

# Does Changing Atmospheric Deposition of N & S Alter Stream DOM Quality & Flux in Northern Forested Watersheds?

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*This research demonstrates that changes in deposition of N and S have the ability to alter carbon cycling and the quality and source of DOM in temperate forested watersheds*

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<http://www.nsrcforest.org>

# Project Summary

## Rationale

Over the last two decades concentrations of dissolved organic matter (DOM), often expressed as dissolved organic carbon (DOC), have increased significantly throughout much of the northern hemisphere, including the northeastern U.S. DOM is ubiquitous within soil solutions and natural waters, important in many processes critical to ecosystem function including soil formation and carbon sequestration, and represents a vector for stream export of C, N and P from temperate ecosystems. The implications for changing DOM flux and quality in temperate forests and beyond are therefore ecologically significant.

## Methods

The Bear Brook Watershed in Maine (BBWM) and Fernow Experimental Forest in West Virginia (FEF) provide unique opportunities to *directly* assess the effects of acid deposition, N enrichment, and recovery from acid deposition on DOM at the decadal time-scale. We used state of the art UV-VIS and fluorescence spectroscopy, and fluid imaging technology (used for rapid and precise enumeration and classification of microbial communities), coupled with measurements of DOC concentration to define changes in DOM source, quality, and flux and microbial populations in response to (a) 22+ years of experimental acidification with  $(\text{NH}_4)_2\text{SO}_4$  in the treated watersheds at BBWM and FEF, (b) recovery from elevated S deposition in reference watersheds, and (c) seasonal changes in hydrology and climate.

## Major Findings

This research demonstrates that changes in deposition of N and S have the ability to alter the quality and source of DOM exported to streams and lakes in temperate forested watersheds. Significant differences in DOM characteristics in these experimental watersheds confirm the acidity change mechanism as the driver of alterations in DOC in northern waters.

## Implications for the Northern Forest region

These findings contribute to issues of concern for northeastern U.S. forests that include sustainability and the provision of ecosystem services such as clean water and carbon sequestration in the face of the intensification of management, emerging renewable energy demands, lower rates of S deposition, long-term projections for increased N deposition, and a changing climate.

# Background and Justification

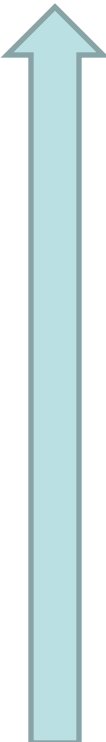
- DOM plays many important roles in the environment
  - Controls the depth of light penetration in water
  - Contains nutrients
  - Can buffer changes in pH
  - DOM can control the fate & transport and bioavailability of metals
  - Reactions with DOM can produce toxic disinfection byproducts during drinking water treatment
  - Part of the global carbon cycle



# DOC is increasing in natural waters—but why?

## What?

Dissolved Organic Carbon (DOC)/  
Dissolved Organic Matter (DOM)



## When?



Last several decades

## Where?



Freshwaters of  
northeastern  
US & Europe





# Possible Drivers of Increased DOM

- Rising atmospheric CO<sub>2</sub> concentrations
- Climate warming
- Changing hydrology
- N deposition
- Decreased sulfate deposition

**Our hypothesis**

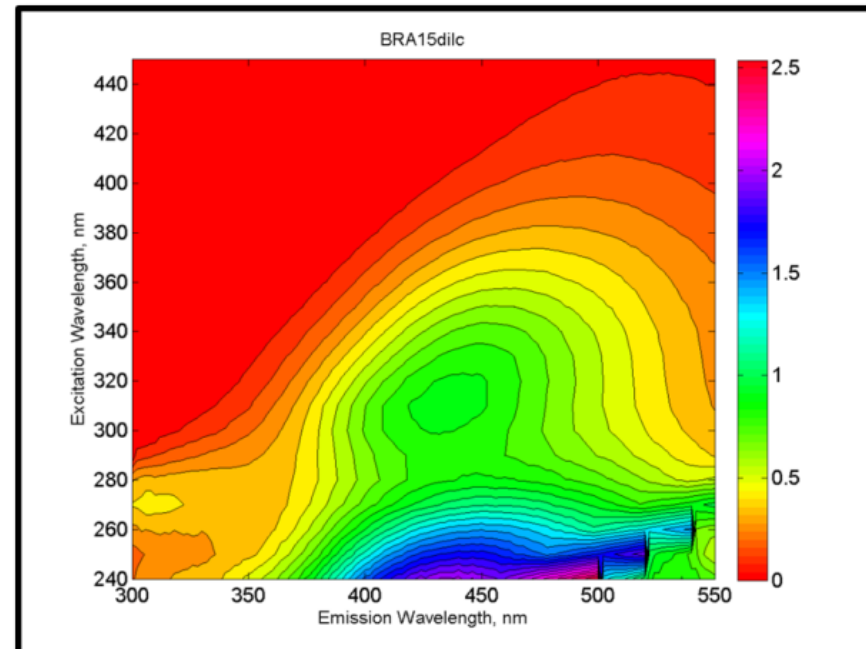
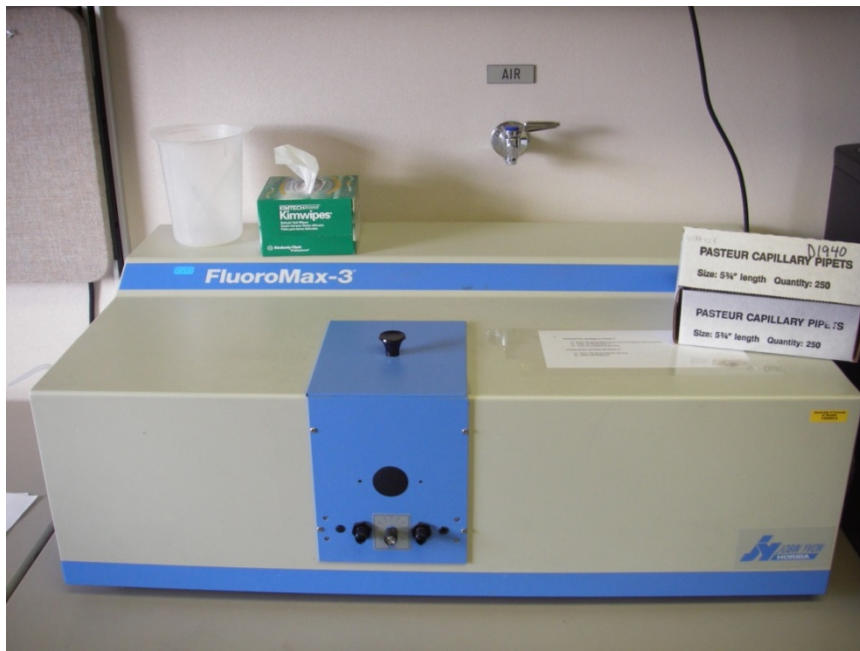


# Methods

The Bear Brook Watershed in Maine (BBWM) and Fernow Experimental Forest in West Virginia (FEF) provide unique opportunities to *directly* assess the effects of acid deposition, N enrichment, and recovery from acid deposition on DOM at the decadal time-scale. We coupled experimental acidification and recovery with fluorescence spectroscopy to assess DOM differences via changes in the fluorescence index (FI), freshness, and humic index of stream water, soil solutions, and soil extracts. (FI data shown here)

Fluorescence Index provides information about the source and quality of DOM

- Higher number = more microbial input, less aromatic (1.8)
- Lower number = more terrestrial (plant) input, more aromatic (1.2)





# Bear Brook Watershed in Maine

**East Bear Brook  
Reference**

Collected stream (~ bi-weekly),  
soil extracts, and soil solution  
samples.

**West Bear Brook  
Treated**

**25+ Years:**

28.8 kg S ha<sup>-1</sup> year<sup>-1</sup>

25.2 kg N ha<sup>-1</sup> year<sup>-1</sup>





# West Virginia

W4 is a reference watershed

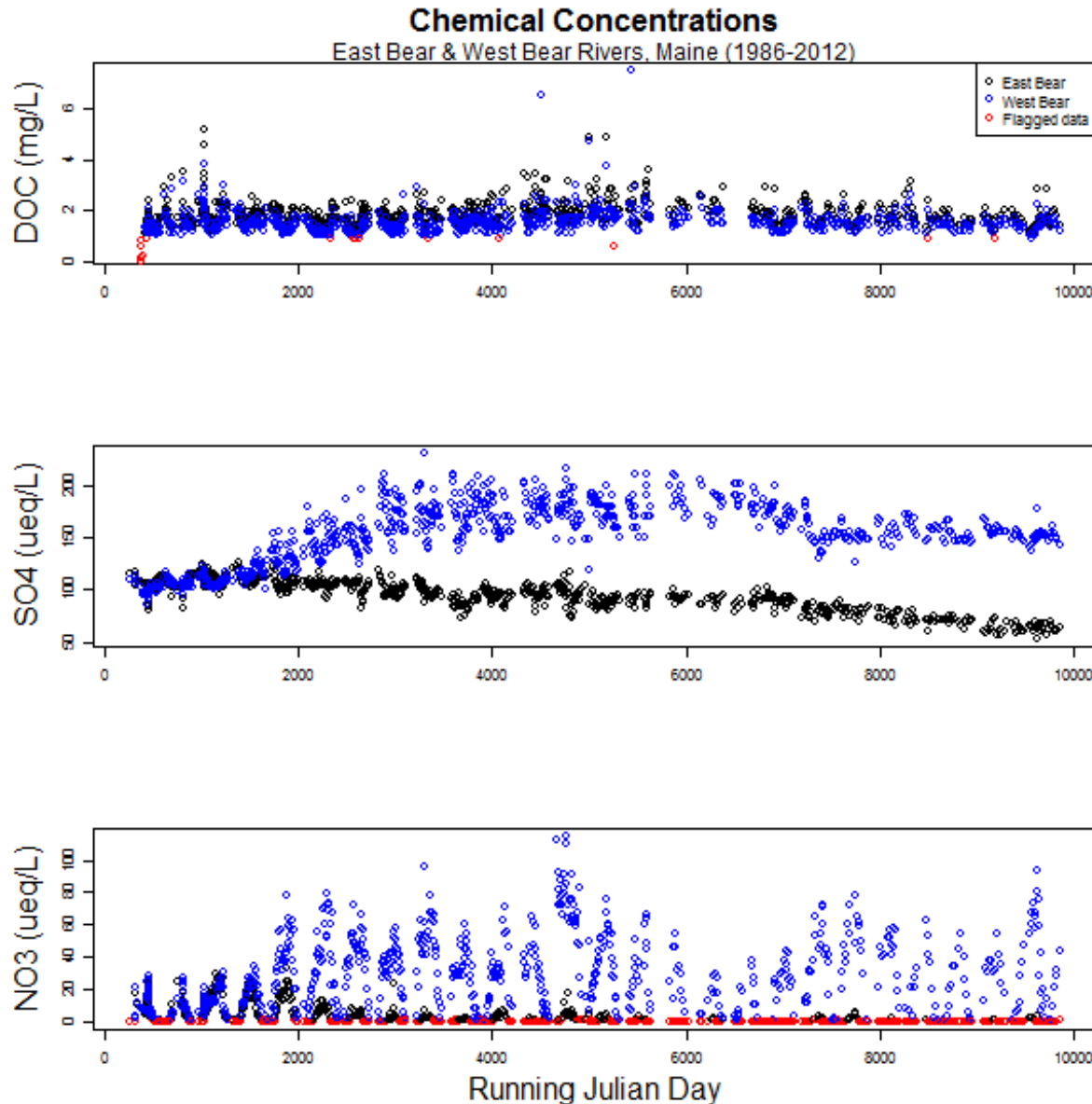
W3 is treated: 25+ years; 40.6 kg S ha<sup>-1</sup> year<sup>-1</sup> 35.4 kg N ha<sup>-1</sup> year<sup>-1</sup>



Collected stream (~ bi-weekly), soil extracts, and soil solution samples

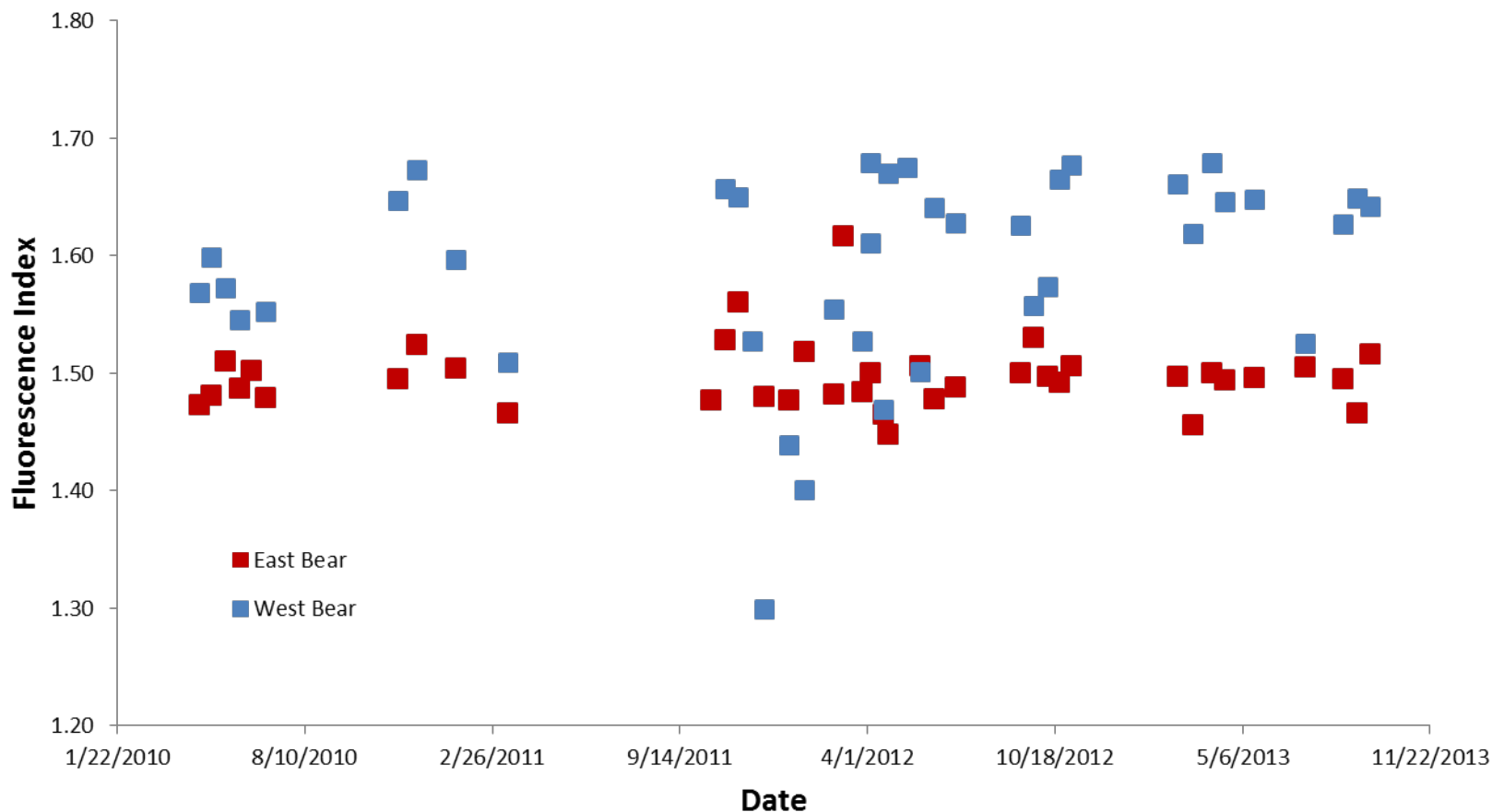


# Results/Project Outcomes



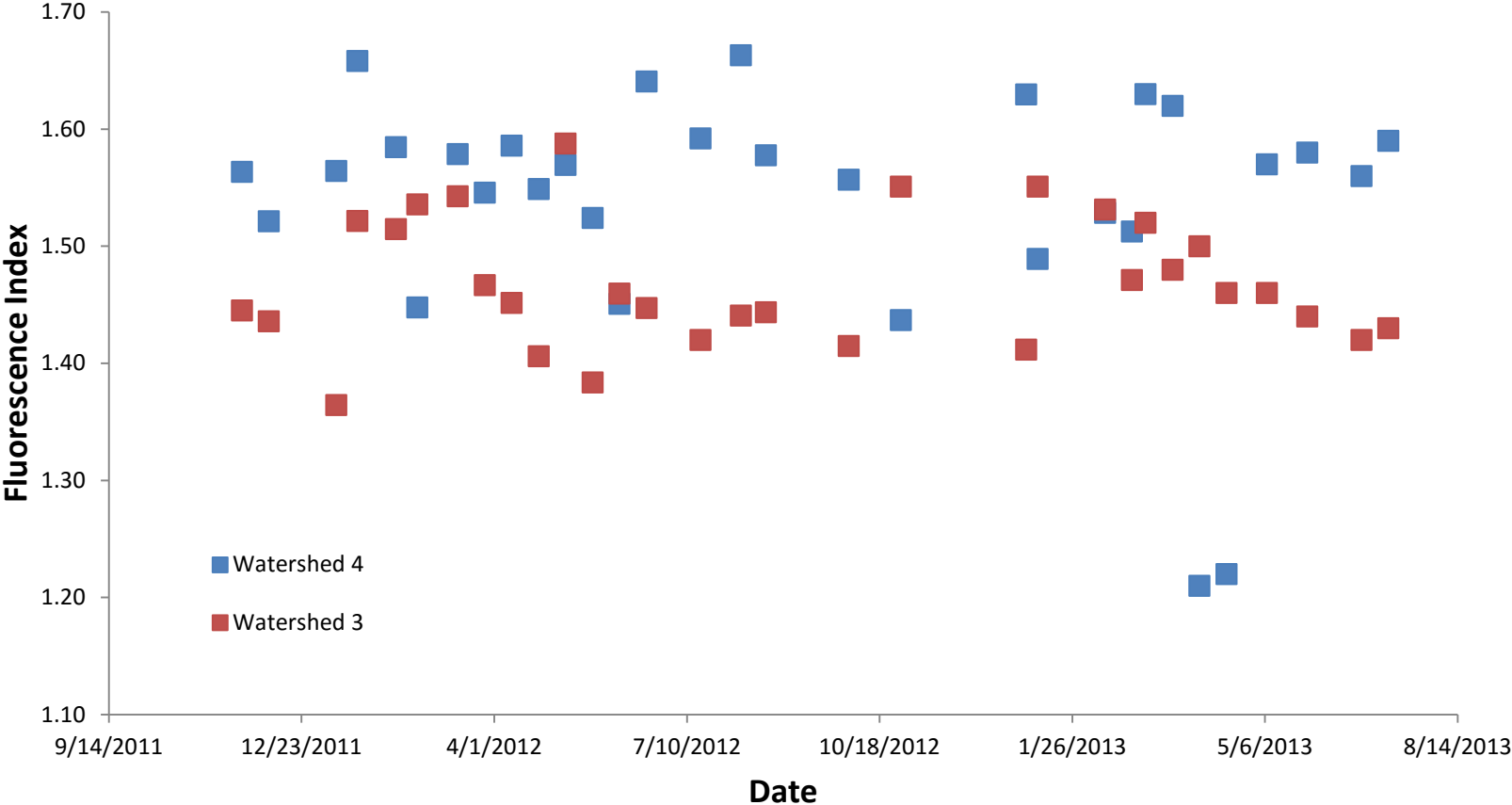
Concentrations of DOC,  $\text{SO}_4$ , and  $\text{NO}_3$  at East and West Bear from 1986-2012. Preliminarily, analysis of these records finds no significant difference in DOC concentrations over time. We hypothesized that while concentrations of DOC in these first order streams may not have changed, the quality of DOM as measured by fluorescence spectroscopy would demonstrate a shift in quality and source.

Fluorescence Index values from East Bear and West Bear streams. FI values, for East Bear (the reference watershed), are significantly lower ( $p < .005$ ) than those collected in West Bear. These data demonstrate the effect of acidification and recovery on DOM quality and source in these experimental watersheds. Lower FI values indicate more aromatic DOM derived from terrestrial material while higher values indicate a greater proportion of DOM derived from in-stream microbial sources.

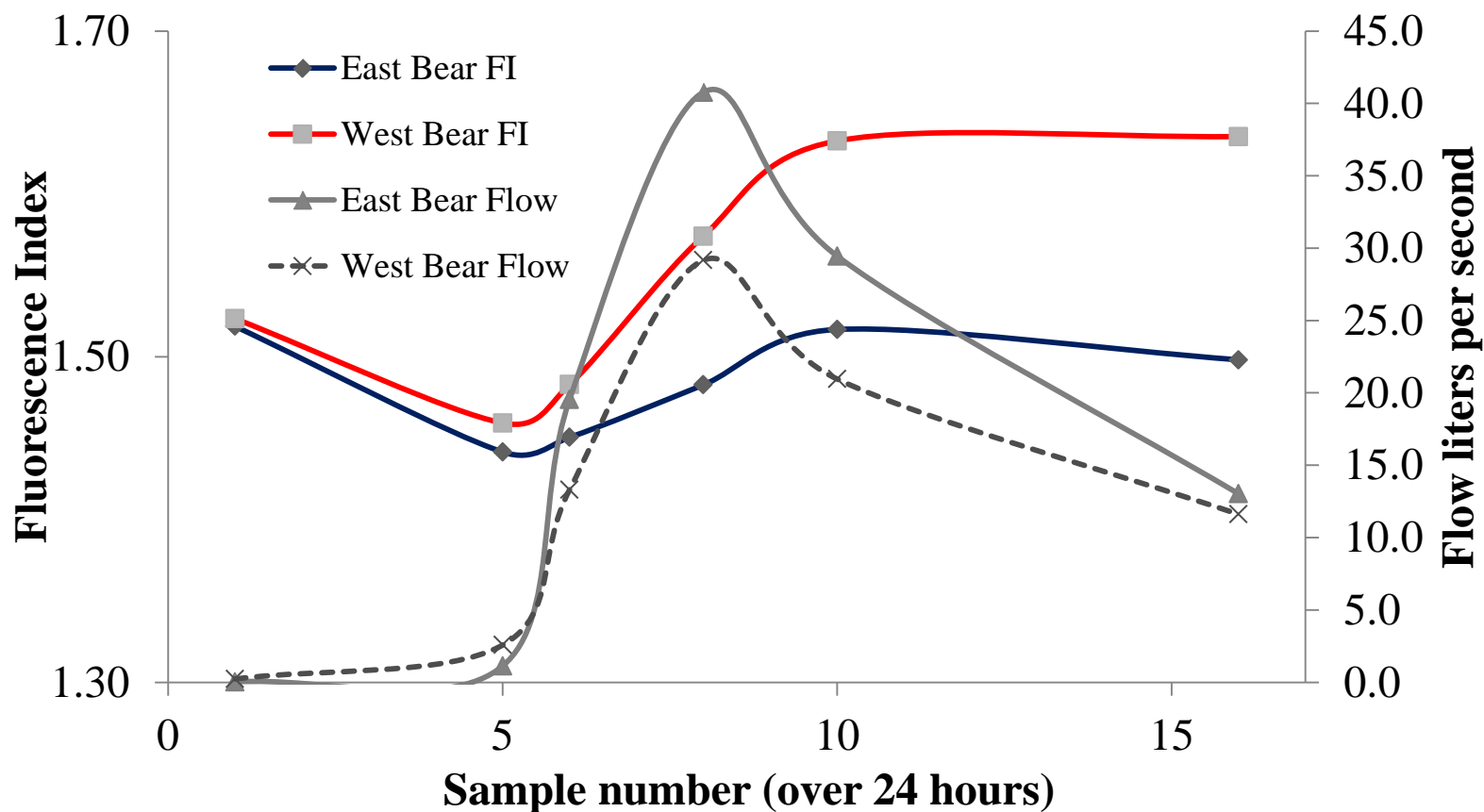




Fluorescence Index values from Watershed 4 and Watershed 3 streams. FI values, for Watershed 3 (the reference watershed), are significantly lower ( $p < .005$ ) than those collected in Watershed 4. These data demonstrate the effect of acidification and recovery on DOM quality and source in these experimental watersheds. Lower FI values indicate more aromatic DOM derived from terrestrial material while higher values indicate a greater proportion of DOM derived from in-stream microbial sources.



Example of event based sampling from the Bear Brook Watershed in Maine. Note the identical fluorescence index values at extremely low flow when stream waters reflect deep groundwater. As the event progresses, flow increases, and stream water inputs pass through upper soil horizons. DOM from upper soil horizons then reflects the effect of acidification and recovery on soils which is captured in the shift in DOM values in the streams with East Bear having more aromatic DOM.





# Implications and Application in the Northern Forest region

This research provides landscape-scale experimental evidence of the effects of environmental policy on carbon cycling in northern forests and surface waters. The changes in DOM source, flux, and quality demonstrate that changes in anthropogenic deposition, or less directly, policies that affect acid and nutrient loading, have the ability to alter DOM cycling in temperate forested ecosystems.



# Future Directions

- Continue to investigate the use of fluorescence spectroscopy as a tool for understanding terrestrial-aquatic linkages under a changing physical and chemical climate.
- Continue to explore event-based dynamics of DOM as they appear to exert unique and transient characteristics at high frequency intervals not readily evident from low frequency monitoring.



# List of Products

- **Presentations**

- SanClements, M.D., Fernandez, I.J., Adams, M.B., Robert, J., Rue, G., McKnight, D.M. Using Fluorescence Spectroscopy to Link Changes in Soil Chemistry and Stream Dissolved Organic Matter. Soil Science Society of America Annual Meeting. Minneapolis, MN. November 14-18, 2015..
- SanClements, M.D., Oelsner, G.P., McKnight, D.M., Fernandez, I.J., Nelson, S.J., Adams, M.B., Mineau, M., Simon, K.S. The effects of acidification and recovery on DOM quality and source in temperate forested watersheds. North American Forest Soils Conference. Whitefish, MT June 2013.
- SanClements, M.D., Oelsner, G.P., McKnight, D.M., Fernandez, I.J., Nelson, S.J., Adams, M.B., Mineau, M., Simon, K.S. The effects of acidification and recovery on DOM quality and source in temperate forested watersheds. BIOGEOMON 7<sup>th</sup> International Symposium on Ecosystem Behavior. Camden, ME, August 2012.
- **Manuscripts in preparation** (*titles and author order subject to change*)
- SanClements, M.D., Fernandez, I.J., Adams, M.B., McKnight, D.M. Whole watershed experimental confirmation of sulfate as a driver of additional DOM source in first order streams. *In preparation for Environmental Science and Technology.*
- It is expected a second manuscript focusing on DOM seasonality at Bear Brook will follow.