**Biogeosciences
Discussions**

Interactive comment on "Constraints on oceanic N balance/imbalance from sedimentary^{15}N records" *by* M. A. Altabet

M. Lehmann (Referee)

lehmann.moritz@uqam.ca

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In this paper, M. Altabet provides theoretical considerations to evaluate the impact of changes in the rates of major global marine N-cycle reactions (N_2 fixation, water column denitrification, benthic denitrification) on the N-isotopic composition of the marine N pool, and its implication for the interpretation of δ^{15}N records in late Holocene and glacial-interglacial-transition marine sediments.

Although interesting to read, this paper seems to be rather a byproduct of Altabet's work, elegantly digesting his and other's previous work but not adding really original components. The paper gives the impression of being written under time constraints, with lots of little flaws and typos, and unattractive illustrations. Nevertheless, it is

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a good and stimulating paper that deserves publication as it refines and rectifies previously published ideas. It comes at the right moment, at a time when the question regarding the annual rates of various global N-fluxes is a matter of hot debate, and shortly after the community has discovered that the N isotopic composition of oceanic nitrate can theoretically be used to infer the relative importance of various N-cycling reactions, such as benthic versus water column denitrification and N_2 fixation, regionally (Sigman et al. 2003, 2005; Lehmann et al. 2005) or globally (Brandes and Devol 2002). Thus, it highlights the potential of stable N isotopes as valuable tracers of N-cycle processes and fluxes, which integrate over large spatial scales.

In essence, there is nothing wrong with the paper and advocating balance or imbalance of the modern N budget is, these days, a matter of contention. Simply some points, I find, should be stressed more or should be presented in a more critical way.

Nitrate N-isotope approach to quantify major global N fluxes

Brandes and Devol's (2002) revised estimate on global benthic denitrification roots in the assumption that, during water column denitrification, N gas is lost with a N isotopic composition that is 25 permil lower than that of mean ocean nitrate, that is, -20 permil. Similarly, Sigman et al. (2003) used an isotope effect of 25 permil for water column denitrification to infer the relative importance of benthic denitrification relative to water column denitrification in the Santa Barbara Basin. While Deutsch et al. (2004) already suggested that assuming an effective N isotope effect equal or similar to the organism-scale, or intrinsic, N isotope effect of denitrification is incorrect, Altabet clarifies why the organism-scale N isotope effect is not pertinent to the calculation of N-isotope balances, pointing to open system processes and the fact that the nitrate pool in denitrification zones, from which N_2 is lost, is significantly depleted and thus already enriched in ^{15}N. He plausibly argues that the effective N isotope effect to be considered in N isotope balances is 12 permil rather than 25 permil. At the same time he barely emphasize the implication of this lowered N isotope effect for isotope-balanced derived N budgets.

Following the line of argumentation by Brandes and Devol (2002) and using an apparent N isotope effect for water column denitrification of 12 permil instead of 25 permil, reported values for global sedimentary denitrification of up to 300Tg N per year would drop to approximately 100Tg N per year, bringing the total N loss by denitrification to approximately 170 Tg N per year - much closer to previous estimates by N. Gruber and colleagues and much lower than postulated by L. Codispoti in his manuscript also submitted to the special volume of Biogeosciences (see Biogeosciences Discussions). As a result, the modern N budget would not be that much out of balance as proposed by Lou Codispoti. These are important deliberations that should be clarified in a revised manuscript.

Again, I will not argue whether the N isotope balance is in or out of balance, nor about the size of the global denitrification sink, because I believe we are still lacking the constraints (modeling, but even more important, observational) that would allow us to precisely assess modern global N fluxes. The mean ocean nitrate approach may be promising, but how realistic is it that it will help us to really get close to the real rates of N loss? The sensitivity of the integrative isotope approach to the robustness of end member N isotope effects for benthic and water column denitrification, respectively, should at least be highlighted more clearly in a revised manuscript. The uncertainty in the water column N isotope effect directly translates into large errors for global denitrification rates, disclosing the actual weakness of the nitrate-N isotope approach. We simply do not have sufficient constraints on the biological N isotope fractionation during water column denitrification in order to assume a robust intrinsic N isotope effect of 25 permil to work with. I hope will get there with time. Similarly, uncertainties in the estimates of the apparent isotope effect of benthic denitrification (0-3 permil), and the possible effect of remineralization and nitrification that can lead to significant efflux of ammonium enriched in ^{15}N, represent even greater biases to isotope-budget-derived rates of denitrification. Moreover, the N-isotope effects of alternative modes of suboxic N_2 production on the average δ^{15}N of the global fixed N pool are not known and, if important, are likely to have a strong impact on N-isotope based N-flux calculation. Once

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more, I feel that the author should stress more the limitations of the N-isotope balance approach.

I find one observation intriguing: From equations 7 and 8, we can expect that enhanced denitrification, with higher nitrate removal under steady state, reduces the apparent N isotope effect. As a consequence, elevated water column denitrification would result in an increase in δ^{15}N of N_2 that is lost from the ocean and a decrease in ocean average nitrate δ^{15}N. While indeed counterintuitive, this result makes sense. The author speculates that increasing water column denitrification, however, is likely to expand the volume of actively denitrifying waters in a way that the fractional removal remains the same. I am not so sure about this, and this issue should be addressed (through collaborations) using global biogeochemical model simulations. Model simulations could also address to which extent benthic and water column denitrification indeed evolve in parallel or not, in response to changes in environmental conditions (upwelling intensity, O_2 and nutrient concentrations). I do not find it implausible that water column and benthic denitrification could vary independently.

Implications for sedimentary $\delta^{15}N$ records

The modeling is very simple and the information gained is somewhat trivial. However, the model results help to gain an idea of what kind of changes in global N fluxes are required to obtain observed changes in δ^{15}N in sedimentary organic matter. An important message of the paper, which does not seem to have reached paleo-oceanographers yet, is that changes in sedimentary denitrification alone (i.e., in an unbalanced global N-cycle) cannot change the N isotopic composition of the N-pool, and, thus, does not produce shifts in sedimentary δ^{15}N records. Only changes in the water column denitrification/ N_2 fixation ratio are capable to change the mean nitrate δ^{15}N and to produce variations in the sedimentary δ^{15}N record. This is an important point stressed by the author. Yet, although he theoretically considers the possible effects of more or less benthic or water column denitrification and N_2 fixation, Altabet

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essentially overlooks the obvious implications for the use of sedimentary δ^{15}N records as means to reconstruct past changes in the global N-cycle and to gain constraints as to whether the global N-budget was in or out of balance in the geologic past. For example, Altabet himself draws scenarios where, on the one hand, the mean nitrate δ^{15}N would not change with an increase/decrease in water column denitrification if the marine N budget remains in balance, whereas changes in denitrification would produce δ^{15}N changes in the sediment records if not compensated by N_2 fixation. In the same context, while changes in sedimentary denitrification have barely any effect on the δ^{15}N of the global N-pool if the N-budget were out of balance, it would lead to δ^{15}N changes in a balanced N-cycle, where N_2 fixation rates change accordingly. While I have no doubt that sedimentary δ^{15}N variations record local/regional changes in the degree of denitrification, nitrate assimilation, or N_2 fixation, I hesitate to believe that we can gain conclusive evidence from sediment records as to the N cycle being in or out of balance in the past, even if we pick the right coring locations (remote from HNLC and denitrification regions). Although presenting the arguments against organic matter δ^{15}N being a reliable global N-cycle proxy, the paper fails to point to the obvious ambivalence of sedimentary N isotope records. Unchanged marine records of δ^{15}N over the last 3 ky may suggest a balanced and stable N budget (at least on average over longer time-scales), but does certainly not provide conclusive evidence for it. Moreover, the fact that the invariable ^{15}N is different in various locations points to the fact that these regions have their own regional N-cycles and budgets. How can local and global signals be disentangled?

Recommendation

I recommend publication of this manuscript after minor revisions (see below). It clearly fits the scope of Biogeosciences, and is, in general, well written and to the point. While the paper does neither present new data nor completely original ideas, it nevertheless contains novel and interesting aspects. The comments above represent

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recommendations to the author that do not necessarily require his response. Minor points are listed below.

Minor points: p. 1123, l.14: The estimate on the combined global N inventory is wrong, on the order of three magnitudes.

p. 1124, l.3: This sentence is not very clear. Also, "sedimentary denitrification" should be "sedimentary N loss".

p. 1126, l. 8: Fractionation factor is not the right term. Rather: enrichment factor or isotope effect.

p. 1126, l. 23-27; p. 1127, l.4: This section is written in memo style. The use of the semicolons is confusing. No exclamation mark.

p. 1127, l. 16: I do not think that the acronym for a reference is acceptable.

p. 1128: A reference should be provided for the equations 7 and 8 (Mariotti et al., 1981?), or the author should explain in more detail how he derived the equations and explain them better.

p.1129, l.5: add unit " permil"

p. 1129, l.18: manifested; l.22: remove "that"

p. 1130: Figures 3 and 4 are mixed up, or at least their legends.

p.1130: It is not really surprising that a change in sedimentary denitrification alone does not produce a change in oceanic d15N. This has been suggested and shown by several previous studies.

p.1132, l.2: add "approximately" 1 residence time

p.1135, l.16: "seems"

p. 1135, l.18-20: There is something missing in this sentence. Also, clarify to what extent the link between phosphate sequestration and denitrification can offset the postulated parallel development of water column vs. sedimentary denitrification.

p. 1136, l.14: "feedback"

p.1136, l. 20: What make a good or excellent δ^{15}N record?

l. 21: "suggest" instead of "show"

l. 21: Based on the previous discussion, what does "increases in denitrification" really mean? More water column denitrification?

p. 1138, l. 1: The N cycle was not necessarily out of balance during the last deglaciation. I am not saying, that it was in balance. But, clearly, scenarios are possible where the ^{15}N records would show variations, even if the N budget were balanced (see general comments above).

p. 1138: Some phrases in the concluding section are simply repetitions of what was said in the introduction, and can be omitted.

p. 1138, l. 17: Rather than nil, the N isotope effect associated with benthic N loss lies closer to 3 permil.

p. 1140, l. 3: "may have" produced

References:

Brandes, J.A. and Devol, A.H., 2002. A global marine-fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling. Global Biogeochem. Cy., 16(4): art. no.-1120.

Deutsch, C., Sigman, D.M., Thunell, R.C., Meckler, A.N. and Haug, G.H., 2004. Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget. Global Biogeochem Cy., 18(4).

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Sigman, D.M. et al., 2005. Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin. Global Biogeochem. Cy., 19(4).

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