Biogeosciences Discuss., 5, S1955–S1962, 2008
www.biogeosciences-discuss.net/5/S1955/2008/

Biogeosciences
Discussions

Interactive comment on “Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments” *by* H. Thomas et al.

A. Hofmann (Referee)

a.hofmann@nioo.knaw.nl

Received and published: 15 October 2008

The main conclusion Thomas et al. draw from their extensive North Sea data set (measurements of A_T, DIC, and $p\text{CO}_2$) is that anaerobic organic matter degrading processes such as sulfate reduction and, most of all, denitrification irreversibly generate enough alkalinity to significantly increase the CO_2 uptake capacity of coastal seas. They show that this anaerobic pump - part of the continental shelf pump - could be a key player in antropogenic carbon sequestration, even on global scale.

This scientifically relevant topic is presented in a concise and generally well written way which makes the manuscript a valuable contribution to BG, provided the authors respond to the comments below.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1 Comments regarding the content of the manuscript

- In line 22 of page 3578 the autors cite Goldman and Brewer (1980) to justify that (biogeochemical) NO_3^- consumption and production has an effect on A_T. However, this is a very sloppy way of expressing something different: Consumption or production of every mole of NO_3^- is either balanced by H^+ syn-transport or OH^- anti-transport. This ensures charge conservacy: otherwise the consumption or production of the anion NO_3^- would charge both the surrounding solution and the organism performing the consumption or production. Subsequently, it does not matter if there is H^+ syn-transport or OH^- anti-transport: both processes increase A_T by one equivalent if one molecule of NO_3^- is consumed ($\frac{-\Delta NO_3^-}{\Delta A_T} = 1$), this is what Goldmann and Brewer (1980) confirm in their experiments. It is very important to note that NO_3^- consumption or production itself has no effect on A_T since it is conservative over realistic marine pH ranges and $[NO_3^-]$ is not part of Dickson's definition of total alkalinity (Dickson, 1981). However, the parallel consumption or production of H^+ or OH^- does affect A_T. This fact should be made clear in the manuscript.

A charge balanced stoichiometric equation of oxic mineralisation (combined with nitrification) and primary production (based on nitrate: i.e. combined with ammonification) could solve this issue and facilitate the explanation of terms in Equation 1 (γ signifies the $\frac{C}{N}$ ratio of organic matter: 6.625 for Redfield stoichiometry):

$$(CH_2O)_\gamma NH_3 + (\gamma+2)O_2 \rightleftharpoons \gamma CO_2 + NO_3^- + H^+ + (\gamma+1)H_2O \qquad (1)$$

The authors then could state that their terms $\delta A_T($ x $NO_3^-)$ are the effects of the above reaction net reacting either from left to right or from right to left using different pools either to source NO_3^- from or to deliver NO_3^- to. A_T is affected via H^+ in the reaction equation above.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

- On page 3580 the authors cite Chen and Wang (1999) for the influences of denitrification and sulfate reduction on A_T. Chen and Wang (1999) use the equations

$$(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 84.8\mathrm{HNO_3} \rightarrow 106\mathrm{CO_2} + 42.4\mathrm{N_2} + 148.4\mathrm{H_2O} + 16\mathrm{NH_3} + \mathrm{H_3PO_4} \quad (2)$$

$$(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 53\mathrm{SO_4^{2-}} + 106\mathrm{H^+} \rightarrow 106\mathrm{CO_2} + 106\mathrm{H_2O} + 53\mathrm{H_2S} + 16\mathrm{NH_3} + \mathrm{H_3PO_4} \quad (3)$$

Aside from the fact that denitrification should be written in terms of $\mathrm{NO_3^-}$ and $\mathrm{H^+}$ to derive the production of 83.8 mol of A_T per mol organic carbon (otherwise $[\mathrm{HNO_3}]$ needs to be consistently included into the definition of A_T; however, it is common practise to assume that $[\mathrm{HNO_3}] = 0$ and $\mathrm{NO_3^-}$ is conservative (i.e. does not protonate) along natural marine pH values), Chen and Wang (1999) neglect the effect of ammonia production by both reactions on A_T (although $[\mathrm{NH_3}]$ is part of Dicksons definition of total alkalinity). If one would include the effect of $\mathrm{NH_3}$ production on A_T, denitrification would produce 1.18 moles of A_T per mole $\mathrm{NO_3^-}$ denitrified and sulfate reduction would produce 2.28 moles of A_T per mole of $\mathrm{SO_4^{2-}}$ reduced, instead of the 0.99 moles and 1.98 moles mentioned here. This means the potential A_T production by denitrification and sulfate reduction exceeds the identified A_T flux even more than mentioned by the authors in line 6 of page 3581.

However, taking into account anaerobic ammonioum oxidation (e.g adapted from Chen and Wang (1999))

$$5\mathrm{NH_3} + 3(\mathrm{H^+} + \mathrm{NO_3^-}) \rightarrow 4\mathrm{N_2} + 9\mathrm{H_2O} \quad (4)$$

which consumes 0.4 moles of A_T per mole of $\mathrm{NH_3}$ oxidised and (in oxygenated watermasses) nitrification

$$\mathrm{NH_3} + 2\mathrm{O_2} \rightarrow \mathrm{NO_3^-} + \mathrm{H_2O} + \mathrm{H^+} \quad (5)$$

which consumes 2 moles of A_T per mole of $\mathrm{NH_3}$ oxidised, additionally to sulfide reoxidation

$$\mathrm{H_2S} + \mathrm{O_2} \rightarrow \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \quad (6)$$

which consumes 2 moles of A_T per mole of H_2S oxidised and is already mentioned by the authors, might ease that dilemma.

- The authors state that they assume that 20-50 % of the riverine nitrate undergoes denitrification, leaving only 50-80 % available for new production. However, improving water quality (increasing oxygen concentrations) might have changed this situation. For the Scheldt estuary, we show (Hofmann et al., 2008) that in the years 2001 to 2004 on average 10 % of total nitrogen is lost to the atmosphere while in the seventies this number still amounted to 40 %. Furthermore, estuaries themselves might be a source of nitrate due to nitrification activity: in the Scheldt estuary, around 1.5 times more nitrate was exported to the North Sea during the years 2001 to 2004 than was imported by the river.
- The authors assume that sulfate reduction irreversibly produces a considerable amount of A_T because a large portion of the sulfur that is reduced by sulfate reduction gets buried in the sediment in the form of pyrite. However, according to e.g. Jorgensen (1982, 1983), 80 - 95 % of the H_2S produced by sulfate reduction diffuses back to the sediment surface where it is subject to re-oxidation. A process which, as correctly stated by the authors, consumes A_T. In turn that means that just around 5 to 20 % of the A_T generated by sulfate reduction is in fact generated irreversibly.
- On page 3580, line 25 ff., the discussion of dissolution of $CaCO_3$ which has been produced in the Wadden Sea itself might not be necessary - as the authors correctly mention, it is obvious that the effect of production and subsequent dissolution of $CaCO_3$ on A_T is zero. However, it might be interesting to discuss if there is a net dissolution or production, i.e. if the $CaCO_3$ inventory of the system changes over time (see e.g. Milliman, 1993; Berelson et al., 2007, etc.).
- In line 29 on page 3582 the authors state that there is substantial A_T production by benthic denitrification in the North Sea proper. The fact that a term for this A_T

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

generation by benthic denitrification is missing in Eq. 1 may lead to an overestimation of the A_T contribution from the Wadden Sea which has been calculated as a closure term of Eq. 1.

- As already mentioned by Prof. Chen, it might be wise to cite Chen (2002).

2 Technical remarks

- While being informative and concise in the data gathering part, the Methods section is rather brief and confusing while explaining what has been calculated. Especially sentences like the one beginning in line 18 of page 3578 where two quantities are introduced and the second one is explained before the first one do not facilitate the reader's understanding. I would propose a table containing all terms in Eq. 1 and explaining what those terms mean and how they have been calculated. For example, although it is not mentioned in the methods section, I can infer from the caption of Tab. 1 that riverine and atmospheric nitrate values (for the $\delta A_T(\text{ x NO}_3^-)$ terms) stem from literature, but it is not clear to me yet where the water column nitrate values stem from.

- The values for ΔA_T were obviously calculated from measured data and all other terms in Eq. 1, except for $\delta A_T(\text{WaddenSea})$, have been calculated from data or literature. These terms then have been used to calculate $\delta A_T(\text{WaddenSea})$ according to the formulation

  $$\delta A_T(\text{WaddenSea}) = \Delta A_T - (...) \qquad (7)$$

  Hence I would change the text beginning from line 10 on page 3578 into something like:

"Following relation for ΔA_T has been assumed:
- Eq. 1 -.
The terms ... have been calculated from ... which allowed for calculating $\delta A_T(\mathrm{WaddenSea})$ from Eq. 1"

- In lines 19 and 20 of page 3581 the authors use “DIC uptake" and "NO_3^- uptake" to refer to the effects of primary production. I would recommend to name these two processes in such a way that it is clear that they are related to primary production.
- In general, the authors use the term "uptake" ambiguously: sometimes it means uptake or incorporation (of e.g. NO_3^-) into an organism or organic matter molecule and sometimes it means ocean uptake, i.e. transfer of chemical species (CO_2) from the atmosphere to the ocean. For these different processes different terms should be used.
- In general, the use of stoichiometric equations for all relevant processes would greatly facilitate the readers understanding of influences of those processes on A_T.
- Either "nitrate" or "NO_3^-" should be used instead of "NO_3" especially since the authors do use "SO_4^{2-}".
- Perhaps a schematic drawing of the considered box model containing the terms of Equation 1 would facilitate the readers' understanding.
- To be consistent with line 26 f. on page 3579, the order of the terms $\delta A_T($ riv. $NO_3^-)$ and $\delta A_T($ column $NO_3^-)$ should be switched in Equation 1.
- The brackets and their content on line 14 of page 3580 should be removed - the reader should know that 1 Gmol = 10^9 mol

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

- In Fig. 2 I would rather use the same units for A_T and δA_T, i.e. see δA_T as an offset not as a rate.
- On page 3580, line 20, the total of 99 Gmol A_T should already be mentioned in the sentence in line 15.
- It might be helpful to mention deviations of what value "anomalies of A_T" stands for.
- On page 3579, lines 19 and 20, in "to open North Sea" a "the" is missing.

Comment to the editorial office: Using the final layout (with all the figures and tables in the text) also for the discussion version would greatly simplify reviewing the manuscript: reading-flow disrupting turning back and forth of pages would be obsolete!

Andreas F. Hofmann

References

Berelson, W. M., Balch, W. M., Najjar, R., Feely, R. A., Sabine, C., and Lee, K.: Relating estimates of CaCO3 production, export, and dissolution in the water column to measurements of CaCO3 rain into sediment traps and dissolution on the sea floor: A revised global carbonate budget, Global Biogeochemical Cycles, 21, –, `<GotoISI>://000245187000001`, 2007.

Chen, C. T. A.: Shelf-vs. dissolution-generated alkalinity above the chemical lysocline, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 49, 5365–5375, `<GotoISI>://000179008300006`, 2002.

Chen, C. T. A. and Wang, S. L.: Carbon, alkalinity and nutrient budgets on the East China Sea continental shelf, Journal of Geophysical Research-Oceans, 104, 20 675–20 686, `<GotoISI>://000083473200013`, 1999.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Dickson, A. G.: An Exact Definition of Total Alkalinity and a Procedure for the Estimation of Alkalinity and Total Inorganic Carbon from Titration Data, Deep-Sea Research Part a-Oceanographic Research Papers, 28, 609–623, `<GotoISI>://A1981LY51900007`, 1981.

Goldman, J. C. and Brewer, P. G.: Effect of Nitrogen-Source and Growth-Rate on Phytoplankton-Mediated Changes in Alkalinity, Limnology and Oceanography, 25, 352–357, `<GotoISI>://A1980JN56000013`, 1980.

Hofmann, A. F., Soetaert, K., and Middelburg, J. J.: Present nitrogen and carbon dynamics in the Scheldt estuary using a novel 1-D model, Biogeosciences J1 - BG, 5, 981–1006, `http://www.biogeosciences.net/5/981/2008/L1-http://www.biogeosciences.net/5/981/2008/bg-5-981-2008.pdf`, 2008.

Jorgensen, B. B.: Mineralization of Organic-Matter in the Sea Bed - the Role of Sulfate Reduction, Nature, 296, 643–645, `<GotoISI>://A1982NK38700041`, 1982.

Jorgensen, B. B.: Processes at the Sediment - Water Interface, in: The Major Biogeochemical Cycles and Their Interactions, edited by Bolin, B. and Cook, R. B., pp. 477–509, SCOPE, 1983.

Milliman, J. D.: Production and Accumulation of Calcium-Carbonate in the Ocean - Budget of a Nonsteady State, Global Biogeochemical Cycles, 7, 927–957, `<GotoISI>://A1993MM23400011`, 1993.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper