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Biogeosciences

Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments

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Abstract. The coastal ocean is a crucial link between land, the open ocean and the atmosphere. The shallowness of the water column permits close interactions between the sedimentary, aquatic and atmospheric compartments, which otherwise are decoupled at long time scales (≅1000 yr) in the open oceans. Despite the prominent role of the coastal oceans in absorbing atmospheric CO_2 and transferring it into the deep oceans via the continental shelf pump, the underlying mechanisms remain only partly understood. Evaluating observations from the North Sea, a NW European shelf sea, we provide evidence that anaerobic degradation of organic matter, fuelled from land and ocean, generates total alkalinity (A_T) and increases the CO_2 buffer capacity of seawater. At both the basin wide and annual scales anaerobic A_T generation in the North Sea's tidal mud flat area irreversibly facilitates 7–10%, or taking into consideration benthic denitrification in the North Sea, 20–25% of the North Sea's overall CO_2 uptake. At the global scale, anaerobic A_T generation could be accountable for as much as 60% of the uptake of CO_2 in shelf and marginal seas, making this process, the anaerobic pump, a key player in the biological carbon pump. Under future high CO_2 conditions oceanic CO_2 storage via the anaerobic pump may even gain further relevance because of stimulated ocean productivity.

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1 Introduction

Shelf and marginal seas constitute biogeochemically active environments linking fluxes of energy and matter between land, the open ocean and the atmosphere. These areas host high biological activity, which is fuelled by nutrient inputs from all three interfacing compartments (e.g. Wollast, 1998; Thomas et al., 2003; Pätsch and Kühn, 2008; Liu et al., 2009). Furthermore, shallow seas, in which the water column is mixed at the seasonal or annual time scale, establish a close link between surface sediments and the atmosphere. This permits relatively direct interactions between both the sedimentary and atmospheric compartments, which are otherwise strictly separated at long time scales (≅1000 yr) in the open oceans. It has been proposed that shelf and marginal seas, such as the East China Sea and North Sea, act as continental shelf pumps, transferring atmospheric CO_2 into deeper layers of the open ocean via physical or biological processes, or a combination of the two (Tsunogai et al., 1999; Thomas et al., 2004). However, as recently summarized (Borges, 2005; Borges et al., 2005, 2006; Cai et al., 2006), a conclusive understanding has yet to be achieved on the role of shelf and marginal seas as sinks or sources for atmospheric CO_2 and of the underlying mechanisms.

Recent investigations describe the North Sea, in the NW European Shelf, as a strong continental shelf pump, facilitated through intense interaction between the deeper northern North Sea and the adjacent North Atlantic (Thomas et al., 2004, 2005a; Bozec et al., 2006). On the other hand, the North Sea's shallow southern part is strongly affected by terrestrial influences such as riverine inputs (Borges and

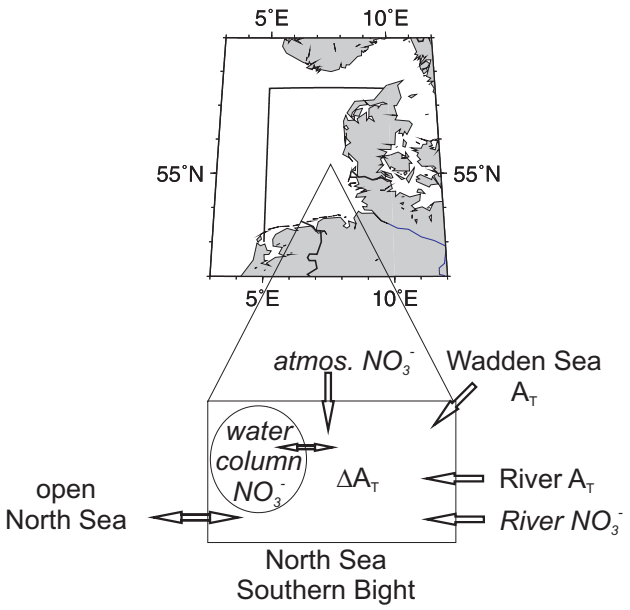

Fig. 1. Total Alkalinity budget of the southeastern bight of the North Sea. The upper panel shows the investigation area. The lower panel reveals the major fluxes, contributing to the alkalinity (A_T) budget. Direct A_T transports are shown as normal font, while A_T changes due to uptake/release of NO_3^- are shown in italics.

Frankignoulle, 2002; Schiettecatte et al., 2006, 2007). Earlier studies indicate that the Wadden Sea, a tidal mud flat area, bordering the southeastern region of the North Sea, might influence carbon cycling in the Southern North Sea (Hoppema, 1990; Brasse et al., 1999; Reimer et al., 1999). In the present study, we unravel the seasonal variability of total alkalinity (A_T) and pH in the North Sea, assess A_T generation in tidal mud flat areas, and evaluate the effects of this A_T generation on CO_2 uptake in the North Sea at basin wide, annual scales.

2 Methods

This study is based on an extensive field data set collected in 2001/2002 with spatial coverage over the whole North Sea region. The data set includes the full carbonate system and related parameters. The cruises were carried out on R/V Pelagia during all four seasons consecutively in August/September and November 2001 and February and May 2002. The entire North Sea was sampled by an adapted 1° by 1° grid of 97 identical stations resulting in high-resolution data sets appropriate for assessing seasonal variability (e.g. Bozec et al., 2006). Approximately 750 samples per cruise were analyzed for A_T by potentiometric determination and for dissolved inorganic carbon (DIC) by coulometric determination (Johnson et al., 1993). Uncertainties were estimated in the range of 2–3 μmol kg^{-1} (≅0.1%) for A_T and 1.5 μmol kg^{-1} (≅0.08%) for DIC. Surface water partial pressure of CO_2 (pCO_2) was determined continuously (Körtzinger et al., 1996) with approximately 20 000 data points per cruise, and the uncertainty was estimated to be 1ppm (≈0.3%). Atmospheric pCO_2 was measured hourly. The pH was calculated from DIC and pCO_2 (Dickson and Millero, 1987). More detailed descriptions of the methods used have been reported elsewhere (e.g. Bozec et al., 2006).

The variation of A_T (ΔA_T) in the southeastern bight of the North Sea (Fig. 1) was computed with the following equation:

$$\Delta A_T = \delta A_T(\text{mix}) + \delta A_T(\text{Riv}) + \delta A_T(\text{Wadden Sea}) + \delta A_T(\text{column } NO_3^-) + \delta A_T(\text{riv. } NO_3^-) + \delta A_T(\text{atm. } NO_3^-) \quad (1)$$

where δA_T (mix) represents the exchange between the southeastern bight and the adjacent central North Sea. The δA_T (mix) was computed by considering that the water in the southeastern bight is mixed at time scales of six weeks with water of the adjacent open North Sea (Lenhart et al., 1995). The southeastern bight encompasses areas south of 57.5° N and east of 5° E (Figs. 1, 2). The concentrations of the adjacent Central North Sea were averaged from data obtained in an area between 2° E to 5° E and 55° N to 57.5° N. The A_T was linearly interpolated between the measurements obtained every 3 months. The δA_T (Riv) represents the riverine inputs and was computed for the observational time period according to Pätsch and Lenhart (2004). The alkalinity inputs from the Wadden Sea (δA_T(WaddenSea)) are computed as closing term of Eq. (1). Furthermore, we consider the effect of nitrate (NO_3^-) uptake and release during new production and aerobic respiration of organic matter on A_T (Goldman and Brewer, 1980). In the view of Dickson's definition (Dickson, 1981), A_T is altered by the uptake/release of H^+, paralleling the uptake/release of NO_3^- because of the required conservation of electrical charges. Sources of NO_3^- include the water column inventory (δA_T (column NO_3^-)), rivers (δA_T (riv. NO_3^-)) and the atmosphere (δA_T (atm. NO_3^-)). The NO_3^- water column inventories were obtained from our observations (e.g. Bozec et al., 2006), while riverine and atmospheric inputs were computed according to Pätsch and Kühn (2008). We assumed that δA_T (Riv), δA_T (column NO_3^-) and δA_T (riv. NO_3^-) are constant over two mixing periods. We considered δA_T (atm. NO_3^-) constant over the full annual cycle. The magnitude of atmospheric deposition of ammonia (Pätsch and Kühn, 2008) is even smaller than that of nitrate and was neglected in the present evaluation (see Fig. 3 or Table 1). Fluxes of NO_3^- due to water mass exchange between the Southern North Sea and the adjacent open North Sea have been neglected, since NO_3^- observations are similar for both regions.

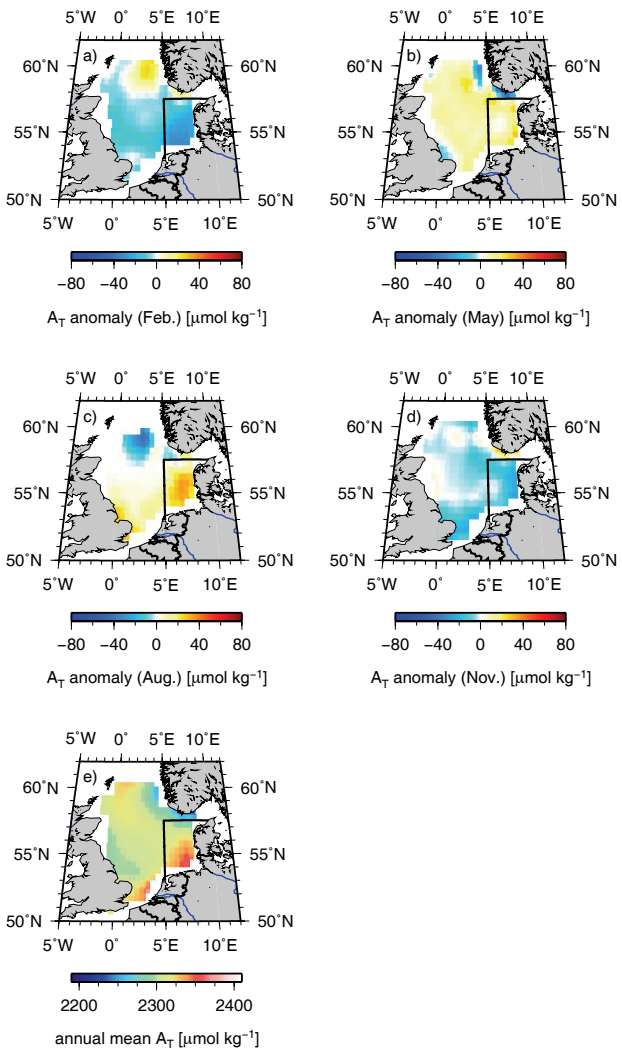

Fig. 2. Seasonality of total alkalinity. Seasonal anomalies of A_T, **(a)** winter (February), **(b)** spring (May), **(c)** summer (August/September) and **(d)** autumn (November) from observations. Panel **(e)** shows the annual mean distribution of A_T, relative to which the anomalies have been computed. The box borders the southeastern bight (see methods for details). The color scale is identical in all panels (a–d). The surface area and volume of the southeastern bight are 150 392 km^2 and 4512 km^3, respectively, computed from the bottom depth distribution (Thomas et al., 2005b). The surface area and volume of the remainder of the North Sea surface waters are 424 908 km^2 and 12 747 km^3, assuming a 30 m deep surface layer and a total surface area of the North Sea of 575 300 km^2 (Thomas et al., 2005a). The area of the Wadden Sea has been estimated at 5000 km^2.

3 Results and discussion

The A_T shows relatively homogenous distributions during each of the seasons in most parts of the North Sea (Fig. 2). In general, the seasonal variability of A_T is relatively low

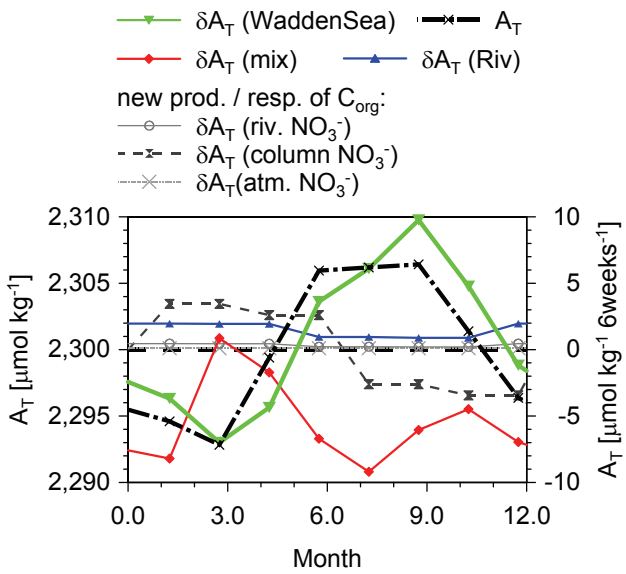

Fig. 3. Processes controlling the seasonal variability of total alkalinity in the southeastern bight of the North Sea according to Eq. (1). The seasonal cycle of A_T (black line and symbols), as well as the seasonal cycle of the Wadden Sea A_T input (δA_T (Wadden Sea), green line and symbols), riverine A_T inputs (δA_T (Riv), blue line and symbols) as well as the A_T release to the Central North Sea (δA_T (mix) , red lines and symbols) are shown. The grey lines and symbols denote A_T changes due to biological uptake of the water column NO_3^-, (δA_T (column NO_3^-), riverine NO_3^-, (δA_T (riv. NO_3^-), and atmospheric NO_3^- inputs (δA_T (atm. NO_3^-).

compared to the seasonal variability of DIC as reported by Thomas et al. (2005b) or Bozec et al. (2006). This signal is perturbed in the southeastern bight, in particular during spring and summer, when high values of A_T were observed. Furthermore, reduced A_T concentrations were observed during spring, and to a lesser extent, in summer in the northeastern area, which can be attributed to enhanced river and Baltic Sea runoff due to the low A_T concentrations of Scandinavian rivers discharging into the Baltic Sea (Thomas et al., 2003). The seasonal cycle of A_T in the southeastern bight of the North Sea reveals increasing concentrations from spring to late summer, with maximum values observed in August (Figs. 2, 3). In autumn and winter, the A_T concentrations decline to minimum values observed in February. In order to evaluate the processes governing the seasonal variability of A_T in the southeastern bight, we consider the terms of Eq. (1) as the relevant drivers (Fig. 3, Table 1). River inputs make the highest contributions during late winter and spring, with declining relevance from late spring until the following winter. With the exception of the rather homogenous winter situation, the open North Sea reveals lower A_T concentrations than the southeastern bight throughout the entire year as indicated by the negative values of the δA_T (mix) term, hence, the southeastern bight releases A_T to the open North

Table 1. Seasonality of total alkalinity in the Southern Bight of the North Sea. A_T release from the Wadden Sea and from rivers entering the southeastern bight to the North Sea according to Eq. (1) (see also Fig. 2). For comparison, we give the A_T changes due to nitrate uptake during (new) nitrate assimilation for selected nitrate sources. Negative values correspond to export to the adjacent North Sea and to NO_3^- release during aerobic respiration of organic matter, respectively. We assumed that 50–80% of the riverine nitrate is available for new production, while 20–50% undergoes denitrification (Beusekom and de Jonge, 2002). All units are in [Gmol A_T].

[Gmol A_T] A_T release from:	February to May	May to August	August to November	November to February	Entire year
Wadden Sea	−102.5	87.7	131.2	−43.9	72.5
Rivers[a]	35.0	16.1	16.0	35.4	103.8
Adjacent North Sea	−3.8	−71.8	−47.5	−68.4	−191.5
A_T change due to:					
Water column nitrate uptake	31.1	23.5	−23.5	−31.1	0
Riverine nitrate inputs [a]	6.2–10.0	3.1–4.9	2.9–4.6	6.3–10.1	19–30
Atmospheric Nitrate inputs [b]	1	1	1	1	4

[a] Pätsch and Lenhart (2004);
[b] Pätsch and Kühn (2008).

Sea. Input from the Wadden Sea makes a positive contribution to A_T from late spring until late autumn, while the Wadden Sea acts as a sink for A_T during winter and early spring. Assimilation of new nitrate increases A_T from late winter until late spring, while aerobic respiration releases nitrate and consequently lowers A_T during the remainder of the year (δA_T (column NO_3^-)). The contribution from nitrate assimilation or respiration is weaker than, and approximately six months (i.e., 180 degrees) out of phase with the Wadden Sea A_T release. The final two terms in Eq. (1), uptake of riverine and atmospheric nitrate, play a minor role in controlling A_T in the southeastern bight of the North Sea.

Several processes can account for the generation of A_T in the Wadden Sea, part of which is linked to the anaerobic degradation of organic matter. In the relatively well-ventilated Wadden Sea, only anaerobic processes can irreversibly generate A_T, which yield products, either resisting or escaping re-oxidation by oxygen. The primary candidates for these processes are

a) denitrification, which generates quasi-inert elemental nitrogen (N_2), which in turn can then escape to the atmosphere; and

b) sulfate reduction, which generates dihydrogensulfide (H_2S), which can either escape to the atmosphere, when sediments are exposed at low tide (Kristensen et al., 2000), or which can be buried as pyrite.

Sulfate reduction releases 1.98 mol A_T per mol SO_4^{2-} reduced (Chen and Wang, 1999) and has been estimated in a range of 6–13 Gmol S yr^{-1} in the Wadden Sea area (Kristensen et al., 2000; de Beer et al., 2005), which corresponds to a production of 12–26 Gmol A_T yr^{-1} (1 Gmol=10^9 mol). Denitrification, which releases 0.99 mol A_T per mol N denitrified (Chen and Wang, 1999), has been estimated in the Wadden Sea to be approximately 100 Gmol N yr^{-1} (Jensen et al., 1996), yielding a release of 99 Gmol A_T yr^{-1}. Denitrification in the Wadden Sea is partly fuelled by riverine nitrate inputs (37 Gmol N yr^{-1} from major rivers, Pätsch and Lenhart, 2004), of which approximately 20–50% are denitrified within the Wadden Sea itself (Beusekom and de Jonge, 2002; Seitzinger et al., 2006), thus contributing up to 19 Gmol A_T yr^{-1} to the total of 99 Gmol A_T yr^{-1}. Further nitrate can be supplied from the open North Sea, smaller rivers or ground water (Slater and Capone, 1987). A further process, which releases A_T, is the dissolution of calcium carbonate ($CaCO_3$). This dissolution is due to the acidification of pore waters related either to the release of CO_2 by respiration, or to the release of H^+ from the oxidation of H_2S within the oxic sediment layers (Jahnke and Jahnke, 2000). The estimated production of calcareous shells, that could be dissolved in the Wadden Sea, is quite low – on the order of 1 mol $CaCO_3$ m^{-2} yr^{-1}, or 5 Gmol $CaCO_3$ yr^{-1} (Beukema, 1982). Moreover, the autochthonous production of $CaCO_3$ would equal more or less the dissolution of $CaCO_3$, hence would not yield any net A_T gain of the Wadden Sea at the complete annual cycle. Otherwise to the best of our knowledge, the supply of allochthonuous $CaCO_3$ to the Wadden Sea has not been reported and therefore is not further considered.

The estimates of the potential A_T sources from denitrification and sulfate reduction in the Wadden Sea slightly exceed the identified A_T fluxes (Table 1). However, there is some uncertainty inherent to these estimates as well as to our assessment, for example related to the exchange time of the southern bight or to the temporal coverage of our study (e.g., Schiettecatte et al., 2007). As pointed out by Hofmann (2008), Chen and Wang (1999) neglect the contribution of ammonia release to the A_T generation. Accordingly, the release of ammonia by denitrification and sulfate reduction would add approximately another 10% to the A_T release. On the other hand, part of this ammonia would be subject to oxidation (nitrification) or biological assimilation, which in turn consumes A_T. Moreover, our results indicate that the southeastern bight acts as a sink for A_T during autumn and winter, which can be attributed to the re-oxidation of the products of sulfate reduction (Luff and Moll, 2004; de Beer et al., 2005). In autumn and winter, weather conditions enforce the intrusion of oxygen into the shallow surface sediments, permitting the re-oxidation of H_2S to become the dominant process, while denitrification and sulfate reduction activity is lower due to the decrease in temperature and supply of organic matter. Earlier studies for example show that the oxidation of H_2S may range from 80–95% of the H_2S generated by sulfate reduction (e.g. Jorgensen, 1982), however it has to be noted here that this particular study focuses on sediments, which are continuously covered by water, thus preventing H_2S from escaping to the atmosphere. We therefore argue that the current assessment might serve as a conservative, lower bound of the A_T release from the Wadden Sea to the open North Sea. It can be concluded that in the North Sea, and particularly in its shallower areas, A_T exerts a much stronger seasonal control on pH (Fig. 4) and surface pCO_2 than in open ocean areas, where the seasonality of DIC dominates. During the transition from winter to spring in the southeastern bight of the North Sea, the DIC uptake (Bozec et al., 2006), and the related A_T increase (due to NO_3^- uptake) synergistically raise the pH and lower the pCO_2. In spring, when large amounts of freshly produced organic matter are available, anaerobic degradation stimulates the release of large amounts of A_T. This supports the efficient DIC drawdown in maintaining low pCO_2 concentrations, as seen in late spring (Thomas et al., 2004). In the summer period, the effect of DIC release by decaying phytoplankton blooms is buffered by the increasing release of A_T from the tidal flat area. This buffering prevents a strong pH decline and acts to maintain low to neutral air-sea fluxes of CO_2, despite higher summer temperatures and degradation of organic matter (Bozec et al., 2006). Outside the southeastern bight, i.e. in areas remote from the tidal mud flat areas, the control of DIC on pH and pCO_2 becomes more significant. This is evident, for example, in the enhanced summer values of pH in the Northern North Sea (Fig. 4) (see also Thomas et al., 2004), or from the declining summer values of pH in the Southwestern North Sea, respectively: in the Northern North Sea the biologically driven CO_2 export out of the surface layer maintains higher pH conditions, while the southwestern region is hardly affected by any A_T release and thus reveals declining pH conditions because of organic matter degradation in a permanently mixed compartment.

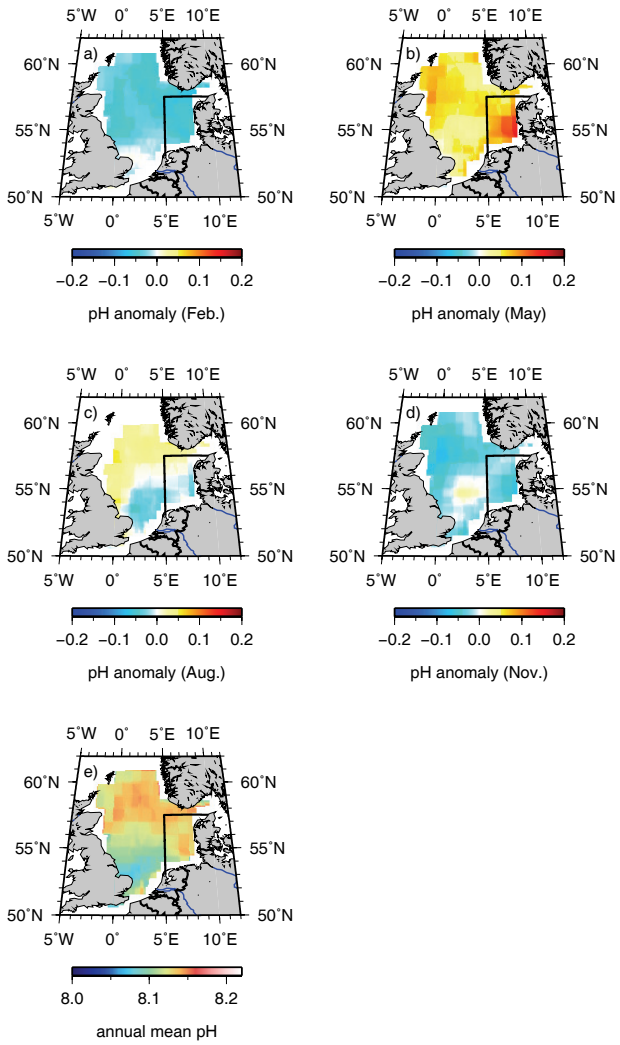

Fig. 4. Seasonality of pH. Seasonal anomalies of pH, **(a)** winter (February), **(b)** spring (May), **(c)** summer (August/September) and **(d)** autumn (November) calculated from observations. The box borders the southeastern bight (see methods for details). The color scale is identical in all panels (a–d). Panel **(e)** shows the annual mean distribution of pH, relative to which the anomalies were computed.

The difference between anaerobic and aerobic degradation of organic matter plays a crucial role in governing CO_2 air-sea fluxes. This is of particular importance on shelves and in shelf sea regions, where the surface sediments, acting as sinks for organic matter and sources of CO_2, are in direct or close contact to the atmosphere. This is in contrast to the open ocean situation, where there is no interaction

between the atmosphere and the sediment at short time scales (<1000 yr). Aerobic degradation has only a minor effect on A_T through nitrate release: considering Redfield stoichiometry, aerobic degradation decreases A_T by 16/106 mol per mol organic carbon remineralized. Aerobic degradation thus releases DIC that is virtually unbuffered, i.e., without a significant change of A_T, thereby largely cancelling out biological DIC drawdown during the preceding production of organic matter at the annual scale. In case of anaerobic degradation of organic matter, for example by denitrification or sulfate reduction, the DIC release is well buffered, i.e., DIC is released together with A_T. Since denitrification, and to some extent, sulfate reduction, are irreversible, if their products are buried or escape to the atmosphere, anaerobic degradation of organic matter constitutes a net A_T gain at the annual scale. This net gain of A_T then facilitates net CO_2 uptake from the atmosphere.

The release of 73 Gmol A_T from the Wadden Sea, which has an area of approximately 1% of the North Sea surface area, facilitates approximately 7–10% (0.2 mol C m^{-2} yr^{-1}) of the annual CO_2 uptake of the North Sea (Thomas et al., 2004). Considering the recent estimate for benthic denitrification in the entire North Sea (excluding the Wadden Sea) of 120 Gmol N yr^{-1} (Pätsch and Kühn, 2008), this corresponds to an A_T release of 119 Gmol yr^{-1}, or in turn may account for circa 15% of the annual CO_2 uptake. In total, anaerobic organic matter degradation has the potential to irreversibly facilitate as much as 20–25% of the CO_2 uptake of the North Sea. The global marine denitrification in shelf areas has recently been estimated at 250 Tg N yr^{-1} (18 Tmol N yr^{-1}) (Seitzinger et al., 2006), which corresponds to a potential CO_2 uptake of 15 Tmol CO_2, or 0.6 mol CO_2 m^{-2} yr^{-1}, assuming a Revelle factor of 11. Our estimate thus covers the lower bound of the independent estimate by Chen (2002). This corresponds to circa 60% of the total CO_2 uptake in shelf and marginal seas (0.3 Pg C yr^{-1}) (Borges, 2005; Borges et al., 2005; Cai et al., 2006; Liu et al., 2009), thus exceeding the effects of both atmospheric reactive nitrogen and sulfur depositions on the carbon cycle in the coastal ocean by one to two orders of magnitude (Doney et al., 2007). Benthic A_T generation may therefore constitute an anaerobic pump that is a major driver for the uptake of atmospheric CO_2 on shelves and in shelf sea regions.

The evolution of riverine A_T inputs to the ocean under future anthropogenic or climate change scenarios remains uncertain. Damming of rivers tends to hinder A_T transfer to the coastal ocean (e.g. Humborg et al., 2002), while on the other hand higher erosion in the catchment area related to land use changes might enhance A_T delivery to these regions (Raymond and Cole, 2003). With regard to benthic A_T release, recent findings reporting a stimulation of organic matter production by rising CO_2 concentrations, become relevant (Riebesell et al., 2007). This enhanced organic matter supply has the potential to stimulate benthic, anaerobic respiration with subsequent A_T release and (net−) CO_2 uptake. Furthermore, global warming has the potential to intensify stratification. This would favour the expansion of oxygen depleted zones and in turn stimulate anaerobic processes. Finally, primary production in near-shore shallow coastal environments is expended to continue to increase due to eutrophication (e.g. Mackenzie et al., 2004) with strong impacts on the carbonate chemistry and air-sea CO_2 fluxes (Mackenzie et al., 2004; Gypens et al., 2008). The increase of primary production due to eutrophication is also expected to enhance anaerobic A_T generation. The enhancement of benthic A_T generation would thus result in negative feedbacks to rising atmospheric CO_2 conditions, by enhancing the capacity of coastal oceans to uptake anthropogenic CO_2 establishing a further pathway for the continental shelf pump.

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References

Beukema, J. J.: Calcimass and carbonate production by mollusks on the tidal flats in the Dutch Wadden Sea, 2. The edible-cockle, Cerastoderma edule, Neth. J. Sea Res., 15, 391–405, 1982.

Beusekom, J. E. E. and de Jonge, V. N.: Long-term changes in Wadden Sea nutrient cycles: importance of organic matter import from the North Sea, Hydrobiologica, 475/476, 185–194, 2002.

Borges, A. V., Delille, B., and Frankignoulle, M.: Budgeting sinks and sources of CO_2 in the coastal ocean: Diversity of ecosystems counts, Geophys. Res. Lett., 32, L14601, doi:10.1029/2005GL023053, 2005.

Borges, A. V., Schiettecatte, L.-S., Abril, G., Delille, B., and Gazeau, F.: Carbon dioxide in European coastal waters, Estuarine, Coastal and Shelf Science, 70(3), 375–387, 2006.

Borges, A. V.: Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the Coastal Ocean?, Estuaries, 28(1), 3–27, 2005.

Borges, A. V. and Frankignoulle, M.: Distribution of surface carbon dioxide and air-sea exchange in the English Channel and adjacent areas, J. Geophys. Res., 108(C8), 3140, doi:10.1029/2000JC000571, 2003.

Borges, A. V. and Frankignoulle, M.: Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast, Biogeochemistry, 59(1–2), 41–67, 2002.

Bozec, Y., Thomas, H., Schiettecatte, L.-S., Borges, A. V., Elkalay, K., and de Baar, H. J. W.: Assessment of the processes controlling the seasonal variations of dissolved inorganic carbon in the North Sea, Limnol. Oceanogr., 51, 2746–2762, 2006.

Brasse, S., Reimer, A. Seifert, R., and Michaelis, W.: The influence of intertidal mudflats on the dissolved inorganic carbon and total alkalinity distribution in the German Bight, southeastern North Sea, J. Sea Res., 42, 93–103, 1999.

Cai, W.-J., Dai, M. H., and Wang, Y. C.: Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis, Geophys. Res. Lett., 33, L12603, doi:10.1029/2006GL026219, 2006.

Chen, C.-T. A.: Shelf-vs. dissolution-generated alkalinity above the chemical lysocline, Deep-Sea Res. II, 49, 5365–5375, 2002.

Chen, C.-T. A. and Wang, S.-L.: Carbon, alkalinity and nutrient budgets on the East China Sea continental shelf, J. Geophys. Res., 104, 20675–20686, 1999.

deBeer, D., Wenzhöfer, F., Ferdelman, T. G., Boehme, S. E., Huettel, M., van Beusekom, J. E. E., Böttcher, M. E., Musat, N., and Dubilier, N.: Transport and mineralization rates in North Sea sandy intertidal sediments, Sylt-Romo basin, Wadden Sea, Limnol. Oceanogr., 50, 113–127, 2005.

Doney, S. C., Mahowald, N., Lima, I., Feely, R. A., Mackenzie, F. T., Lamarque, J.-F., and Rasch, P. J.: Impact of anthropogenic atmospheric nitrogen and sulphur deposition on ocean acidification and the inorganic carbon system, P. Natl. Acad. Sci., 104, 14580–14585, 2007.

Dickson, A. G., and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987.

Goldman, J. C. and Brewer, P. G.: Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity, Limnol. Oceanogr., 25(2), 352–357, 1980.

Gypens, N., Borges, A. V., and Lancelot, C.: Effect of eutrophication on air-sea CO_2 fluxes in the coastal Southern North Sea: a model study of the past 50 years, Global Change Biol., doi:10.1111/j.1365-2486.2008.01773, in press, 2009.

Hofmann, A.: Interactive comment on "Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments" by H. Thomas et al., Biogeosciences Discuss., 5, S1955–S1962, 2008.

Hoppema, J. M. J.: The distribution and seasonal variation of alkalinity in the southern bight of the North Sea and in the western Wadden Sea, Neth. J. Sea Res., 26(1), 11–23, 1990.

Humborg, C., Blomqvist, S., Avsan, E., Bergensund, Y., Smedberg, E., Brink, J., and Mörth, C.-M.: Hydrological alterations with river damming in northern Sweden: Implications for weathering and river biogeochemistry, Glob. Biogeochem. Cy., 16(3), 1039, doi:10.1029/2000GB001369, 2002.

Jahnke, R. A. and Jahnke, D. B.: Rates of C, N, P and Si recycling and denitrification at the US Mid-Atlantic continental slope depocenter, Deep-Sea Res. I, 47, 1405–1428, 2000.

Jensen, K. M., Jensen, M. H., and Kristensen, E.: Nitrification and denitrification in Wadden Sea sediments (Konigshafen, Island of Sylt, Germany) as measured by nitrogen isotope pairing and dilution, Aquat. Microb. Ecol., 11, 181–191, 1996.

Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., and Wong, C. S.: Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector, Mar. Chem., 44, 167–187, 1993.

Jorgensen, B. B.: Mineralization of Organic Matter in the Sea Bed – the Role of Sulfate Reduc-tion, Nature, 296, 643–645, 1982.

Körtzinger, A., Thomas, H., Schneider, B., Gronau, N., Mintrop, L., and Duinker, J. C.: At-sea intercomparison of two newly designed underway pCO_2 systems – encouraging results, Mar. Chem., 52, 133–145, 1996.

Kristensen, E., Bodenbender, J., Jensen, M. H., Rennenberg, H., and Jensen, K. M.: Sulfur Cycling of intertidal Wadden Sea sediments (Konigshafen, Island of Sylt, Germany): sulfate reduction and sulfur gas emission, J. Sea Res., 43, 93–104, 2000.

Lenhart, H.-J., Radach, G., Backhaus, J. O., and Pohlmann, T.: Simulations of the North Sea circulation, its variability, and its implementation as hydrodynamical forcing in ERSEM, Neth. J. Sea Res., 33, 271–299, 1995.

Liu, K.-K., Atkinson, L., Quiñones, R., and Talaue-McManus, L.: Biogeochemistry of continental margins in a global context, in: Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis, edited by: Liu, K.-K., Atkinson, L., Quiñones, R., and Talaue-McManus, L., IGBP Book Series, Berlin: Springer, in press, 2009.

Luff, R. and Moll, A.: Seasonal dynamics of the North Sea sediments using a three-dimensional coupled water-sediment model system, Cont. Shelf Res., 24, 1099–1127, 2004.

Mackenzie, F. T., Lerman, A., and Andersson, A. J.: Past and present of sediment and carbon biogeochemical cycling models, Biogeosciences, 1, 11–32, 2004, http://www.biogeosciences.net/1/11/2004/.

Pätsch, J. and Lenhart, H.-J.: Daily Loads of Nutrients, Total Alkalinity, Dissolved Inorganic Carbon and Dissolved Organic Carbon of the European Continental Rivers for the Years 1977–2002, Berichte aus dem Zentrum für Meeres- und Klimaforschung, Reihe B, Ozeanographie, 48, 159 pp., 2004.

Pätsch, J. and Kühn, W.: Nitrogen and carbon cycling in the North Sea and exchange with the North Atlantic – a model study Part I: Nitrogen budget and fuxes, Cont. Shelf Res., 28, 767–787, 2008.

Raymond, P. A. and Cole, J. J.: Increase in the export of alkalinity from North America's largest river, Science, 301, 88–91, 2003.

Reimer, A., Brasse, S., Doerfer, R., Dürselen, C.-D., Kempe, S., Michaelis, W., Rick, H.-J., and Seifert, R.: Carbon cycling in the German Bight: An estimate of transformation processes and transport, German Journal of Hydrography, 51, 313–329, 1999.

Riebesell, U., Schulz, K. G., Bellerby, R. G. J., Botros, M., Fritsche, P., Meyerhöfer, M., Neill, C., Nondal, G., Oschlies, A., Wohlers, J., and Zöllner, E.: Enhanced biological carbon consumption in a high CO_2 Ocean, Nature, 450, 545–548, doi:10.1038/nature06267, 2007.

Schiettecatte, L.-S., Gazeau, F., van der Zee, C., Brion, N., and Borges, A. V.: Time series of the partial pressure of carbon dioxide (2001–2004) and preliminary inorganic carbon budget in the Scheldt plume (Belgian coast waters), Geochem. Geophy. Geosy., 7, Q06009, doi:10.1029/2005GC001161, 2006.

Schiettecatte, L.-S., Thomas, H., Bozec, Y., and Borges, A. V.: High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea, Mar. Chem., 106, 161–173, doi:10.1016/j.marchem.2007.01.001, 2007.

Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B., Tobias, C., and van Drecht, G.: Denitrification across landscapes and waterscapes: a synthesis, Ecol. Appl., 16(6), 2064–2090, 2006.

Slater, J. M. and Capone, D. G.: Denitrification in aquifer soils and nearshore marine sediments influenced by groundwater nitrate, Appl. Environ. Microb., 53, 1292–1297, 1987.

Thomas, H., Pempkowiak, J., Wulff, F., and Nagel, K.: Autotrophy, nitrogen accumulation and nitrogen limitation in the Baltic Sea: a paradox or a buffer for eutrophication?, Geophys. Res. Lett., 30, 2130, doi:10.1029/2003GL017937, 2003.

Thomas, H., Bozec, Y., Elkalay, K., and de Baar, H. J. W.: Enhanced open ocean storage of CO_2 from shelf sea pumping, Science, 304, 1005–1008, doi:10.1126/science.1095491, 2004.

Thomas, H., Bozec, Y., de Baar, H. J. W., Elkalay, K., Frankignoulle, M., Schiettecatte, L.-S., Kattner, G., and Borges, A. V.: The carbon budget of the North Sea, Biogeosciences, 2, 87–96, 2005a, http://www.biogeosciences.net/2/87/2005/.

Thomas, H., Bozec, Y., Elkalay, K., de Baar, H. J. W., Borges, A. V., and Schiettecatte, L.-S.: Controls of the surface water partial pressure of CO_2 in the North Sea, Biogeosciences, 2, 323–334, 2005b, http://www.biogeosciences.net/2/323/2005/.

Tsunogai, S., Watanabe, S., and Sato, T.: Is there a continental shelf pump for the absorption of atmospheric CO_2?, Tellus B, 51, 701–712, 1999.

Wollast, R.: Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, in: The Global Coastal Ocean, edited by: Brink, K. H. and Robinson, A. R., John Wiley & Sons, 213–252, 1998.