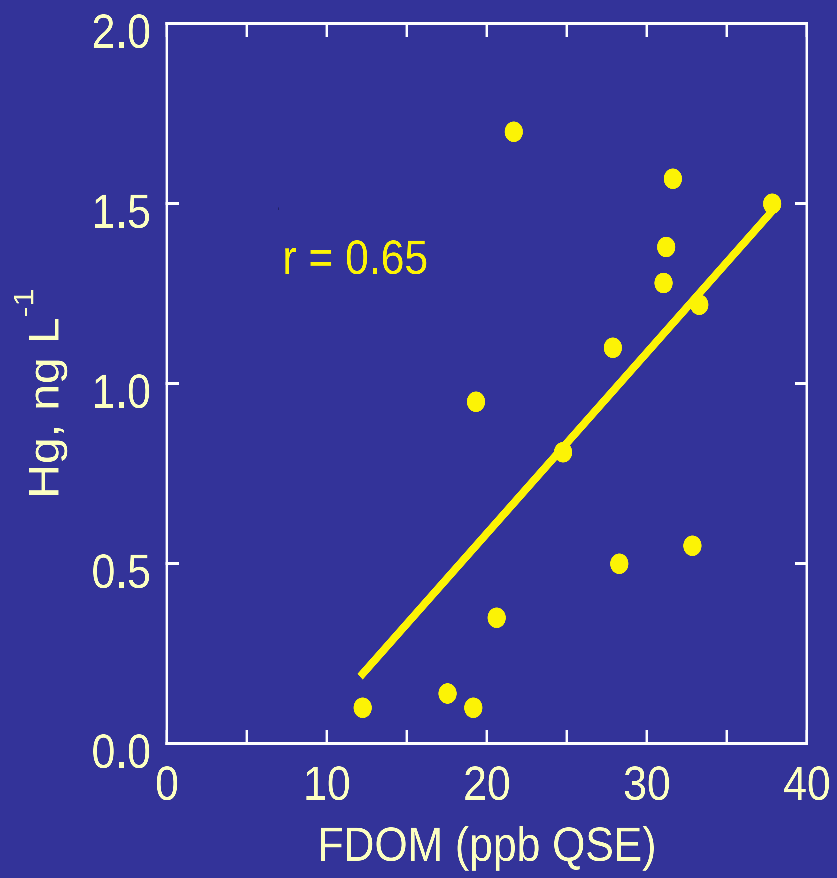




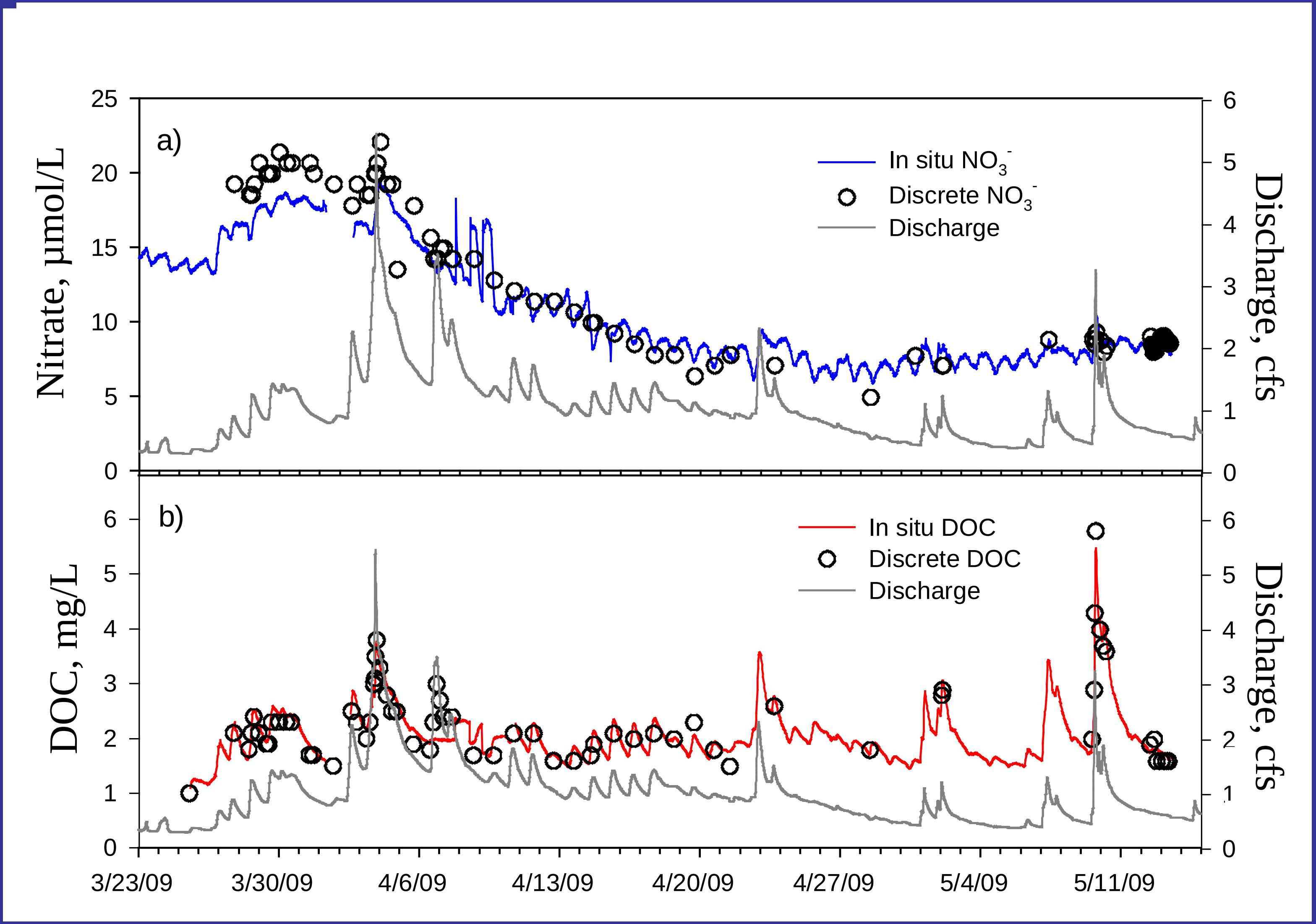


FDOM -- proxy for dissolved Hg

Sleepers River, VT



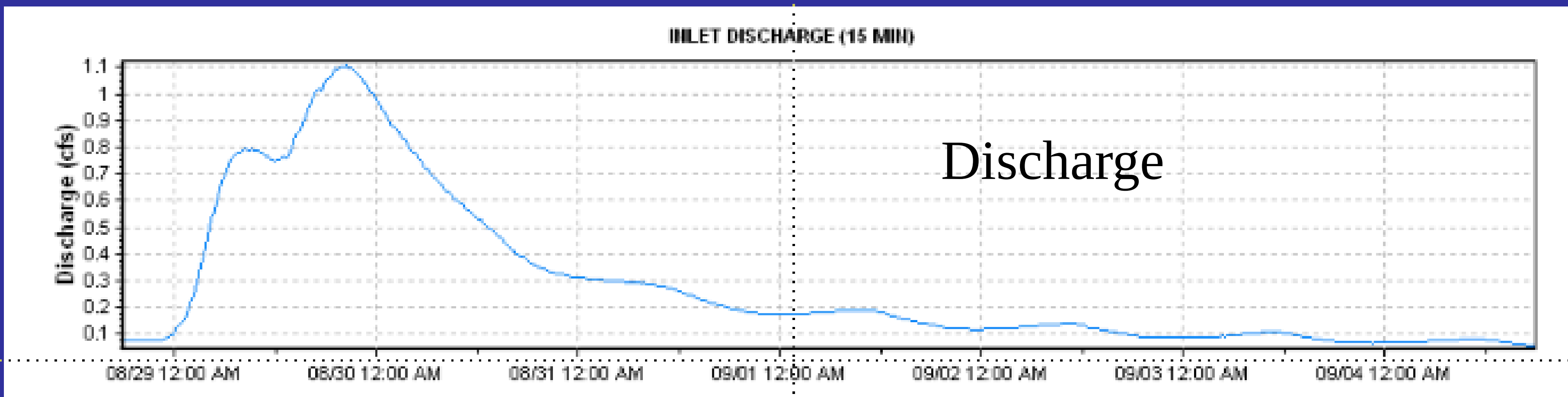
DOC and nitrate from in situ sensors Sleepers River snowmelt 2009

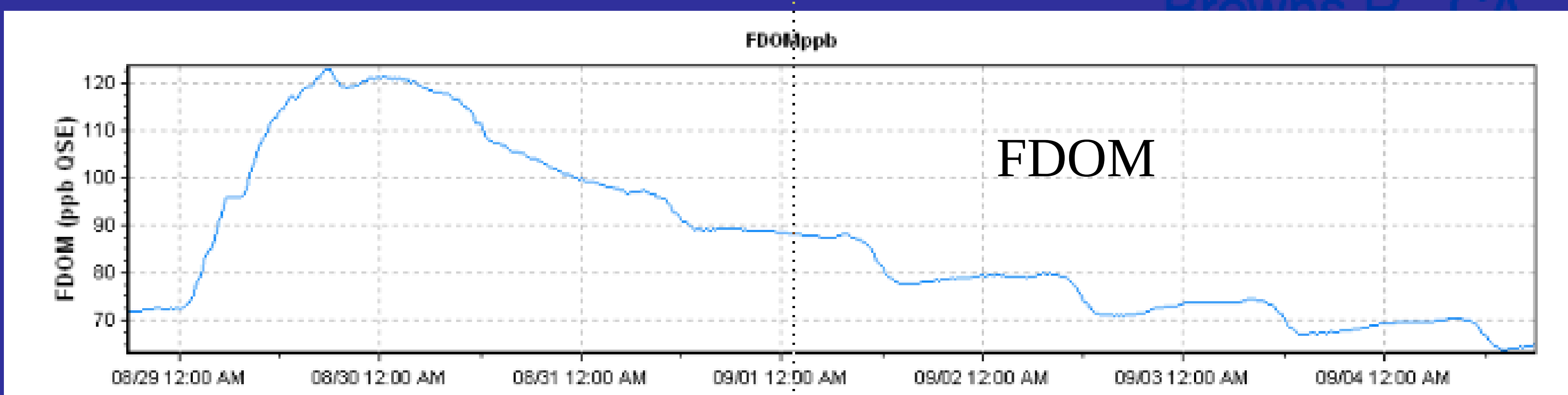


Implications and applications in the Northern Forest region

- This project was a proof-of-concept that fluorometers, nitrate sensors, and other new-generation sensors have strong potential as inexpensive monitoring approaches in the Northern Forest region, even under adverse winter weather conditions.
- Regional DOC concentrations have been on the rise for a decade or more due to some combination of climatic warming and shifts in atmospheric deposition chemistry. Optical sensors are a tool to track further developments in this trend, as changes in carbon cycling have strong relevance to climate change
- Regional mercury emissions have declined considerably, but deposition has remained fairly steady and stream export may even have increased along with the increasing DOC. Given the numerous regionwide advisories on fish consumption due to mercury, the capability for inexpensive monitoring with optical sensors is appealing,
- These sensors generate and can potentially transmit data every 15 minutes, 24 hours a day. The ability to display raw data, or even concentration values computed from proxy measurements, in real time on the internet will help generate excitement and draw attention to these important environmental issues.

Our data on the real-time website at Arbutus





Future directions

- Having demonstrated proof-of-concept at a few sites, the next step would be to involve more scientists at more sites. However, although the data are easy to collect, quality control and troubleshooting ability come with experience, so deployment should proceed at a measured pace.
- It would be prudent to improve and refine our efforts at the sites where we are already working, and we have funding to do so through 2012.
- On the technical site, we are working out some quality control metrics that can be logged and transmitted so we can evaluate sensor performance in near real-time, and either service the sensor, correct the data retroactively, or both, as appropriate.
- Showcasing the data on a realtime user-friendly and well-conceived website, would be the among the best ways to generate excitement and demonstrate the relevance of this approach. Hopefully we can achieve this within the current funding cycle.

List of products

- Three peer-reviewed papers are in progress as a result of this project:

- Pellerin, B.A., Saraceno, JF., Shanley, J.B., Sebestyen, S.D., Aiken, G.R., and Bergamaschi, B.A. 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. Accepted, in revision. Expect to submit final version December 2010.

- Pellerin, B.A., Shanley, J.B., Aiken, G.R., McGuire, K., Saraceno, JF., and Sebestyen, S.D. DOC dynamics in forested headwater streams as inferred from in situ fluorometers. In preparation. Expect to submit January 2011.

- Shanley, J.B., Aiken, G.R., Driscoll, C.T., Pellerin, B.A., Saraceno, JF., and Sebestyen, S.D. Stream mercury export from forested headwaters; continuous optical proxy measurements provide accurate fluxes and process insight. Expect to submit April 2011.

List of products

- 2 USGS publications:

- Pellerin, B.A., Bergamaschi, B.A., Aiken, G.R., Downing, B.D., Fleck, J.A., Saraceno, JF., and Shanley, J.B. In situ optical sensors for monitoring the Nation's water quality. USGS Fact Sheep, 4 pp. In review. Expected completion April 2011.

- Bergamaschi, B.A., Downing, B.D., Pellerin, B.A., and Saraceno, JF. In Situ Sensors for Dissolved Organic Matter Fluorescence: Bringing the Lab to the Field. In: USGS WRD Instrument News, Spring 2010.

List of products

- Abstracts/Conferences 1/2
  - Shanley, J.B., Aiken, G.R., Bergamaschi, B.A., Driscoll, C.T., Pellerin, B.A., Saraceno, JF., and Sebestyen, S.D. In situ optical sensors track mobile mercury on the cheap. 10th International Conference on Mercury as a Global Pollutant. Halifax, NS. July 25-29, 2011. (invited)
  - Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Saraceno, J., Fleck, J.A., Kraus, T.E.C., Shanley, J.B. and Aiken, G. In situ CDOM fluorescence measurements: A continuous proxy for dissolved organic carbon concentration in rivers and streams? AGU Fall Meeting, San Francisco, CA, December 17, 2010.
  - Shanley, J.B., Pellerin, B.A., Saraceno, JF., Aiken, G.R., Sebestyen, S.D., McGuire, K., Dittman, J., and Driscoll, C.T. Faster, cheaper, and better? Real-time *in situ* optical sensors advance biogeochemical investigations in Northern Forest fresh waters. NERC meeting, Saratoga, NY Nov. 8-10, 2010.
  - Shanley, J.B. Taking the Pulse of Headwater Streams -- Real-Time Proxies for DOC and Mercury. Hubbard Brook Annual Cooperators' Meeting, July 8-9, 2010.
  - Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Saraceno, J., Fleck, J.A., Shanley, J.B., Aiken, G., Boss, E. and Fujii, R. Seeing the light: Applications of in situ optical measurements for understanding DOM dynamics in river systems. National Monitoring Conference, April 2010, Denver, CO.
  - Shanley, J.B., G.R. Aiken, J.A. Dittman, C.T. Driscoll, B. Pellerin, J.F. Saraceno, A. Riscassi, D.A. Burns. Carbon quality strongly influences mercury export from forested upland catchments. Swedish University of Agricultural Sciences, Uppsala, Sweden, April 9, 2010. (invited)

List of products

- Abstracts/Conferences 2/2

- Shanley, J.B., G.R. Aiken, J.A. Dittman, C.T. Driscoll, B. Pellerin, J.F. Saraceno, A. Riscassi, D.A. Burns. Carbon quality strongly influences mercury export from forested upland catchments. GSA Northeast/Southeast meeting, Baltimore, March 11-13, 2010. (invited)

- Pellerin, B.A., Bergamaschi, B.A, Downing, B.D., Saraceno, JF., Fleck, J., Shanley, J.B., Aiken, G.R., Boss, E., and Fujii, R. Seeing the light: the application of in situ optical measurements for DOM studies in riverine systems. Fall Meeting, AGU San Francisco, Dec. 14-18, 2009. (invited)

- Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Saraceno, J., Fleck, J.A., Shanley, J.B., Aiken, G., Boss, E. and Fujii, R. Seeing the light: Applications of in situ optical measurements for understanding DOM dynamics in river systems. UC-Merced, Environmental Systems Seminar. Dec. 2, 2009 (invited).

- Shanley, J.B. Use of in situ optical sensors to improve stream biogeochemical flux esrtimates. Aquatic Environment and Watershed Science seminar series, Rubenstein School of Natural Resources, Univ. Vermont, Nov. 22, 2009.

- Shanley, J.B. In situ sensors – applications in Northern Forest watersheds. Informal presentation at Optical Sensor workshop, Burlington, VT, August 2-5, 2009.

- Shanley, J.B., G.R. Aiken, C.T. Driscoll, J.A. Dittman, S.D. Sebestyen, B. Pellerin, M. Marvin-DiPasquale, P.F. Schuster, 2009. Total mercury and methylmercury export from terrestrial uplands in a changing climate. Spring Meeting, AGU Toronto May 24-27, 2009. (invited)