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Interactive comment on “The nitrogen isotope effect of benthic remineralization-nitrification-denitrification coupling in an estuarine environment” by M. Alkhatib et al.

Anonymous Referee #3

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General Comments:

This article presents a unique study of the $\delta^{15}\text{N}$ of dissolved nitrogen species in the St. Lawrence Estuary and Gulf of St. Lawrence sediment pore waters, which were used to calculate the isotope effects for benthic remineralization-nitrification-denitrification coupling (ϵ_{sed} and ϵ_{app}). The study site was ideal for this analysis because they were able to collect samples from a variety of environmental conditions, including varied organic matter reactivity and bottom water dissolved oxygen. They showed that these conditions have an effect on the expressed isotope effect. This study was also the

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first to include actual measurements of $\delta^{15}\text{N}$ of $\text{DON}+\text{NH}_4^+$ into the calculation of the ϵ_{sed} . They measured an ϵ_{sed} of $4.6 \pm 2.5\%$, which is higher than deep water values but consistent with projections by Lehman et al. 2007. A higher ϵ_{sed} causes the global fixed nitrogen budget to have a greater imbalance, with losses far outweighing inputs.

Overall this paper merits publication in Biogeosciences. The data is of good quality and adds never before measured parameters (^{15}N -RDN) and samples to calculating expressed nitrogen isotope effects in sediments. The study sites and sampling scheme were well suited for measuring expressed isotope effects of benthic remineralization-nitrification-denitrification coupling and their variation between different environmental conditions. For the most part they present a clear and correct analysis of the data. With that said, I do think the paper could be strengthened by revising some sections to have a clearer explanation of benthic nitrogen isotope systematics and the calculations of ϵ_{sed} and ϵ_{app} . Suggestions on improving the clarity of the paper are below within the specific comments.

Also, I would have liked to see a more detailed analysis of how the errors associated with the concentration and isotope measurements would propagate into calculation of the ϵ_{sed} and ϵ_{app} . These errors should be shown within the figures, as well. Secondly, the core incubations feel out of place in the paper and I question whether any significant result comes from only 4 incubations in which the replicates that have different results.

Specific Comments:

Terminology: Throughout the paper the terms for reduced dissolved nitrogen species, including RDN, $\text{DON}+\text{NH}_4^+$, just DON or just NH_4^+ are interchanged repeatedly. In some instances it makes sense why one or the other RDN species is being referred to, but in many others it isn't explained why the statement refers to DON rather than NH_4^+ or both. It would be helpful to always make it clear which species you are talking about and why.

Terminology: The phrase "nitrate elimination" is confusing; I would use denitrification

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and anammox or fixed nitrogen loss.

Introduction: I would've liked a more clear explanation and definition of ϵ_{sed} and ϵ_{app} early in the paper. A diagram and equations for both would be helpful.

11691, line 6: Consider using the term "oxygen deficient zones" when referring to the global geographic area of low oxygen and "oxygen minimum zone" when referring to oxygen concentration minimum in a water column profile.

11694, line 2: Table 1 should be Table 2.

11697, line 21-23: How do you know the ammonium loss is from ammonia oxidation? Also this probably belongs in the discussion.

11698, line 5: Should be Figure 2 and 5 (not 4)

Fig 2: It would help to make the station number and the legend larger and more noticeable. Also could you add dissolved oxygen profiles to this figure? Since the WCS method can give inaccurate ammonium concentrations deeper in the profile, maybe these samples should be marked in a different symbol to indicate that it may be falsely enriched.

Section 3.3, 11699 line 15: Why did you use exponential and linear fits?

Table 2: When you propagate the error from the concentration and isotope measurements, do you still know the ϵ_{sed} and ϵ_{app} to 2 decimal places? Could you put a standard deviation on these calculated values.

11699, line 20: I would be interested to see the $\delta^{15}\text{N-NO}_3$ flux values in a table.

11700, line 10: Where is the efflux of low $\delta^{15}\text{N-DIN}$ coming from?

11700, line 2-13: I'm confused by the analysis of these core incubations. Since there are only 4 and the replicates seemed to disagree, I would be hesitant to make any conclusions from them. Could there be some incubation bottle effects or other issues

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coming into play?

Fig. 4: Could you use the same symbols for nitrate and ammonium as you did on Fig. 1? Also, is it possible to keep the y scale bar the same? This would help the comparison among incubations.

11700, line 22: What “change” are you referring to? Be more specific.

11700, line 24: What do you mean by N isotope exchange?

11701, lines 1-5: It would be helpful to see the equation for ϵ_{sed} written out.

11702, line 9: Isn't DON a component of RDN, what do you mean by RDN/DON pool?

11702, lines 21-24: Could anammox be a source of ^{15}N -enriched RDN?

11703, lines 16-20: Is there a way to discriminate between nitrate diffusion and incomplete nitrification as causes for the suppressed biological isotope effect?

11705, lines 3-4: I'm not sure if these incubations prove that the sediments are a source of ^{15}N -depleted DIN. Only the 16B incubation showed significant ^{15}N depletion.

11706, line 25: Table 1 should be Table 2.

11708, lines 7-10: What would the average ϵ_{sed} be for the ocean? How much do these higher ϵ_{sed} in coastal areas affect the overall budget?

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