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Discussions

Interactive comment on "Effects of cyanobacterial-driven pH increases on sediment nutrient fluxes and coupled nitrification-denitrification in a shallow fresh water estuary" *by* Y. Gao et al.

Anonymous Referee #2

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Review of Gao et al – Biogeosciences General comments: Gao et al present an interesting experimental test of the effects of elevated pH on sediment N cycling with particular focus on coupled nitrification-denitrification. The topic is relevant, given the effects of high rates of primary production in productive marine or estuarine sediments can lead to localized substantial changes in pH, despite the strong buffering capacity of seawater. Investigating both the physical-chemical effects, e.g., on NH4+ adsorption, and physiological effects, e.g., on nitrifying bacteria, of such changes is quite relevant and has not been examined much in estuarine systems. Thus, this study contributes new and relevant insights into factors affecting estuarine N cycling. I applaud the authors' experimental approach that includes both aspects. It would strengthen the story even more if the authors could provide insights as to what degree of the pH induced changes in rates can be attributed directly to physical-chemical changes (e.g., NH4+ desorption) versus physiological effects where possible.

The calculation of diffusive flux rates for SRP and sumNH4+really contributes nicely to the study and to the believability of the experimental results. This is especially strong in the case where substantial concentrations of NH4+ and NH3 occur together under elevated pH and the diffusive flux calculation supports (and explains) the experimentally measured enhanced fluxes. The stoichiometric calculation in regards to the DIN and O2 fluxes are similar nice, supplementary considerations.

While I find the study quite interesting, relevant and presumably ultimately worthy of publication, there are some problems, including some major issues, that need to be addressed before final publication. I will try to outline these below. First, considering the experimental treatment, is the difference in elevated pH's (9.2 vs. 9.4-9.5) large enough to be considered different? Would have been nicer to have a pH value in mid 8's and low 10's. Please comment on why this might not have been possible. Discuss this also in light of the pKb for NH3. Also, given the starting pH's of your sampling sites, you should elaborate more on what are normal vs. extreme pH's at these sites. The point of departure for the Powerline site was not pH=7, so calling pH=7 a "control" may in fact be misleading in this case. The highest experimental pH was in fact the "control" in this situation.

I like the comparison of the two different approaches to measure nitrification. Compare and discuss them in discussion, however, and not the methods section (p. 1168, lines 16-18). (Alternatively, include this comparison as an important point in the introduction). Unfortunately there is a confusing discrepancy between the results text (p. 1172, lines 1-9) and Figure 1. The text refers to Powerline (P) but the figure text says Budds Landing (BL). I assume the latter is correct as only the design used at BL allowed pore-

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water sampling at elevated pH conditions. But aren't there also some porewater date for P as well? Are they not presented? Please clarify and correct the methods section if necessary. Note, the letters (A-F) are missing from the figure as well which doesn't make things less confusing.

There are other annoying and confusing discrepancies in the data presented. For example, the SRP and NH4+ flux data at the high pH treatment for BL presented in Table 4 and Figure 3 do not match. It seems likes sites were switched. On the other hand, they were not switched for the control pH level. Such inconsistencies lead me to doubt whether when the authors present the correct data for the right sites, treatments, etc.

Please explain better the "cause" of the pH error bars in the NH4+ adsorption-desorption experiments (Fig. 2). What "error" or variability is actually shown? Min-max pH? s.d.? It is not stated in the figure text. Also discuss whether these observed changes in pH are consistent (can be solely explained) by the acid-base chemistry of the NH4+-NH3 reaction. Or are other factors affecting pH during these incubations? Also, state what model is being fit in Fig. 2A and B. Where do the solid lines come from and how are they estimated? A similar comment can be made about Fig. 5A. Is that line in any way related to the kinetics discussed on p. 1176, lines 22-23 for nitrification? Nothing is stated in either the manuscript or figure text.

The presentation (p. 1177, lines 18-20) of the data in Fig. 5B is also confusing. Is what is shown in Figure 5B the augmented NH4+ flux rates (with inhibitor) or the calculated (by difference) nitrification rate? The figure text indicates the latter, but the discussion in the text seems to imply the former (and a nitrification rate of ∼30 umol m-2 h-1). Which is it? It has importance re NH4+levance for understanding the N2 flux data later. It is not clear to me why a pH driven release of adsorbed NH4+ would inhibit nitrification per se (p. 1178, lines 2-3). If that NH4+ is not lost, then this should still be available (unless adsorbed NH4+is actually more available for nitrifiers). This inhibition of nitrification at higher pH's must also be physiological, as argued with NH3 inhibition, or that NH4+ is

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lost via diffusive fluxes before it could be nitrified. I am not sure whether the authors can come with some insights or calculations about the relative rates of these fates of NH4+ once desorbed, but it would be appreciated.

The discussion of the controls of denitrification (3.11) and its relationship to nitrification as well as physiological tolerances for pH are good and insightful. The points about the contribution of DNRA to NH4+ fluxes is interesting, but could be made more quantitative if it is possible to calculate how much of the elevated diffusive fluxes (Table 4) were supported by porewater NH4+ (Fig. 1) increased due to pH-induced NH4+ desorption (Fig. 2). I am not sure if this calculation can be made precisely without a model, but it seems to me like you have the parts in place of a good first order calculation.

Why not move the presentation of the effects of pH on SRP flux (3.7) closer to the section on SRP profiles (3.1)? It seems awkward to separate them and it breaks up the flow of discussion on N processes (sections 3.4-3.11). Placed here this section seems just like an afterthought.

The t-test used to test for effects of pH on SRP and NH4+ fluxes (3.7 and 3.8) is inappropriate. You have 3 treatments and thus these should be considered simultaneously using an ANOVA. That ANOVA can then be followed up by multiple pairwise comparisons using Tukey's HSD, for example. Why were statistical tests not conducted for other parameters tested (e.g., O2 flux, potential nitrification, etc.)? Furthermore, no mention is made of whether the data was tested for distributional considerations (normality and homogeneity) necessary before applying parametric statistics. This must also be stated.

I appreciate the conclusion and ecological implication section. It is the only place where the authors attempt to pull the individual processes, discussed individually, together. But I feel that the first section on harmful algal blooms is too long and is too much like an introduction. What is important here is to tell us that such blooms do affect N cycling and thus help promote themselves by enhancing nutrient availability. I would

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like the authors to state more clearly whether the pH effect on benthic N or P release is greater; it seems like the latter (on a relative basis) and thus while this manuscript has mostly focused on N cycling that in fact the enhanced P flux is a greater effect and will help maintain N-fixing cyanobacteria blooms. This, together with less denitrification (this ms), will lead to even greater N input to the estuary, continuing eutrophication, primary production, and even faster element cycling overall. This does appear to be a troublesome positive feedback system.

Overall this is a good study and it provides new, experimental information about the response of estuarine ecosystems to eutrophication stress and its effects via enhanced primary production (blooms) with subsequent effects (increased pH) on nutrient cycling processes. It is thus both interesting and relevant, particularly in heavily impacted systems such as the Chesapeake. I hope that the authors can address the issues raised above and submit an improved manuscript for publication. I am confident that they can do so and eliminate the problems and uncertainties I identified in this version. Below are some minor comments that will also hopefully improve a revised version. I look forward to seeing a revised manuscript published.

Detailed Comments: p. 1164, line 13-14. What is water depth of collection sites? (move to here)

p. 1164, line 20-21. What was the effect of this bubbling on pH in the water?

p. 1166, line 9-11. Need to state somewhere that they cores were sealed (and how). The whole flow-through system is not very well described. Were peristaltic pumps used? How was this controlled?

p. 1166, line 23-25. Mention already here that they were sectioned under anoxic conditions.

p. 1167, line 13. Were sectioning intervals 1 cm? This is unclear.

p. 1171, line 1. I could not find the reference citation (Larsen et al 2001).

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p. 1171, line 10. 65 °C is quite low for sediment water content. 105°C is more typical.

p. 1178, line 22. Change “consisted” to “consistent”.

p. 1192. Figure 1. Letters (A-F) are missing.

p. 1193 & 1196. Figure 2 & 5A. Inform us what the fitted lines/curves are.

p. 1194-5. Figures 3 & 4. Here you use s.d. and elsewhere you use s.e. What is the logic? Be consistent (and use s.e.).

Interactive comment on Biogeosciences Discuss., 9, 1161, 2012.