Do ratios of dissolved organic carbon and nitrogen in aquatic ecosystems remain stable over time or are they impacted by atmospheric acid deposition?

Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition

Citation Rodriguez-Cardona, B. M. Wymore, A. S., Argerich, A., Barnes, R. T., Bernal, S., Brookshire, E. N. J., Coble, A. A., Dodds, W. K., Fazekas, H. M., Helton, A. M., Johnes, P. J., Johnson, S. L., Jones, J. B., Kaushal, S. S., Kortelainen, P., Lopez-Lloreda, C., Spencer, R. G. M., & McDowell, W. H. (2022). Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition. *Global Change Biology*, 28: 98-114.
https://doi.org/10.1111/gcb.15965

What are long-term trends in dissolved organic carbon and nitrogen and do their ratios remain stable?

For aquatic ecosystems, dissolved organic matter (DOM) is an important nutrient and energy source. Past work has assumed that changes in dissolved organic nitrogen and carbon (DON and DOC) are correlated. The authors performed a global study to determine long-term trends in DOC and DON in streams and rivers in the northern hemisphere across six biomes. They hypothesized that changes in DON would be positively correlated with DOC and that DOM stoichiometry (DOC:DON ratio) would remain stable.

How did DOC and DON change over time and did they trend consistently with each other?

- Trends of DOC and DON were not consistent across sites and at most streams DOC and DOC:DON did not vary statistically over time. While a majority of sites had significant DOC trends over time, the direction of change was not consistent.
- DON trends were not consistent with DOC trends. At 93% of sites, the two trends did not covary even when they changed in the same direction.

Were long-term trends in DOC or DOC:DON affected by a history of acid deposition?

- Acid deposition history did not affect long-term DOC trends or DOC:DON trends between sites. However, DON trends were greater in deposition sites than in non-deposition sites.

Which models best explained variability in DOC, DON, and DOC:DON?

- The largest portion of variability in DOC trends was explained by the stream chemistry model (66%), and then in similar amount by acid deposition (34%) and watershed characteristics (32%).
- Local characteristics are important for the long-term DOC patterns, where present. There was no long-term pattern in DOC at the majority of the sites.
- For DON, variability was explained by stream chemistry (27%) and acid deposition (34%). No watershed characteristics variables were selected.
- Variability in DOC:DON was not as well explained by the models. Stream chemistry (10%), watershed characteristics (18%), and acid deposition (1%) explained less than a third of the variability.

Which variables were important for model fit?

- Important stream chemistry variables in the models were Ca^{2+}, DOC, DON, ambient NO_3^-, inorganic N, and peak NO_3^- or SO_4^- deposition.
- Important variables describing watershed characteristics are mean annual temperature, watershed elevation, geology or bedrock type, and soil type.

What factors influenced DOM stoichiometry over time and which types of ecosystems may be most impacted?

- The desynchronicity of DOC and DON over time may be caused by the variety of sources of DOM among sites. Where DOM stoichiometry changed, the amount of C increased and the amount of N decreased. Therefore, ecosystem scale energy and nutrient balances may be changing over time.
- At most sites with changing DOM stoichiometry, the change was driven by increasing DOC or decreasing DON. A temporal trend in DOM stoichiometry was driven by a relative increase in DON at only one site.
- Ecosystems with low DOM, such as tall grass prairies and tropical rainforests, may be most impacted by changing DOM composition because small changes in C or N could cause large proportional changes.

What impact will changing DOM stoichiometry have on other ecosystem processes? How did acid deposition history impact current nutrient balances?

- Changes in DOC:DON will likely impact other biogeochemical cycles that influence nutrient export and trophic assemblages in the local stream as well as downstream aquatic areas.
- In sites recovering from acidified atmospheric deposition, DOC and DON increased and DOM stoichiometry was relatively stable. The ecosystems had greater nutrient input while the proportionate relationships changed little.

How important is understanding the ways that climate change may impact DOM stoichiometry on a global scale and how could that understanding be achieved?

- Understanding changes in DOM related to climate change on a global scale is imperative for future ecosystem models and watershed management approaches.
- Continued monitoring of DOM concentration and stoichiometry over long time scales relative to climate and landscape variables is necessary to understand how nutrient cycling and availability of DOM may change globally in freshwater systems.

Research Approach/Methods

- The authors collected DOC and DON data from 72 individual waterways at 7 different sites. Sample locations spanned 42 degrees of latitude in the northern hemisphere and time series ranged from 8 to 45 years.
- They evaluated long-term trends in DON, DOC, and DON:DOC with a nonparametric regression that outputs a median change over time. They then used mutual information, a nonparametric method to evaluate the inter-dependence of two time series, to determine if DON and DOC covary over time.

- To determine whether acid deposition impacted DOM, the authors used deposition data to classify sites and compared DOM trends between sites with and without atmospheric deposition.
- They used a Kruskal-Wallis rank sum test to evaluate differences between groups for DOC, DON, and DOC:DON and a 1-sample t-test to determine if means differed from 0.
- The researchers used an elastic-net analysis, a penalized regression, to identify the most influential predictor variables for DOC, DON, and DOC:DON. They focused on variables in three categories: watershed characteristics, acid deposition history, and stream chemistry.

Keywords atmospheric acid deposition, C:N stoichiometry, dissolved organic carbon, dissolved organic matter, dissolved organic nitrogen, long-term trends, streams

Images

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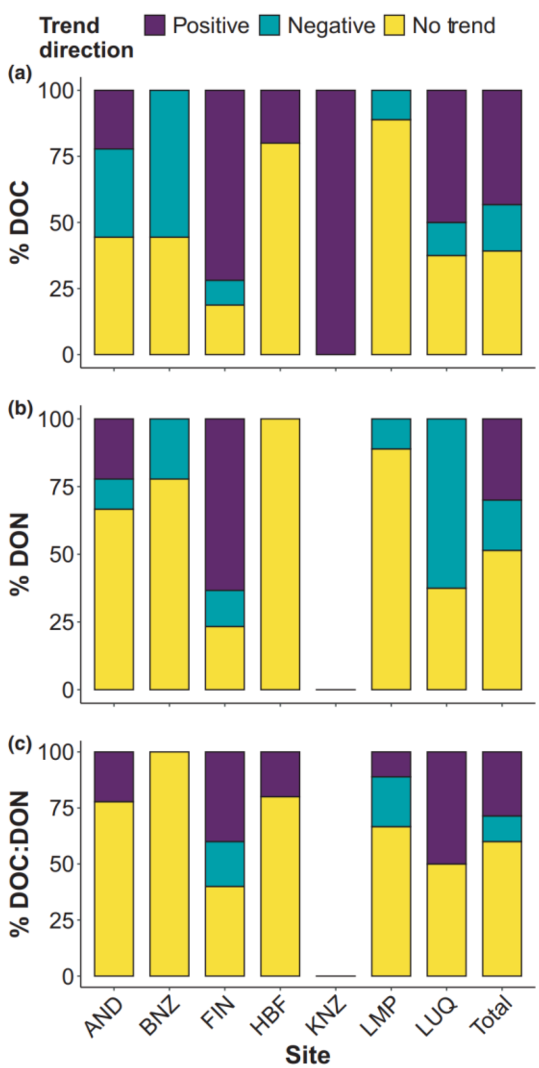

Figure 4 from Rodriguez-Cardona et al. 2022. Percent of (a) DOC, (b) DON, and (c) DOC:DON ratios trends with positive (purple), negative (blue), or no trend (yellow) per site based on Sen slope p < .05. Note KNZ and 2 Finnish streams (YLIJOKI 1 and Vuoksi Vastuupuomi 061) were excluded from (b) and (c) due to no DON data available.

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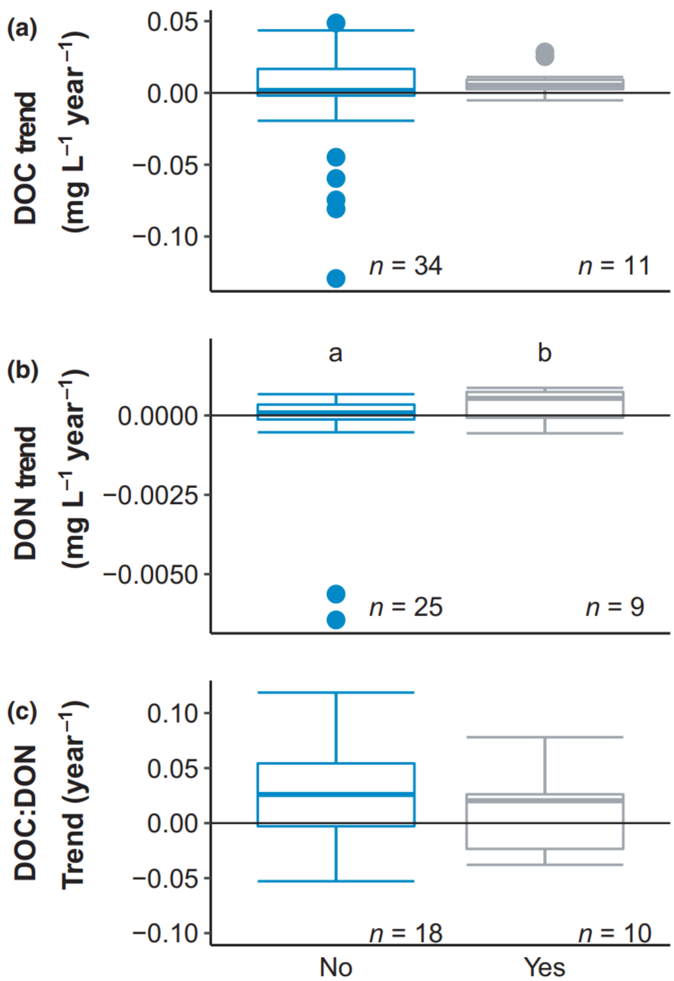

Figure 6 from Rodriguez-Cardona et al. 2022. Significant Sen slopes (p < .05) in (a) DOC, (b) DON, and (c) DOC:DON ratios grouped by history of acid deposition where sites affected by acid deposition are in grey (FIN, HBF, LMP, KNZ) and sites not affected by acid deposition (CPC, AND, LUQ) are in blue. There is an outlier point in the DOC:DON trends for sites not affected by acid deposition that was excluded from the figure and statistics, the value is 0.96 year−1 from HBF. Letters denote statistically significant differences determined by Kruskall– Wallis rank-sum test (DOC p = .38; DON p = .05, and DOC:DON p = .56). p-values for one-sample t-test, to determine if means are different from 0 for DOC in acid deposition affected sites p = .008 and no acid deposition p = .35; DON in acid deposition affected sites p = .05 and no acid deposition p = .41; DOC:DON in acid deposition affected sites p = .29 and no acid deposition p = .008.

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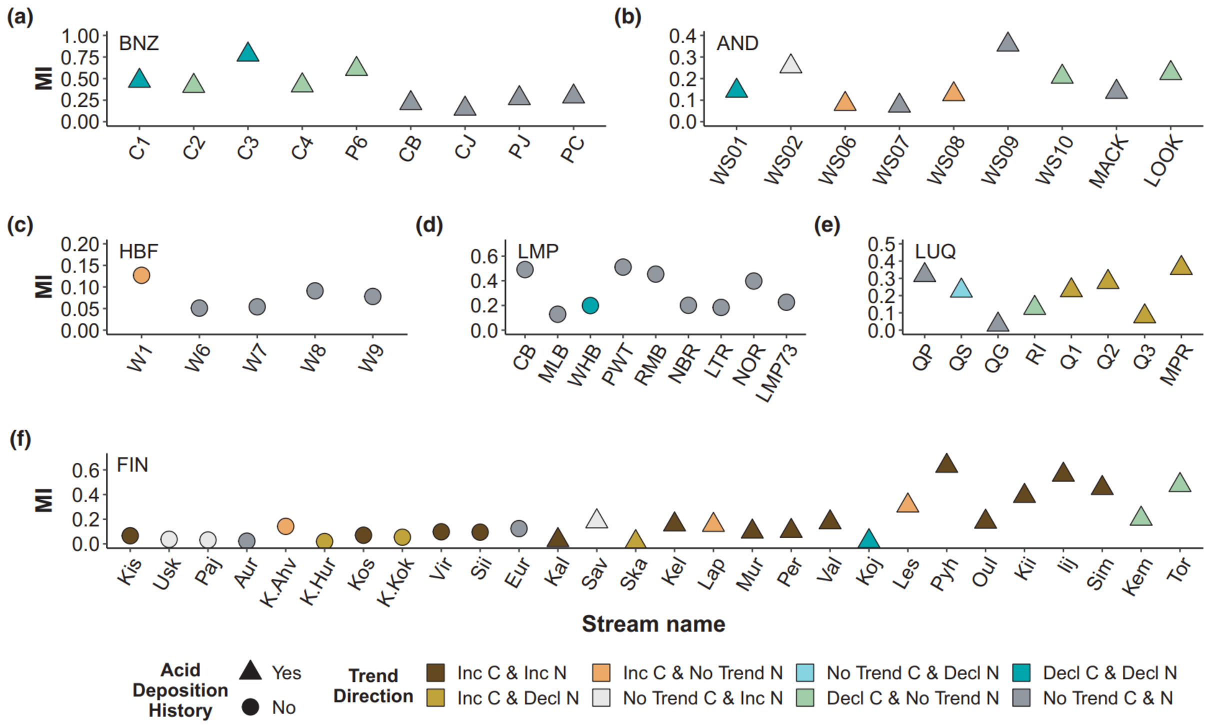

Figure 5 from Rodriguez-Cardona et al. 2022. Mutual information values (MI) for DOC and DON. Shapes describe the acid deposition history by site, circles represent sites with a history of acid deposition and triangles are for sites that have not been affected by acid deposition. Colors represent the directional trend of DOC and DON based on their Sen slope where no trend are streams with a Sen slope with p > .05. Note Konza and 4 Finnish streams (YLIJOKI 1, Vuoksi Vastuupuomi 061, KOTIOJA 1, and Kivipuro 39) were excluded due to limited DON data available for these streams.

*Note: The shape description in the figure legend matches the designation of affected or not affected by acid deposition in the text of the paper. The key at the bottom of the figure shows the opposite.