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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 #1

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The paper by Alkhatib et al. investigates the N-isotope fractionation effect associated with denitrification and organic matter remineralisation in sediments of the St. Lawrence Estuary. Bottom and pore waters were taken along a transect of coring sites and bracketing gradients of water depth, oxygen saturation in bottom waters, and reactivity of sedimentary organic matter. The authors analysed nutrient concentrations and 15N/14N ratios of nitrate (actually of nitrate +nitrite) and – apparently as a novelty - reduced dissolved nitrogen (comprising ammonia and dissolved organic nitrogen species). They use the data to establish the isotope fractionation effect associated

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with sedimentary N-cycling. The major conclusion/postulate is that benthic remineralisation (denitrification/nitrification, ammonia efflux and DON efflux) causes a significant isotope fractionation effect (epsilon_sed). The authors essentially argue that efflux of DON with high d15N from sediments has so far been neglected in global N-isotope budgets and that may affect estimates of global source and sink isotope and mass balances.

Their data confirm previous work in the Bering Sea that the gross effect of benthic denitrification/nitrification is relatively small overall (permil fractionation factor epsilon_app <3‰, but varies as a function of oxygen penetration depth, which in turn is a function of sedimentation rate (see below), organic matter availability, and organic matter quality. This low apparent fractionation factor is enlarged when considering the reduced products of N cycling in the balance (epsilon_sed). The bulk fractionation factor calculated from this data set represents an important sedimentary environment, because continental margin sediments collect a large share of all organic matter deposited in the ocean, and have a proportionally large role in the global turnover of reactive nitrogen. The authors argue that, based on their and previous data, the expanded data set on isotopic effects associated with sedimentary denitrification (which accounts for something like 70% of all denitrification in the global ocean) implies that the global ocean N-isotope balance between sources (N-fixation) and sinks (denitrification, which is associated with a large fractionation factor in mid-water oxygen minimum zones and – as demonstrated again here – smaller isotope effect when occurring in sediments) is very sensitive to any significant upward revision in estimates of the gross sedimentary fractionation factor epsilon_sed.

Although I grappled hard with the paper, lost it a couple of times and intuitively feel that its main point is overstated, I found it interesting and stimulating. In my assessment the paper thus merits publication in Biogeochemistry: It expands on previous work by some of the same authors in a different environment and enlarges the sparse global data set to an important and quantitatively relevant hemipelagic to estuarine sediment

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province. It also appears to be the first to include dissolved organic nitrogen in the isotope budgets (I have no knowledge of other studies on this) of sediment-water exchange, and this is what makes the paper stimulating and complicated. Below are some general ramblings that the authors may chose to and some detailed points that the authors should consider in their revision.

1) I would have liked to see a schematic diagram of the processes that are referred to in the paper, possibly as a new figure 1. That would have made the different epsilon-terms and sink/source effects on the isotopic net balance more comprehensible to readers.

2) Figures are really difficult to read and please consider using color codes or composite diagrams for each site in an Appendix

3) (rambling) Key here is the inclusion of RDN in the entire budget, or more specifically, the inclusion of DON efflux into and further fate of DON in the water column (ammonia is not significant in the SWI budget for the study area). Now, that DON is a legacy of previously deposited organic matter that has undergone hydrolysis and de-amination and associated fractionation. DON turnover itself and possible fractionation on the way through the sediment cannot be traced with the current data set. The authors chose to evaluate the RDN concentrations and d15N only for the upper 2 cm of sediment, while data from deeper down in the sediment are obviously available but somehow flawed. The RDN flux across the 0-2 cm sediment interval is what remains of DON/NH4 produced below that interval, plus any addition from OM mineralisation in the interval, minus any nitrification, minus any anammox, minus any DON/ammonia taken up by bacteria (rupturing of which apparently biased the sediments below 2 cm), minus any adsorption. The entire concept of epsilon_sed thus is a huge can of worms, and importantly, is not instantaneous in time and most liekely not even in steady state (what about temperature effects?), but integrates activities in that can of worms over unknown periods of time (years to probably decades or centuries). I don't even want to argue about lateral advection, which is frequent in coastal and margin sediments. I find it exceedingly difficult to convince myself that a) the DON fluxing out of the sediment

is the kind that is eventually nitrified and may affect the global nitrate (isotope) budget, and b) that you can derive a fractionation factor epsilon_sed that is globally valid (which is why they are useful) and peg it on organic matter quality and oxygen concentration in bottom water. I am convinced that for any site it is most likely time-variable and more generally, that it is specific to each sedimentary environment o0r even sediment patch. If you don't share that view, I'd like to know why.

4) Main factors for spatial (and sediment specific) differences in fractionation factors discussed are oxygen concentrations in bottom water and organic matter quality ("sediment reactivity" is not appropriate in my understanding). What about sedimentation rates and bioturbation? Suppose you bury the same type of OM at the same bottom-water oxygen concentration in sediments with differing sedimentation rates and/or bioturbation intensity (as in the paper below)? What will the diagenetic profiles look like and how will that affect fluxes? OM degradation is a time-dependent chemical process, and sedimentation rate sets the age of any OM at a given depth. (Authors allude to oxygen exposure time on page 11706, line 5, which implies some sort of time constraint, but do not expand on this). An interesting paper I came across on this is Sloth, N.P. et al., 1995. Nitrogen cycling in sediments with different organic loading. MEPS 116:163-170

5) Paragraph 3.3. (line 22 ff) Although I read this a couple of times, and looked up Lehmann et al. (2007) this paragraph left me puzzled. I initialy had a problem rationalising why there should be a difference for the two isotopes at all, if diffusivities are the same. What is the reason that NO3 is drained from bottom water that is more depleted than the bottom water nitrate? Or do you add nitrate at one point along z that is lighter (from nitrification or so) and what you are saying is that at $z=-1$, $z=0$, $z=+1$ you have different nitrate 15N/14N which – expressed as fluxes along the concentration gradient - add up to an epsilon_app? That means that epsilon_app is essentially a function of path length and whatever value along z you chose as end points in Delta14N-NO3 and and Delta15N-NO3? Which portion (Delta z) of the profiles in Delta14N-NO3 and

Delta15N-NO3 did you fit? Why did you chose a mix of exponential and linear fits? Afterwards I wondered if paragraph 3.3. is not either much too brief (although I at least have a basic grasp I spent much too long trying to understand what it was about), or if one could do with a few sentences (it doesn't really go beyond Lehmann et al., 2007 anyway). And is it necessary to include the core incubations (which again make an appearance only briefly in the Discussion)? At this point in the paper, they are not necessary and no one will argue with the epsilon_app once properly explained. Just to ease my mind, it would be nice to have nitrite concentrations displayed or tabulated.

6) Terminology: You frequently term this "underexpression of the N-isotope fractionation during benthic N-elimination", which admittedly sounds great. But N is not eliminated, and what you mean by N-elimination here is only denitrification (correct?) and (as you discuss later) N-isotope fractionation during denitrification only occurs when there is nitrate left. I suggest that you consider using something like "the net effect" or so.

Frequently you use the expression "at the scale of sediment-water exchange". What do you mean by scale? Or do you mean "during"?

Some detailed points: Page 11703 Line 10: epsilon_app in my view does not "quantify the degree of under-expression", because that would be a term quantifying the difference between epsilon_cell and epsilon_app. But epsilon_app is the sum of several processes. Line 13: Is "albeit" used correctly? Line 16: the "apparent suppression" is really either due to kinetic/concentration effects, or a masking by nitrification. Suppression to me means that the denitrifiers are in some way affected. Line 21: are generally found Line 25 lowest instead of least

Page 11704 Line 9: through Line 12ff: I would argue that OPD, epsilon_app as calculated here, and depth of denitrification are intrinsically linked to sedimentation rate. I would also argue that the CI is linked to oxygen at the sediment-water interface and length of time that chlorins are exposed to oxygen in the diagenetic gradient (=sed

rate). It all boils down to the steepness of the nitrate gradient shaped by denitrification/nitrification and diffusion. . ..

Line 17 at low levels of what?

Line 20 ff: What is "reactive station"? The instantaneous OM reactivity along the gradient is a result of its degradation history, which in my view is a function of oxygen and sedimentation rates or time represented by your samples. (It would probably be interesting to estimate chlorin degradation rates for each downcore profile at each of the sites. . . I predict that they all would follow the same power function, as in Middelburg's paper some 20 years ago).

Page 11705 Line 9 Nitrate remineralisation? Page 11697, line 13: delete comma before "did". Page 11698, line 21 ff: delete, this is speculation and there are many other putative reasons. . . Page 11701 4.1. heading: delete "the". "Solorzano" in reference list

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