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Interactive comment on "Sources and cycling of nitrogen in a New England river discerned from nitrate isotope ratios" *by* Veronica R. Rollinson et al.

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Interactive comment on "Sources and cycling of nitrogen in a New England river discerned from nitrate isotope ratios" by Veronica R. Rollinson et al. Anonymous Referee #1

Received and published: 13 November 2020 Review of "Sources and Cycling of nitrogen in a New England river discerned from nitrate isotope ratios" by Rollinson et al.

Summary Rollinson and colleagues present a comprehensive examination of nitrogen

(N) loading dynamics in a New England watershed. The analysis includes measurements of DIN including nitrate (NO3-), nitrite (NO2-) and ammonium (NH4+) as we all as dissolved organic (DON) and particulate (PN) forms. In contrast to previous studies of N loading in this watershed, the authors also leverage the use of nitrate N and O isotopes for constraining confounding influences of source mixing and cycling mechanisms. Together with various temporal and spatial perspectives (seasonal transects of the whole river, weekly site sampling, river discharge measures and point source characterization), they stitch together a comprehensive picture of N sources and controls on loading from the watershed into the estuary. The study indicates very little uncycled atmospheric N loading and identifies underlying drivers of N loading that stem from differing hydrologic regimes (e.g., base flow conditions vs. shallow flow influences). They authors also outline how nitrate N and O isotopes are expected to behave in the framework of 'nutrient spiraling' – and use the differential behaviors of N and O isotopes to constrain cycling and source partitioning.

Major comments Overall, the manuscript is very well-written and covers a lot of ground. The data are of high quality and the analysis and interpretation of the data is sound.

One criticism I have is that the manuscript is probably overly long-winded in some aspects and might benefit from some trimming and tightening to make it more approachable to a broader audience. I did appreciate the application of the data to the broader understanding of sources and cycling phenomena in the watershed and the thoroughness of this discussion (sections 4.2), but thought that the discussion of loading (4.3), for example, could be condensed. We concur with the Reviewer's assessment. We have condensed section 4.3.

My only other critique is that there were times when I was left wondering about the error on some of the endmember estimates and flux terms. My guess is that the small distinctions in average endmember isotopic compositions might be overwhelmed by natural variability in sample population (and/or in the intercept on the modified Keeling plot)? Also, for example, it is not clear how 'close' the flux comparison between the 2018 data in this study may compare the historical 2002 data from Fulweiler and Nixon (Lines 680 to 689). While it seems clear that the drastically disparate hydrologic regimes of the two years underlie the major changes in N fluxes, having a better understanding of the magnitude of the error associated with these watershed scale flux estimates would help readers put the assessment in to a clearer context. We consider that our N flux terms are well constrained, as these derive from highly resolved discharge measurements (from the river flux gauges), and temporally well-resolved concentration estimates (weekly). We imposed some statistical rigor to the flux estimates by using Beale's ratio estimator, which is cited to provide high estimation accuracy and relatively low bias of total nitrogen and nitrate (e.g., Lee et al. 2016; J. Hydrol). Indeed, the bias correction factor was 1 for all computations (i.e., the term in parentheses in Eq. 3a). Nevertheless, to approximate the potential uncertainty in the flux estimates, we conducted an additional bootstrap of the N flux estimates, and posted the resulting standard deviation of respective terms in Table 2. We added text to the methods to describe the bootstrapping exercise. The resulting uncertainty of the flux estimates is relatively modest, particularly for DIN (<10%), less so for DON and corresponding TN ($\leq$17%). In light of this uncertainty, flux estimates remain distinct between 2018 and 2001.

Similarly, the estimates of endmember concentrations (L692) should have some indication of confidence. By some measures, 50 and 65 are not all that different, for example. Finally, the same can be said for the estimates of endmember _15N and _18O values (for example, L457; L490 to L500).

The reviewer raises a valid point. The low-flow [NO3-] end-member was "guesstimated" and devoid of confidence estimates. To remedy this, we derived the low-flow end-member [NO3-] from the best fit of Equation 4 to the observations, stipulating a low base flow asymptote of 2.2 x 108 L d-1 (the lowest observed discharge in 2018) and a concentration increase of 26 μmoles per L, yielding an end-member value of 64 $\pm$ 9 μM.

While we did not obtain the data from the Fulweiler & Nixon study for direct comparison; nevertheless, the low flow [NO3-] reported therein is undeniably lower in 2002 than in 2018.

With regard to the isotopic end-members, we now report the standard error for the intercepts of the modified Keeling Plots, which are relatively small. We considered performing an additional jackknife of the regression analyses, but concluded that the interpretations of the study are not contingent on the absolute values of the intercept, only whether these were higher or lower than observed at low base flow.

To be clear I am not trying to insinuate that the data and findings are suspect in any way – just that more attention could be given to presenting the error intrinsic to such endmember estimation.

Minor comments L99: Sigman et al 2019 reference – missing? Corrected to Sigman and Fripiat, 2019. L101: what is meant by 'inherent' cycling? The word was unnecessary. We removed it for simplification.

L265: 'barring a single outlying value. . .' We changed to "notwithstanding a single outlying value."

L303: were highly anti-correlated (?) We changed to "...were similar in grab vs. composite samples." It might be useful to understand whether the WWTFs are of the combined-sewer overflow type or not, which plays into the residence time of waste in the facilities – and hence N speciation. There is a clear seasonality in the WWTF speciation data that is not really highlighted or addressed. So, while the DIN and TON fluxes from the WWTF are remarkably constant, the NH4+ and NO3- fluxes would not necessarily be constant. It isn't clear whether this really plays into any of the overall findings. It appears that the WWTF samples were not analyzed for nitrate isotopes? This would be a unique dataset and could offer some interesting insights. Given the large shifts in total N speciation in the WWTF – I suspect there would be some substantial variation in the N and O isotopes of WW effluent as well. While these data are not necessarily paramount to the conclusions presented in the paper, knowing more about isotopic variability associated with annual WWTF operations and effluent would be valuable to the riverine N biogeochemistry community in general. Side question – was nitrite measured or reported from WWTF samples? The Westerly-WWTF does not have combined sewer overflow. As pointed out by the reviewer, we neglected to discuss the N speciation and associated dynamics of the W-WWTF effluent, out of concern for the length of the manuscript. And although we originally intended to, we ultimately did not conduct isotope ratio analyses of nitrate in the effluent, deciding these were not central to our study. That said, we intend to further exploit the WWTF data and measure the isotope ratios in our collected effluent samples for an upcoming study of N cycling within the estuary proper.

L377:. . . would admittedly arise from loading by point sources to the degree that a point source has elevated conductivity. Not necessarily. The conductivity of deeper groundwater is generally higher than that of shallow groundwater, because it is in contact with the substrate and bedrock for longer. One could envision groundwater that has a lower nutrient concentration than shallower groundwater, such that nutrients from a point source are less diluted at low base flow. That said, we do not think this is the case, but cannot rule out this possibility entirely.

L456: Refer to Figure 8. The line refers to Figure 2, which was described in the Results, such that it need not be re-iterated in this part of the discussion, where we summarize salient results.

L498: ". . . values of NO3- in rainwater." We added this qualifier to the text.

L500: . . . with higher discharge can thus be partially explained. . . We modified the clause to "...The increase in δ18ONO3 with increasing discharge..."

L507: Kendall is misspelled. Fixed.

L516 to L522. Consider splitting this sentence into two sentences. We split it into two

sentences.

L529-531: Please include reference here. We added a reference.

L542: which limited light penetration. Fixed.

L620: to primarily reflect Added "primarily."

L640: there was little to no accumulated snow in March 2019 Fixed.

L645: I think it would be good to state that no samples were taken from Kenyon Industries much earlier – when it is introduced as a potential point source. We added this information at line 161 in the Methods.

Please also note the supplement to this comment:
https://bg.copernicus.org/preprints/bg-2020-390/bg-2020-390-AC1-supplement.pdf

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