

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

M. Alkhatib et al.

moritz.lehmann@unibas.ch

Received and published: 29 February 2012

AC: We thank the referees for their valuable comments, which will be very helpful when preparing an amended version of the submitted manuscript. The three reviewers acknowledge the significance and scientific quality of the discussion paper. The reviewers all agreed that the first-time assessment of the benthic fluxes of reduced dissolved N isotope (DRN = DON+ammonium) and its integration in the calculations of the total sedimentary N isotopic effect of combined benthic N transformations (remineralization-nitrification-denitrification) represent an important step forward in ongoing efforts to

C5909

use N isotope signatures in marine /estuarine environments to gain information about global or regional N fluxes. The reviewers comments underscore that the study area was well-chosen. The St. Lawrence estuarine-marine gradients in dissolved oxygen (DO) and sediment organic matter (OM) reactivity made this environment ideal for studying the controls of these environmental conditions on the N isotopic effects of sedimentary N cycling on the N isotopic composition of the water column fixed N pool. All three reviewers came to the conclusion that the quality of our study merits publication in Biogeosciences. Nevertheless, they asked for clarifications on some specific points and suggested corrections, which may help to further improve the manuscript. Below, we address the reviewers' concerns point-by-point (AC: author comment; RC: reviewer comment).

Referee #1

RC: 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.

AC: We plan to include a scheme depicting the most important processes that control benthic DIN/DON exchange. The figure will be an adaption of Fig. 1 of Lehmann et al. (2004) (Coupling the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate as a constraint on benthic nitrogen cycling, *Marine Chemistry* 88 (2004) 1–20), complemented by DON-relevant components

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

AC: We plan to revise the color code so that distinguishing between single profiles/stations will be easier.

RC: Key here is the inclusion of RDN in the entire budget, or more specifically, the

C5910

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 $\delta^{15}\text{N}$ 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/ NH_4 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 ϵ_{sed} thus is a huge can of worms, and importantly, is not instantaneous in time and most likely 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 ϵ_{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 or even sediment patch. If you don't share that view, I'd like to know why.

AC: We agree that there are multiple processes, which will affect the size and the N isotopic composition of the porewater DON pool, and we acknowledge (here and in the original manuscript) that our data set will not help to address these processes. We do not say that processes below 2 cm will not have an effect on the DON isotope exchange at the SWI. We just mention that the way we extract porewater DON/DIN includes the risk that samples below 2 cm may be compromised. Still, the DON/RDN that fluxes out

C5911

of the sediments is the result of these combined processes and we can measure it. Disregarding the driving forces behind the observed isotopic composition of RDN fluxes, all ϵ_{sed} values were significantly above the previously assumed value of $\sim 0\%$. That it will vary with space is likely, and we in fact discuss possible mechanisms that lead to these spatial changes. As for temporal changes, we can only speculate. However, the study site was chosen to represent a relatively broad spectrum of environmental conditions (O_2 , reactivity, surface productivity), so that the average calculated ϵ_{sed} values are probably representative. Especially in the Gulf, where we report the comparatively high ϵ_{sed} , environmental conditions are very similar to those found in most continental margin sediment. Therefore, we are confident that our results can be extrapolated to a global scale.

Regarding the fate of the DON from the sediments, there are several studies that report on the dynamic nature of DON in the ocean water column and the susceptibility of DON to bacterial enzymatic remineralization. As a result, a dominant fraction of DON that fluxes out of marine sediments is likely to undergo rapid oxidation and to add to the oceanic DIN pool. (e.g. Burdige 2007, *Chem. Rev.* 107, 467-485). DON is a significant source of N that supports both auto- and heterotrophic production in marine environments, and there is evidence that DON concentrations fluctuate significantly on seasonal time scale in near shore waters and on annual time scale in open ocean (Engeland et al., 2010, *Estuarine, Coastal and Shelf Science*, 89, 31-42). In addition, the C/N ratio of DOM flux from the St. Lawrence sediments is very low (4-10, Alkhatib et al., in preparation), which is an accepted indicator of relatively high DOM reactivity.

As for temperature effects and advection: Temperature is not an issue as all stations display almost the same bottom water temperature. The sediment texture is dominated by silty to clay sediments (see review by Gobeil 2006; *Hdb Env Chem Vol. 5, Part H*, 121-147), so that advective processes likely do not play a significant role. This clearly changes when the sediments are bioturbated and bioirrigated, simplifying benthic solute exchange. However, Lehmann et al. (2004) (*Coupling the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$*

C5912

of nitrate as a constraint on benthic nitrogen cycling, *Marine Chemistry* 88 (2004) 1–20) observed that even in bioturbated sediments, diffusion limitation can lead to the observed suppression of nitrate N isotope effect for denitrification. The effect on the RDN isotope flux out of the sediments is uncertain. We will mention this aspect in the revised version of the manuscript. Also, see comment below.

RC: 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 bottomwater 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.

AC: “Sediment reactivity” is often used in organic geochemistry literature, and we think it is clear what it refers to. The sedimentation rate differences will most probably affect the sediment POM reactivity, and along the Laurentian Channel (see Table 1) the sedimentation rates vary significantly, as does sediment POM reactivity. We show that POM reactivity plays a role in ϵ_{sed} values. The possible aspects of bioturbation in this context remain uncertain (see comment above). Bioirrigation and bioturbation can have contrasting effects on ϵ_{sed} . Bioirrigation may allow “deeper” DON with higher $\delta^{15}\text{N}$ to escape the sediments, by-passing the diagenetically active reaction zone right below SWI and as a result would increase the ϵ_{sed} , however, it can deepen the oxic layer inside the sediments and as a result can act to reduce the ϵ_{sed} . Also bioturbation/bioirrigation may act to remedy nitrate diffusion limitation in some environments,

C5913

however, even in heavily bioirrigated sediments low ϵ_{sed} values have been observed (Lehmann et al. 2004; see comment above).

RC: 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 initially 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 NO_3 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 $^{15}\text{N}/^{14}\text{N}$ which – expressed as fluxes along the concentration gradient – add up to an ϵ_{app} ? That means that ϵ_{app} is essentially a function of path length and whatever value along z you chose as end points in $\Delta^{14}\text{N}-\text{NO}_3$ and $\Delta^{15}\text{N}-\text{NO}_3$? Which portion (Δz) of the profiles in $\Delta^{14}\text{N}-\text{NO}_3$ and $\Delta^{15}\text{N}-\text{NO}_3$ 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 ϵ_{app} once properly explained. Just to ease my mind, it would be nice to have nitrite concentrations displayed or tabulated.

AC: The isotope effect of diffusion of the nitrate molecules is insignificant. This is due to the fact that nitrate is mostly hydrated and the actual mass difference between hydrated $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ molecules is small. Nevertheless, reactions in the sediments will create isotope gradients (also in the diffusive layer), from which individual isotopologue fluxes can be calculated. It is important to note that the “draining” does not refer to a unidirectional flux of the isotopologues, but a net flow into the sediments. There will be exchange to some extent and an isotope effect on the water column, if there is a $\delta^{15}\text{N}$ gradient across the SWI. However, the gross flux of “heavy” nitrate out of the sediments

C5914

is greatly reduced under diffusion limiting conditions (i.e., quantitative consumption). We think that the approach we employ is clearly described and a reference to the original paper where this approach has been used for the first time is provided. In brief, from the concentration and the $\delta^{15}\text{N}$ values, we can calculate the concentration profiles for the single isotopologues. The choice of the data points for calculating the gradients is indeed important. But as long as the same analogous data points were used for both ^{14}N and ^{15}N , the results are robust. For nitrate, often there is a clear linear trend in the diffusive layer, and a linear regression is used. For RDN profiles, that were clearly not linear in the vicinity of the SWI an exponential regression was used, and the derivative of the function at $z=0$ was used to calculate concentration gradient. Both approaches are valid, as both yield the concentration gradient at the SWI.

We will remove the text/figures that refer to the core incubations. Nitrite does not build up in the sediments, therefore, we find it unnecessary to add yet another depth profile to the figure or tabulated data. Also, if present in traces, $\delta^{15}\text{N}$ -TDN includes the nitrite component.

We will attempt to clarify section 3.3, removing complexity where possible. We will also include a more detailed explanation of how we calculated the N isotope effects (see also comment to Reviewer 3)

RC: 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”?

AC: Correct, nitrate elimination refers to denitrification and/or anammox.

We will identify “underexpression of the N-isotope fractionation during benthic N-

C5915

elimination” as “underexpression of the N-isotope fractionation during benthic N_2 producing reactions” or as you suggest “the net N-isotope effect”.

“at the scale of sediment-water exchange” refers to the spatial scale at which isotope fractionation can be described: enzyme level – organism level – SWI level (i.e., the scale of sediment-water exchange) – the ocean/estuarine basin. ϵ_{app} refers to the extent to which the organism-scale N isotope effect ϵ_{cell} is expressed when looking at the actual isotopologue fluxes into the water column.

RC: Some detailed points:

Page 11703 Line 10: ϵ_{app} in my view does not “quantify the degree of under-expression”, because that would be a term quantifying the difference between ϵ_{cell} and ϵ_{app} . But ϵ_{app} is the sum of several processes.

AC: We agree with the reviewer, the text will be rephrased accordingly

RC: Line 13: Is “albeit” used correctly?

AC: It will be rephrased.

RC: 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.

AC: We do not refer to any biological suppression of cellular mechanisms or functions. We only refer to the apparent lack of ^{15}N enrichment that would be expected from an actively denitrifying environment.

RC: Line 21: are generally found Line 25 lowest instead of least Page 11704 Line 9: through

AC: Will all be changed.

RC: Line 12ff: I would argue that OPD, ϵ_{app} as calculated here, and depth of

C5916

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

AC: In a separate paper we have demonstrated that there are indeed close links between OPD, oxygen exposure time, and OM reactivity along the LC (Alkhatib et al, accepted in ECSS, pending minor modifications). Combined, these factors determine the depth and, equally important, the thickness of the nitrate reduction zone, and hence the steepness of the nitrate gradient, as well as the likelihood of 15-N enrichment signatures from the subsurface being propagated back into the water column (with direct effect on ϵ_{app}). The causal relationships between ϵ_{app} and these parameters will be discussed in the revised manuscript, but have already been addressed in the original submission.

RC: Line 17 at low levels of what?

AC: "at low level" will be deleted

RC: 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 Middelburg0s paper some 20 years ago).

AC: We meant to refer to the station with the highest sediment OM reactivity . We will clarify this in the revised manuscript. The factors controlling the sediment OM reactivity, and the indices that describe OM reactivity are the focus of another paper (Alkhatib et al., , accepted in ECSS, pending minor modifications).

RC: Page 11705 Line 9 Nitrate remineralisation? Page 11697, line 13: delete comma

C5917

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

AC: Will all be changed/deleted.

Referee #2

RC: As stated by the authors, the cause for the depletion of the RDN/DON pool in the subsurface porewater was unclear. I wondered whether the authors had considered the potential role of dissimilatory nitrate reduction to ammonium (DNRA) as a means of shunting isotopically light NO_3^- into the NH_4^+ pool (McCready et al., 1983. Canadian Journal of Microbiology 29:231-234.). While DNRA may not be considered as a major NO_3^- sink mechanism in such sediments, it would seem that the suboxic conditions near the surface could easily support at least some portion of NO_3^- consumption by DNRA (An and Gardener. 2002. Marine Ecology Progress Series 237:41-50). This process would also not necessarily require any interference with the NO_3^- isotope flux, since both DNRA and denitrification would presumably act to increase the ^{15}N of the NO_3^- with increasing depth. While it might be argued that DNRA is only important in sulfidic sediments, new evidence points to an important role of DNRA in non-sulfidic environments including suboxic water columns (Lam et al. 2009. Proceedings of the National Academy of Sciences USA 106:4752-4757) and sediments underlying oxygen minimum zones (Bohlen et al. 2011. Geochimica et Cosmochimica Acta 75:6094-6111). In some cases, it would also appear that the NH_4^+ profiles are at least not inconsistent with this possibility. I think at least consideration of the potential role of DNRA in this context is warranted.

AC: The point made here by the reviewer has been considered during the preparation of the original manuscript, but given that ammonium fluxes outside the sediments as reported by Thibodeau et al. (2010; Estuar. Coast. Shelf S., 90, 195–205) were not very high or absent at all, we decided not to include it in the discussion. Incubation experiments with ^{15}N labeled nitrate performed on whole cores retrieved from the sediments

C5918

at Sta.18 have shown that DNRA is an active process in the Gulf of the St. Lawrence (Thibodeau et al., 2010). However, the potential of DNRA can be masked by complete nitrification of the DNRA-generated ammonium followed by complete denitrification of residual nitrate from DNRA and from nitrified ammonium. One station is insufficient for extrapolation to the whole St. Lawrence system, and it is very speculative to conclude that DNRA is a significant process in the system. But still, as suggested by the reviewer, we will address possible effects of DNRA with regards to the subsurface RDN $\delta^{15}\text{N}$ depletion.

RC: Regarding the calculated TDN flux, in addition to the fact that only the top 2cm of data are used, the TDN (or RDN) profiles in Figure 4 appear quite a bit noisier than the NO_3^- profiles, for example. I'm wondering whether these two aspects play a role in the error estimate of these fluxes and, more importantly, in the calculations of ϵ_{sed} ?

AC: We have calculated the flux of ^{15}N -RDN and ^{14}N -RDN (not TDN) from the concentration gradients just below the sediment-water interface. The greater noise also of the $\delta^{15}\text{N}$ -RDN profiles will translate in a greater error for ϵ_{sed} than for ϵ_{app} . We will mention this in the revised manuscript. Still, even if the overall noise is a bit greater, the trends/gradients seem to be evident and consistent.

RC: The authors mention the fact that calculated values of ϵ_{sed} appear related to $\delta^{15}\text{N}$ of sediment surface organic matter (Pg 17, Ln 10). This brings up an interesting point, the potential importance of which should be adequately addressed. ϵ_{app} relates exclusively to the NO_3^- in the overlying water column and the changes in its isotopic composition due to its consumption by sedimentary processes, all of which represents a internally contained system (i.e., it doesn't matter what the composition of the NO_3^- in the overlying water is, what matters is only its composition relative to the $\delta^{15}\text{N}$ lost due to denitrification). However, regarding ϵ_{sed} , because this incorporates the isotope flux of NH_4^+ and DON, both of which are derived from sediment organic matter, there should be some consideration of the source of this organic matter. Namely, if there is a gradient of sediment organic matter $\delta^{15}\text{N}$ along the estuarine gradient (due to

C5919

variable terrestrial inputs, for example), then this would represent an external factor that could contribute to the variability of RDN $\delta^{15}\text{N}$ and hence, the calculation of ϵ_{sed} . How does the variation in sediment organic matter contribute here? If, as I suspect, this is an important aspect to the fluxes observed, then the extension of these findings to continental shelves worldwide, for example, may not be valid.

AC: Originally, ϵ_{app} , solely related to the changes in the nitrate isotopic composition due to consumption within the sediments, as described by Reviewer 2. However, this approach neglects the fact that ammonium can be oxidized to nitrate (with an isotope effect), so that the ^{15}N -enrichment due to denitrification can be overprinted. If we consider the sediments as a black box, and we just look at the DIN (isotope) fluxes, it is a philosophical question as to what really affects the difference between the $\delta^{15}\text{N}$ of the inflowing N and the $\delta^{15}\text{N}$ of the outflowing N. Independent of the processes at work, this difference gives us a first insight into the N isotope effect of nitrification-denitrification in the sediments. The concept ϵ_{sed} goes one step further as it includes the fluxes of RDN, assuming that RDN eventually adds to the water column nitrate pool. It is ϵ_{sed} that best describes the overall effect of the combined benthic N transformations that ultimately lead to the loss of N_2 . However, including the organic component (POM) bears the problem of integrating processes that may occur at different time scales. The $\delta^{15}\text{N}$ of sediment POM can have an effect on the ϵ_{sed} value. We will clarify this in the revised manuscript.

RC: Finally, I felt that the potential influence of porewater advection on rates of nitrogen transformation could/should be addressed. Were porosity measurements made on collected cores? In sandy sediments, a number of studies have shown that porewater advection largely impacts nitrogen transformation rates. If pertinent, the potential influence of advection on nitrification and denitrification rates/ processes, as determined in the following studies, should be incorporated into the discussion: 1. Rao, et al. 2007. Continental Shelf Research. 27: 1801–1819. 2. Rao, et al. 2008. Continental Shelf Research. 28: 602–613. 3. Gihring, et al. 2010. Limnology and Oceanography 54:

C5920

43-54. 4. H. Gao, et al., 2010. The ISME Journal 4: 417-426.

AC: See comment above

RC: "Benthic isotope exchange" – poor word choice. "Isotope exchange" has a much different connotation that is meant by the usage here. Consider rephrasing? You might want to somehow define ϵ_{app} and ϵ_{sed} in the abstract – or at least be somewhat more clear about what they refer to? (Also – you refer to the "nitrate and TDN" isotope effects – ϵ_{app} and ϵ_{sed} , respectively – when ϵ_{sed} is actually a combined nitrate + TDN isotope effect). Please clarify. "sediment-water exchange" – perhaps change to "sediment porewater-water column exchange?"

AC: We will clarify these points in the revised manuscript, and we will define ϵ_{sed} and ϵ_{sed} in the abstract.

RC: Section 3.3 In general, this section could probably benefit from some clarity. While the authors do use clear explanations for each of the terms, there may be a bit too much reliance on the reader's prior understanding of Lehmann et al., (2007). I think that perhaps a bit more text explaining the calculated NO_3^- flux, ϵ_{app} and ϵ_{sed} would help the reader follow this more easily – including simply reminding the reader, for example, that the " $\delta^{15}N$ of the NO_3^- flux" is the low $\delta^{15}N$ that is lost (as N_2) from the water column via denitrification of water column NO_3^- in the underlying sediments. Pg 10, Ln 9: the latter? Not clear to what this refers?

AC: See above. We will try to clarify section 3.3

RC: Pg 10, Ln 12: Not clear about why/when/where you use an exponential vs linear fit. What does one situation mean versus the other? Again – a revisit to Lehmann et al. (2007) might be in order.

AC: See comment above.

RC: Pg 10, Ln 19: 'drained' – not clear. Consider using "removed."

C5921

AC: Will be changed as suggested.

RC: Pg 10, Ln 13: How valid is the assumption of similar diffusion coefficients? How sensitive are the estimates of ϵ_{sed} to this assumption? If not very, perhaps you can simply state this and get away from the assumption?

AC: See comment above. The isotope effect of diffusion of the nitrate molecules is insignificant. This is due to the fact that nitrate is mostly hydrated and the actual mass difference between hydrated $14NO_3^-$ and $15NO_3^-$ molecules is small. A bigger problem is that we have to assume a common diffusivity for the whole RDN pool. We have addressed this potential shortcoming in the original submission.

RC: Pg 15, Ln 20: The production of low $\delta^{15}N$ NO_3^- from sediments through incomplete oxidation of NH_4^+ efflux has also been observed/interpreted similarly in highly reactive, organic rich estuarine environments (Wankel, et al. 2009. Journal of Geophysical Research 114, G01011, doi:10.1029/2008JG000729.)

AC: We will cite the work by Wankel et al. accordingly.

RC: Other Minor Edits Pg 2, Ln 9: change 'enhance' to 'alter' or 'increase?' Pg 2, Ln 12: elimination from sediments on the fixed oceanic N pool Pg 3, Ln 23: : : : marine nitrate ^{15}N as a tracer of : : : Pg 6, Ln 13: Nalgene 0.2 m (microns not millimeters). Pg 6, Ln 27: 3 M L-1 is improper – use mol L-1 to be consistent. Pg 7, Ln 2, Ln3: Same error. Pg 9, Ln 13: Martin and McCorkle reference not in the Bibliography. Pg 12, Ln 15: While sediments in general violate one of the basic. . . Pg 13, Ln 14: source of ^{15}N -enriched RDN. Pg 13, Ln 21: not associated with any significant. . . Pg 15, Ln 3-5: Redundant. This was just stated on the page before Pg 17, Ln 10: Refer to both Tables 1 and 2. Pg 18, Ln 9: : : :and an input. . . Pg 18, Ln 18: : : :deep sea.

AC: Will all be changed as suggested

RC: Pg 15, Ln 24: What exactly is meant by "nitrate remineralization?"

AC: See above. We will clarify it.

C5922

RC: Pg 11, Ln 20: Might be nice to include the RDN flux in Table 1.

AC: A detailed discussion on RDN fluxes and the environmental controls that modulate them is in preparation. For obvious reasons, we are hesitating to include such a table. But if the Associate Editor would like to see it in the revised version, we will include it.

Referee #3

RC: 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} .

AC: In the methods section we will add more description on the calculations of ϵ_{app} and ϵ_{sed} (We have calculated the $^{15}N/^{14}N$ for sedimentary flux of NO_3^- and RDN using the concentration profiles of $^{15}NO_3^-$, $^{14}NO_3^-$, RD15N, and RD14N and the $\delta^{15}N$ of NO_3^- and RDN. Using the $^{15}N/^{14}N$ for sedimentary flux of NO_3^- and RDN we have determined the $\delta^{15}N$ of the sedimentary NO_3^- and RDN flux across the SWI using the following formula, $[(F_{15N}/F_{14N})/0.003677-1]*1000$, where F_{15N} is the flux of either $^{15}NO_3^-$ or TD15N, F_{14N} is the flux of either TD14N or $^{14}NO_3^-$, and 0.003677 is the natural abundance of ^{15}N in the atmospheric Air. Isotopic effect is then calculated by the difference between the bottom water $\delta^{15}N$ of either RDN or NO_3^- and the respective $\delta^{15}N$ of its flux.).

RC: 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.

AC: We will add more information on the analysis of errors. Also, we will remove the text/figures that refer to the core incubations.

C5923

RC:Terminology: Throughout the paper the terms for reduced dissolved nitrogen species, including RDN, $DON+NH_4^+$, 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.

AC: We will ascertain that this point will be clear in the revised manuscript. In any case, DON dominate the RDN fluxes at most locations, therefore, the discussion concentrates more on DON and to some extent RDN is equivalent to DON, at least close to the SWI.

RC: Terminology: The phrase "nitrate elimination" is confusing; I would use denitrification and anammox or fixed nitrogen loss.

AC: We will use "fixed N loss"

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

AC: See comment above. A more clear definition will be provided in the abstract and/or the method section. But already in the original submission, in sections 3.3 and 3.4, we explained how the two parameters were calculated. In addition, the terms were explained in detail in previous publications (e.g. Brandes and Devol 1997; Lehmann et al., 2007).

RC: 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.

AC: Will be changed as suggested

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

C5924

AC: Will be changed.

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

AC: True, there are multiple sinks for porewater ammonium, but (aerobic or anaerobic) oxidation is most probable. In any case, we will remove this section, as we address the different ammonium pathways in the discussion.

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

AC: Will be changed.

RC: Fig 2: It would help to make the station number and the legend larger and more noticeable.

AC: Will be changed as suggested

RC: 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.

AC: We have included the overlying bottom water [DO], oxygen penetration depth, and oxygen exposure time. These parameters were calculated from sediment DO consumption rates taken from Thibodeau et al. (2010), which were determined from ex-situ whole core incubations. Unfortunately we do not have any microsensor data, nor did we measure we measured [DO] in WCS extracted porewater samples.

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

AC: See comment above. We will try to avoid any irritation that the dual approach seems to produce. In the revised version, we will always use an exponential fit, and change the method section accordingly. Results are not affected.

C5925

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

AC: We will eliminate the second decimal in the revised MS.

RC: 11699, line 20: I would be interested to see the $\delta^{15}\text{N}$ -NO₃ flux values in a table.

AC: Will be changed as suggested

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

AC: From incomplete nitrification of ammonium produced through the organic matter remineralization

RC: 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 coming into play?

AC: We will exclude the incubation experiments from the revised version of the manuscript.

RC: 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.

AC: Will be changed as suggested

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

AC: It refers to the $\delta^{15}\text{N}$ -TDN change with depth. We will clarify this in the revision of the MS

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

AC: It refers to ϵ_{sed} . Will be clarified

C5926

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

AC: ϵ_{sed} refers to the combined RDN plus nitrate isotope flux with respect to the water column DIN pool. We will clarify this in the revised MS.

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

AC: Will be changed to RDN

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

AC: Yes! We know that the anaerobic oxidation of ammonium is associated with a strong ammonium N isotope effect, similar to that of nitrification (Contreras et al., in preparation). If ammonium oxidation is not quantitative, it can influence both ϵ_{app} and ϵ_{sed} , as described in the manuscript.

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

AC: It could have been potentially distinguished if the d^{18}O of nitrate had been measured, for example in the incubation nitrate samples (See Lehmann et al. 2004)

RC: 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.

AC: Incubation data will not be included in the revised manuscript.

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

AC: Will be changed as suggested

RC: 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?

AC: Our data reveal that the biological N isotope effect of estuarine benthic denitrifi-

C5927

cation is highly suppressed but that ϵ_{sed} can still be significantly different from zero. The conditions along the LC, especially in the Gulf of St. Lawrence can be considered representative of coastal and continental shelf environments where a large portion of the global sedimentary denitrification occurs. While our observational data now confirm that ϵ_{sed} values of 5‰ and greater are possible, benthic denitrification in deep sea sediments probably occurs with a lower ϵ_{sed} of ~ 2 ‰ (Lehmann et al., 2007). According to Lehmann et al. (2007), a global mean ϵ_{sed} of ~ 4 ‰ is realistic.

References:

Alkhatib, M., Schubert, C.J., del Giorgio, P., Gelin, Y., and Lehmann, M.F.: Organic matter reactivity indicators in sediments of the St. Lawrence Estuary, Est. Coast. Shelf S., accepted pending minor revisions. Lehmann, M. F., Sigman, D. M., and Berelson, W. M.: Coupling the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate as a constraint on benthic nitrogen cycling, Mar. Chem., 88, 1–20, 2004.

Lehmann, M. F., Sigman, D. M., McCorkle, D. C., Granger, J., Hoffmann, S., Cane, G., and Brunelle, B. G.: The distribution of nitrate $^{15}\text{N}/^{14}\text{N}$ in marine sediments and the impact of benthic nitrogen loss on the isotopic composition of oceanic nitrate, Geochim. Cosmochim. Ac., 71, 5384–5404, 2007.

Thibodeau, B., Lehmann, M. F., Kowarzyk, J., Mucci, A., Gelin, Y., Gilbert, D., Maranger, R., and Alkhatib, M.: Benthic nutrient fluxes along the Laurentian Channel: Environmental controls and impact on the N-budget of the St. Lawrence marine system, Estuar. Coast. Shelf S., 90, 195–205, 2010.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/8/C5909/2012/bgd-8-C5909-2012-supplement.pdf>

Interactive comment on Biogeosciences Discuss., 8, 11689, 2011.

C5928