

## ***Interactive comment on “Nitrogen transformations along a shallow subterranean estuary” by Mathilde Couturier et al.***

### **Anonymous Referee #1**

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This manuscript details a nice study of N-species distributions in the subterranean estuary (STE). It adds a rather regionally-unique site to the large body of coastal groundwater nutrient studies available for lower latitudes on the North America east coast. I think there are two weaknesses of this paper that should be addressed before publication:

First, the assignment of endmembers is critical for interpreting non-conservative mixing behavior. The “fresh groundwater” endmember seems poorly matched to the STE study site because the chemical composition is not similar to any of the low salinity regions within the sampled STE. In addition, it's not clear from the few transect contour plots shown, but some of the data suggest that there may be more than two endmembers that contribute to mixing patterns within this STE. Have the authors considered the possibility of shallow and deep fresh groundwater endmembers? They may have

C1

similar salinity, but spatially separated and chemically-distinct signatures. This clearly complicates the interpretation, but it may be more accurate. For example, for NO<sub>x</sub>, Figs 2 and 3 show a fresh, low NO<sub>x</sub> landward EM; a fresh, high NO<sub>x</sub> deep seaward EM; and a shallow, saline low NO<sub>x</sub> seaward EM. This interpretation means that Fig 4 may not show extensive removal of NO<sub>x</sub>, but simply dominant mixing of low NO<sub>x</sub> fresh groundwater and seawater.

Second, the authors argue variously for N species removal and enrichment. They provide a lot of detailed and well-written general discussion about all the possible sources of this non-conservative behavior, but very limited evidence for which processes are probably responsible for trends at their site. This would be a much stronger contribution if the authors could provide more concrete evidence for occurrence of particular geochemical processes.

These and other comments are detailed below.

L7 p7 and elsewhere. Suggest reporting dissolved oxygen in molar units instead of percent to facilitate comparison with other chemical constituents.

L18 p7. I disagree with the “fresh endmember” choice. Is this really representative of water entering the study STE, especially since the NO<sub>x</sub> and DON mixing lines don't seem consistent with the STE samples (Fig 4)? Seems like the best choice would be from within the site boundaries.

The spatial and salinity patterns almost seem to suggest 3-EM mixing, with Were seasonal or spatial/depth differences greater? In L24 p8, note that assessment of removal or addition depends on 2- vs. 3-EM mixing. Hard to evaluate this further without seeing the spatial distribution of NO<sub>x</sub> and NH<sub>4</sub> similar to Salinity in Fig 2.

The distances in Figs 1-3 don't match. I also don't like Fig 3 (even though 2012 was apparently the most complete with respect to N species) because it doesn't appear to capture the most landward “inventory” site. Or maybe it's just because the distances

C2

are all mixed up.

L25 p8. Does NH<sub>4</sub> really decrease under high O<sub>2</sub> conditions? How was this evaluated? It's not at all apparent from the data shown in Fig 4.

L3 p9. How much water was pumped before stabilization of GW quality parameters (L3 p6)? How much volume was pumped for samples? Could co-existing NO<sub>x</sub> and NH<sub>4</sub> be an artefact of sample volumes that overlap redox boundaries?

The discussion in section 4.1 doesn't really say much about the current study site. So how variable do the authors think that this STE is with respect to salinity and redox conditions? Does the STE structure change temporally relative to the snowmelt period? How did the June sampling periods relate to snowmelt during the study years?

L16 p11. If DNRA depends on Corg availability, would it also be expected to be depressed due to high lignin/low labile DOC?

The discussion of biogeochemical N-transformations is rather speculative. In Section 4.2.1, the NO<sub>x</sub> distribution suggests removal (or maybe not, if there are more than two endmembers, see above). If removal, then reduction to N<sub>2</sub> and reduction to NH<sub>4</sub> are suggested as possibilities. This discussion is well-written, but doesn't really lead to a useful conclusion. In the end, it's not clear to me if any of the discussed pathways are any more likely than the others. ("More work is needed" is not a very satisfying summarizing sentence.) In Section 4.2.2, I agree that the NH<sub>4</sub> source is probably organic matter oxidation, especially considering the sediment layer containing 20% OM. It's not clear to me why it is important whether the NH<sub>4</sub> come from decomposition of DON or POM/sedimentOM, or the importance of the pathway by which organic carbon is oxidized (sulfate reduction, Eq 5, or something else). It would however be useful if the authors could say something about where the NH<sub>4</sub> enrichment occurs in this STE and why (e.g., in Fig 3, at the 15m profile).

L8, p13. I don't see these "hot spots", except maybe deep and seaward in Fig 3. I

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would find this discussion much more interesting if the authors showed and discussed their results in more detail, and limited the speculation. None of the discussion in this section is specific to this location or to the results found in this study.

The nutrient inventory approach to flux estimation seems a bit misguided, given the work by e.g., H. Michael and C. Robinson showing the finer structure in transport through the STE (i.e., not just plug flow). For the nutrient inventories, it appears (Fig 1) that the data are from 2013? Or are data from different years somehow combined? If so, what is the spatial region considered for combining different profile locations?

L12, p15. The "filter" interpretation depends on how you account for dilution. Presumably, the inventories would somehow have to be normalized to salinity? Also, here and the discussion on p16, the non-conservative behavior interpretation (and also flux) depends on endmember assignment. I would argue that the STE is not a sink for terrestrial N because any removal relative to the upland well endmember must have occurred prior to reaching the "onshore" profile (or according to Fig 3, the farthest onshore profile). If anything, the inventories in Fig 5 suggest that groundwater is enriched in N at the HTM profile, and the STE is therefore a source of N to the coastal ocean.

L 2, p17. It's not clear how relevant these comparisons are. For example, the comparison with the St Lawrence River would probably be more appropriate if the authors scale their shoreline fluxes to the shoreline length for the entire nearshore region receiving the river input (assuming this is justified).

Should check significant figures in the tables.

Fig. 4. Suggest using different symbol shapes in addition to color to distinguish oxygen level categories.

Fig. 5. "saline saltwater" is rather redundant wording.

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