

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

**Anonymous Referee #2**

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### Summary

Alkhatib et al. present a study of the impact of sedimentary nitrogen transformation processes along the estuarine gradient of the St. Lawrence Estuary. This estuarine gradient provides other key variations in sediment biogeochemical attributes including organic matter reactivity, bottom water oxygen content and rates of benthic respiration. Hence, this environment provides a contiguous framework in which to evaluate the influence of these environmental parameters on nitrogen transformations and, more specifically, the isotopic expression of these sedimentary processes on the overlying

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water column nitrogen pool. The work is essentially an extension of the former sediment flux work of Lehmann et al. (2004, 2005 and 2007), building off of a nitrate isotope flux model and now integrating measurements of total reduced nitrogen (TDN =  $\text{NH}_4^+$  + DON). As has been demonstrated in prior work, due to diffusion limitation of denitrification (or any other  $\text{NO}_3^-$  consuming process) in sedimentary environments, the expression of the large kinetic isotope effect of denitrification is suppressed in the overlying water resulting in only very small changes in the nitrate  $\delta^{15}\text{N}$  (or  $\delta^{18}\text{O}$ ). Combining the isotopic flux of TDN (for the first time) from the sediments, however, Alkhatib et al. demonstrate that the ‘total nitrogen isotope effect’ of sediment nitrogen transformations may indeed be larger than previously observed. If true, and if extension to global continental shelf environments is valid, this finding has important implications for the global N budget.

The manuscript is very well written, well organized and manages to present the complex isotope systematics of sediment N fluxes in a relatively clear and understandable manner. This being said, there are places where I think some clearer language might help strengthen the message, in particular with regard to the presentation of much of the terminology and calculations. The study seems to have been conducted using a well planned and strategic approach. Further, the data appear to be of good quality and I feel the scientific interpretation is sound. Nonetheless, I do have some comments that, upon consideration by the authors, will hopefully prove to strengthen the manuscript as a whole. In summary, I feel the manuscript warrants publication in Biogeosciences upon consideration of the comments listed below.

### Major Comments

1. 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  $\text{NO}_3^-$  into the  $\text{NH}_4^+$  pool (McCready et al., 1983. Canadian Journal of Microbiology 29:231-234.). While DNRA may not be considered as a major

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NO<sub>3</sub><sup>-</sup> sink mechanism in such sediments, it would seem that the suboxic conditions near the surface could easily support at least some portion of NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> isotope flux, since both DNRA and denitrification would presumably act to increase the  $\delta^{15}\text{N}$  of the NO<sub>3</sub><sup>-</sup> 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<sub>4</sub><sup>+</sup> 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.

2. 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<sub>3</sub><sup>-</sup> 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  $\epsilon_{\text{sed}}$ ?

3. The authors mention the fact that calculated values of  $\epsilon_{\text{sed}}$  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.  $\epsilon_{\text{app}}$  relates exclusively to the NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> in the overlying water is, what matters is only its composition relative to the  $\delta^{15}\text{N}$  lost due to denitrification). However, regarding  $\epsilon_{\text{sed}}$ , because this incorporates the isotope flux of NH<sub>4</sub><sup>+</sup> 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

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to 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  $\epsilon_{\text{sed}}$ . 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.

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

#### Specific Comments

##### Abstract:

“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  $\epsilon_{\text{app}}$  and  $\epsilon_{\text{sed}}$  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 –  $\epsilon_{\text{app}}$  and  $\epsilon_{\text{sed}}$ , respectively – when  $\epsilon_{\text{sed}}$  is actually a combined nitrate + TDN isotope effect). Please clarify. “sediment-water exchange” – perhaps change to “sediment porewater-water column exchange?”

##### 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

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the reader's prior understanding of Lehmann et al., (2007). I think that perhaps a bit more text explaining the calculated NO<sub>3</sub>- flux,  $\epsilon_{app}$  and  $\epsilon_{sed}$  would help the reader follow this more easily – including simply reminding the reader, for example, that the “ $\delta^{15}N$  of the NO<sub>3</sub>- flux” is the low  $\delta^{15}N$  N that is lost (as N<sub>2</sub>) from the water column via denitrification of water column NO<sub>3</sub>- in the underlying sediments. Pg 10, Ln 9: the latter? Not clear to what this refers?

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.

Pg 10, Ln 19: 'drained' – not clear. Consider using “removed.”

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

Pg 15, Ln 20: The production of low  $\delta^{15}N$  NO<sub>3</sub>- from sediments through incomplete oxidation of NH<sub>4</sub><sup>+</sup> 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.)

#### 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  $\delta^{15}N$  as a tracer of ...

Pg 6, Ln 13: Nalgene 0.2  $\mu m$  (microns not millimeters).

Pg 6, Ln 27: 3  $\mu M$  L<sup>-1</sup> is improper – use  $\mu mol$  L<sup>-1</sup> to be consistent.

Pg 7, Ln 2, Ln3: Same error.

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Pg 9, Ln 13: Martin and McCorkle reference not in the Bibliography.

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

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 15, Ln 24: What exactly is meant by “nitrate remineralization?”

Pg 17, Ln 10: Refer to both Tables 1 and 2.

Pg 18, Ln 9: ...and an input...

Pg 18, Ln 18: ...deep sea...

END OF REVIEW

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

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