The effects of acidification & recovery on DOM in temperate forested watersheds

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The Big Picture

What
Dissolved Organic Carbon (DOC)

When
Last several decades

Where
Waters of northeastern US & Europe
Why might changes in DOC (a proxy for DOM) be important from an ecological perspective?
DOM-Composition & Function

• Ubiquitous in natural waters

• Composed of degraded material, by-products, and residues from plant, animal, microbial, and fungal origins

• Important ecological functions
  – Modifies pH
  – Attenuates UV-light
  – Binds nutrients & pollutants
  – Food source
Possible Drivers of Increased DOM

- Rising atmospheric CO$_2$ concentrations
- Climate warming
- Changing hydrology
- N deposition
- Decreased sulfate deposition
Acid Deposition & SOM

• Can change acidity of soils or ionic strength of soil solutions

• Decreased soil acidity leads to more soluble soil organic matter

DOM → Lakes
Can we use long-term monitoring data & archived samples to confirm sulfate as driver of DOC trends?
The primary objective of the LTM is to detect long-term trends in acid/base status of lakes and streams.
Sites & Samples

- Archived samples from 9 lakes in Maine LTM

- Monitoring Data ~1983-2009

- Archived Samples 1993-2009
Methods - Fluorescence & UV-Vis Spectroscopy

- UV-Vis
- Excitation-Emission Matrices (EEMs)
- Numerous corrections
- “Map” of DOM

Fluoromax 3
Methods - Fluorescence Spectroscopy

EEM

- Fluorescence Index (FI)
  - FI is ratio of emission intensity
  - FI is a primarily a measure of DOM source: (terrestrial/microbial)
    - Terrestrial low (~1.3)
    - Microbial high (~1.8)
  - Correlated w/ aromaticity
Can we use long-term monitoring data & archived samples to confirm sulfate as driver of DOC trends?
Regional Trends: Deposition & Lake Chemistry

Wet Deposition

Lake Sulfate

SO$_4^{2-}$ meq L$^{-1}$

<table>
<thead>
<tr>
<th>Date</th>
<th>SO$_4^{2-}$ meq L$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>1/1/1990</td>
<td>40</td>
</tr>
<tr>
<td>1/1/2000</td>
<td>60</td>
</tr>
<tr>
<td>1/1/2010</td>
<td>80</td>
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</tbody>
</table>

SO$_4^{2-}$ meq L$^{-1}$
Is sulfate correlated with lake DOC?

DOC mg C L$^{-1}$

P=0.003
But...where is the DOM from?

- If decreased sulfate deposition is driving > soil DOM fluxes to lakes, we should see a decrease in lake water FI over time

- Because lower FI means stronger terrestrial signature

Did we?
Yes -- sulfate is also correlated with FI

Sulfate

FI

More terrestrial

P = <0.0001

Mud

$\text{SO}_4^{2-}$

20 40 60 80 100

1.3 1.4 1.5 1.6 1.7 1.8

FI
Conclusion

As sulfate decreased, DOM increased and became more terrestrial in source
Is it possible to test this mechanism in the present at the watershed scale?
Answer: Yes.

- Using long-term (22+ year) whole-watershed acidification experiments
  - Bear Brook watershed in Maine (BBWM)
  - Fernow Experimental Forest, West Virginia
Bear Brook Watershed in Maine

22+ Years:
28.8 kg S ha\(^{-1}\) year\(^{-1}\)
25.2 kg N ha\(^{-1}\) year\(^{-1}\)
West Virginia

W4 is a reference watershed
W3 is treated: 22+ years; 40.6 kg S ha\(^{-1}\) year\(^{-1}\); 35.4 kg N ha\(^{-1}\) year\(^{-1}\)
Bear Brook DOC Trends 1988 - 2008

DOC mg L⁻¹

Running Day of Project

Treated
Reference

Treatment Begins
Comparison of BBWM EEMs

Increased fluorescence in amino acid region

Reflects N fertilization and increased amino acids in treated watershed (i.e. changing DOM quality)
Reference watershed has a lower FI (i.e. more terrestrial) with the exception of January 2012---corroborates archive data
Precipitation Events

October 2010—Total time elapsed 31 hours

EB

FI

Flow

0 2 4 6 8

0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6

WB

FI

Flow

0 2 4 6 8

0 0.2 0.4 0.6 0.8 1 1.2 1.4
Fernow response is less clear at this point, but differences in DOM are evident.
Comparing decadal responses of whole-watershed manipulations at the Bear Brook and Fernow experiments

Ivan J. Fernandez · Mary Beth Adams · Michael D. SanClements · Stephen A. Norton
Preliminary Conclusions

Initial data suggests 22+ years of ammonium sulfate additions have altered DOM source & quality in these experimental watersheds
Overall summary

- Recovery from acidification has led to increased DOM from terrestrial sources
- Long-term experimental acidification seems to confirm the acidity-soil mechanism
Future Directions

• Continued bi-weekly stream samples from BBWM and Fernow

• DOM slug additions

• Soil solutions, soil extracts, precipitation, & throughfall

• 22+ years of hydrology and chemistry
Thank you! Questions?

Special thanks to Robert Lee for his help!