How does nitrogen deposition affect in-stream dissolved organic nitrogen processing and its role in regulating watershed nitrogen export?

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• DON uptake in forested headwater streams can be comparable to nitrate uptake

• DIN availability can decouple DOC and DON uptake

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Project Summary

- Human alterations to the global nitrogen (N) cycle have resulted in elevated N deposition that alters ecosystem N dynamics and can result in watershed N saturation. Research on the effects of elevated N deposition has focused on dissolved inorganic N (DIN) despite the fact that dissolved organic N (DON) is frequently the dominant form of N exported from watersheds. We investigated the effect of nitrogen (N) deposition on dissolved organic nitrogen (DON) uptake and the coupling of dissolved organic carbon (DOC) and DON in forested headwater streams in the northeastern US.
- We conducted reach-scale DOC and DON uptake measurements in 6 streams across a gradient of ambient and experimentally elevated N deposition, biofilm microbial enzyme activity measurements, DOC and DON bioavailability assays, and reach-scale DOC and DON uptake measurements with experimental manipulation of nitrate concentration.
- In fall 2012, we found that DON uptake decreased as inorganic nitrogen availability increased across sites but DOC uptake was unrelated to N availability resulting in the decoupling of DOC and DON uptake. However, this pattern did not occur at the same sites during the following summer or fall. We think that N demand was high in fall 2012 due to biofilms accruing following "super storm Sandy" which resulted in the high demand for DON where inorganic N was low. N-acquiring enzyme activity was significantly higher in the stream with the highest ambient DOC. When we experimentally increased nitrate concentration in a stream while simultaneously measuring DOC and DON uptake, we found that DON uptake increased and DOC uptake was not affected.
- We found that DON uptake can be as high or higher than nitrate uptake in these streams and that DOC and DON uptake can be decoupled by N demand and DIN availability. This suggests that headwater streams may play an active role in regulating watershed DON export in the northern forest.

Background and Justification

- Human alterations to the global nitrogen (N) cycle have resulted in elevated N deposition that alters ecosystem N dynamics and can result in watershed N saturation.
- Research on the effects of elevated N deposition has focused on dissolved inorganic N (DIN) despite the fact that dissolved organic N (DON) is frequently the dominant form of N exported from watersheds.
- A better understanding of factors that control stream DON concentrations and watershed export across the region, especially in-stream uptake, is needed.

Methods

• Reach-scale DOC and DON uptake measurements in 6 streams across gradient of ambient and experimentally elevated N deposition.



Methods

• Biofilm microbial enzyme activity measurements







Methods

• DOC and DON bioavailability assays





• DON-DOC uptake:

Results from fall 2012 sampling support the hypothesis that the processing of DOC and DON would decouple as watershed N deposition and ambient stream DIN increases. DON demand (as uptake velocity, V_f) was reduced as DIN availability increased (Figure 1), however we found no relationship between DOC demand and DIN availability. In streams, which are not in wetland dominated catchments, there was an increase in DOC V_f : DON V_f with watershed N deposition. This indicates that as watershed N deposition and DIN availability increase, DOC and DON processing become decoupled and the relative demand for DOC and DON shifts to emphasize C acquisition. This shift was driven by the reduced DON demand rather than increased DOC demand.



Figure 1. Dissolved organic nitrogen uptake velocity (V_f) in relation to ambient dissolved inorganic nitrogen concentration. In fall 2012, DON uptake was measured in 6 headwater streams in forested watersheds along an ambient and experimentally elevated N deposition gradient in the northeastern US.

• DON-DOC uptake (continued):

Unlike fall 2012, we found no relationship between ambient DIN and DON uptake velocity in summer 2013 or fall 2013. The most interesting result relating to DOC uptake was that we observed evidence of priming induced by the added acetate and urea during the uptake measurements. As such, plateau DOC concentrations at the downstream end of the study reach were below background levels in half of the streams during summer 2013.

During fall 2014, we experimentally increased nitrate concentration in a stream while simultaneously measuring DOC and DON uptake; we found that DON uptake increased and DOC uptake was not affected.

We think that N demand was high in fall 2012 due to biofilms accruing following "super storm Sandy" which resulted in the high demand for DON where inorganic N was low.

<u>Enzyme activity:</u> We found no significant difference between samples collected before and during urea+acetate additions so all 6 samples collected in each stream were treated as replicates. Using 2-way ANOVA (factors Season and Stream), we found that β-glucosidase (C acquiring) was lower during the summer compared to the fall (*P* 0.04). In addition, N-acetyl-glucosaminidase (NAG-N acquiring) was significantly higher in HBEF-W9 stream than in the other streams (*P* 0.03). HBEF-W9 has higher DOC than the other streams and increased organic N acquisition, as indicated by higher NAG activity, and may be due to higher C availability. We found no significant trends between C acquiring enzyme activity and DOC uptake or N acquiring enzyme activity and DON uptake.

Implications and applications in the Northern Forest region

- We found that DON uptake is important and can be comparable to inorganic nitrogen uptake in these headwater streams and that inorganic nitrogen availability can drive de-coupling of DOC and DON uptake.
- Headwater streams may play an important role in regulating watershed DON export from forested headwater streams.

Future directions

- Conduct follow-up experiment using isotopically double-labeled (¹⁵N-¹³C) amino acids to assess the effect of inorganic nitrogen availability on DOC-DON coupling in more detail.
- Design study to quantify the magnitude and factors controlling the occurrence of priming effects on DOC uptake in streams.

List of products

Peer reviewed publications:

In review:

Mineau, M. M., W. M. Wollheim, I. D. Buffam, S. E. G. Findlay, R. O. Hall Jr., E. R. Hotshkiss, L. E. Koenig^{*}, W.H. McDowell, and T. B. Parr^{*}. *In Review*. Dissolved organic carbon uptake in streams: A review and assessment of reach scale measurements. Submitted to Journal of Geophysical Research – Biogeosciences on 9/1/2015

In Prep:

Dissolved organic carbon and nitrogen uptake in streams across a nitrogen deposition gradient: Inorganic nitrogen availability can drive de-coupling of DOC and DON. Planned submission early 2016.

Conference presentations:

Mineau, M.M., I.J. Fernandez, W.M. Wollheim, and J.L. Campbell. Elevated nitrogen deposition is associated with decoupling of DOC and DON processing in northeastern USA headwater streams. NERC conference, March 19 – 20 2013, Saratoga Springs, NY. Poster presentation

Mineau, M.M., I.J. Fernandez, W.M. Wollheim, and J.L. Campbell. Elevated nitrogen deposition is associated with decoupling of DOC and DON processing in northeastern USA headwater streams. SFS annual meeting, May 19 - 23 2013, Jacksonville, FL. Oral presentation.

Mineau, M.M., I.J. Fernandez, W.M. Wollheim, and J.L. Campbell. Elevated nitrogen deposition is associated with decoupling of DOC and DON processing in northeastern USA headwater streams. Hubbard Brook Experimental Forest Cooperator annual meeting, July 2013, Oral presentation.

Mineau, M.M. Dissolved organic N & C processing in headwater streams: Priming and patterns across seasons. Hubbard Brook Experimental Forest Cooperator annual meeting, July 2014, Oral presentation.

List of products

• Invited seminars:

Mineau, M.M. Nutrient cycling in headwater streams: The effect of nitrogen deposition on dissolved organic matter retention. Keene State College, February 7th, 2013. Invited presentation.

Mineau, M.M. Effects of human disturbances on nitrogen and carbon cycling in river networks. Brad College December 19th, 2013. Invited presentation

• Outcomes:

Two research assistants have been involved in field and laboratory work for this project. Both research assistants are from underrepresented groups in STEM. One is a student transitioning from community college to UNH and the other a woman. Both gained valuable training, skills, and experience as part of their work on this project.