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

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The main conclusion Thomas et al. draw from their extensive North Sea data set (measurements of \( A_T \), DIC, and \( pCO_2 \)) 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 anthropogenic 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.
1 Comments regarding the content of the manuscript

- In line 22 of page 3578 the authors 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 ($\frac{-\Delta \text{NO}_3^-}{\Delta A_T} = 1$), 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 ($\gamma$ signifies the C:N ratio of organic matter: 6.625 for Redfield stoichiometry):

$$ (\text{CH}_2\text{O})_{\gamma}\text{NH}_3 + (\gamma + 2)\text{O}_2 \rightleftharpoons \gamma\text{CO}_2 + \text{NO}_3^- + \text{H}^+ + (\gamma + 1)\text{H}_2\text{O} \quad (1) $$

The authors then could state that their terms $\delta A_T(\times \text{NO}_3^-)$ 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.

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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

$$\begin{align*}
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 84.8\text{HNO}_3 & \rightarrow 106\text{CO}_2 + 42.4\text{N}_2 + 148.4\text{H}_2\text{O} + 16\text{NH}_3 + \text{H}_3\text{PO}_4^2\quad (2) \\
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53\text{SO}_4^{2-} + 106\text{H}^+ & \rightarrow 106\text{CO}_2 + 106\text{H}_2\text{O} + 53\text{H}_2\text{S} + 16\text{NH}_3 + \text{H}_3\text{PO}_4\quad (3)
\end{align*}$$

Aside from the fact that denitrification should be written in terms of $\text{NO}_3^-$ and $\text{H}^+$ to derive the production of 83.8 mol of $A_T$ per mol organic carbon (otherwise $[\text{HNO}_3]$ needs to be consistently included into the definition of $A_T$; however, it is common practise to assume that $[\text{HNO}_3] = 0$ and $\text{NO}_3^-$ 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 $[\text{NH}_3]$ is part of Dicksons definition of total alkalinity). If one would include the effect of $\text{NH}_3$ production on $A_T$, denitrification would produce 1.18 moles of $A_T$ per mole $\text{NO}_3^-$ denitrified and sulfate reduction would produce 2.28 moles of $A_T$ per mole of $\text{SO}_4^{2-}$ 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 ammonium oxidation (e.g adapted from Chen and Wang (1999))

$$5\text{NH}_3 + 3(\text{H}^+ + \text{NO}_3^-) \rightarrow 4\text{N}_2 + 9\text{H}_2\text{O} \quad (4)$$

which consumes 0.4 moles of $A_T$ per mole of $\text{NH}_3$ oxidised and (in oxygenated watermasses) nitrification

$$\text{NH}_3 + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+ \quad (5)$$

which consumes 2 moles of $A_T$ per mole of $\text{NH}_3$ oxidised, additionally to sulfide reoxidation

$$\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \quad (6)$$
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 $A_T$
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 $\delta A_T(\times NO_3^-)$ terms) stem from literature, but it is not clear to me yet where the water column nitrate values stem from.

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

$$\delta A_T(WaddenSea) = \Delta A_T - (...)$$

(7)

Hence I would change the text beginning from line 10 on page 3578 into something like:
"Following relation for $\Delta A_T$ has been assumed: - Eq. 1 -.
The terms ... have been calculated from ... which allowed for calculating $\delta A_T (\text{WaddenSea})$ 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 $\delta A_T (\text{riv. NO}_3^-)$ and $\delta A_T (\text{column NO}_3^-)$ 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 S1960
• In Fig. 2 I would rather use the same units for $A_T$ and $\delta A_T$, i.e. see $\delta A_T$ 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!

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References


