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Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments

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Abstract

The coastal ocean constitutes the crucial link between land, the open ocean and the atmosphere. Furthermore, its shallow water column permits close interactions between the sedimentary and atmospheric compartments, which otherwise are decoupled at short 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 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.

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. Thomas et al., 2003; Pätsch and Kühn, 2008; Liu et al., 2008). Furthermore, the shallow seas, of which 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

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compartments, which are otherwise strictly separated at short 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). As recently summarized (Borges, 2005; Borges et al., 2005), a conclusive understanding however 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 (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 was built 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

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analyzed for A_T by potentiometric titration, 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} ($\cong$0.1%) for A_T and 1.5 μmol kg^{-1} ($\cong$0.08%) for DIC. Surface water partial pressure of CO_2 (pCO_2) was determined continuously (Körtzinger et al., 1996) with ≈20 000 surface water pCO_2 data points per cruise, and the uncertainty of the pCO_2 data was estimated to be 1 ppm (≈0.3%). Hourly measurements were also made for atmospheric pCO_2, while pH has been 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 variability of A_T (ΔA_T) in the southeastern bight of the North Sea was computed with the following equation:

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

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 a ventilation time for the southeastern bight of 6 weeks (Lenhart et al., 1995). The southeastern bight encompasses areas south of 57.5° N and east of 5° E (Fig. 1). 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 δA_T(Riv) represents the riverine inputs, and δA_T(WaddenSea) the inputs from the Wadden Sea, computed as closing term of Eq. (1). Here, δA_T(Riv) was computed for the observational time period (Pätsch and Lenhart, 2004). 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). 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)). Atmospheric deposition of ammonia is negligible compared to NO_3 (Pätsch and Kühn, 2008) and was ignored in the present evaluation.

3 Results and discussion

Total alkalinity shows a relatively homogenous distribution throughout the year in most parts of the North Sea (Fig. 1). The seasonal variability of A_T is relatively low compared to the seasonal variability of DIC (e.g. Thomas et al., 2005b, Bozec et al., 2006). This fairly uniform 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 (Thomas et al., 2003). The seasonal cycle of A_T in the southeastern bight of the North Sea reveals increasing concentrations from spring to the end of summer, with maximum values observed in August (Figs. 1 and 2). In autumn and winter the A_T concentrations decline to minimum values observed in February. In order to unravel the seasonal variability of A_T in the southeastern bight, we consider the terms of Eq. (1) as the relevant drivers (Fig. 2; 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. The southeastern bight releases A_T to open North 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. Uptake of new nitrogen increases A_T from late winter until late spring, while aerobic respiration releases NO_3 and consequently lowers A_T during the remainder of the year (δA_T (column NO_3)). The contribution from NO_3 uptake/release 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.

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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, which either resist or escape re-oxidation by oxygen. The primary candidates for these processes are:

(a) denitrification, which generates quasi-inert elemental nitrogen (N_2) and which 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). 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 NO_3 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, which would fuel $CaCO_3$ dissolution in the Wadden Sea, is quite low - on the order of 1 mol $CaCO_3$ m^{-2} yr^{-1}, or 5 Gmol CO_3 yr^{-1} (Beukema, 1982). Moreover, the autochthonous production of $CaCO_3$ would equal over the complete annual cycle more

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or less the dissolution of $CaCO_3$, hence not yield a 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. 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 the sulfate reduction (Luff and Moll, 2004; de Beer et al., 2005). 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 of temperature and supply of organic matter. 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. 3) 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 have become available, anaerobic degradation stimulates the release of large amounts of A_T. This supports the efficient DIC drawdown while maintaining the low pCO_2 concentrations seen in late spring. 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. 3) (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 the A_T release and thus reveals declining pH conditions because of organic matter degradation in a permanently mixed compartment.

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 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 canceling 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 ≈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

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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. This corresponds to circa 60% of the total CO_2 uptake in shelf and marginal seas (0.3 Pg C yr^{-1}) (Liu et al., 2008), thus exceeding the effects of both atmospheric 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 as an anaerobic pump 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 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. The enhancement of benthic A_T generation would thus result in a negative feedback 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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Table 1. Seasonality of 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 production for selected nitrate sources. Negative values correspond to NO_3 release during aerobic respiration of organic matter. 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 [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
A_T change due to uptake of:					
Water column nitrate	31.1	23.5	−23.5	−31.3	0
Riverine nitrate [a]	6.2–10.0	3.1–4.9	2.9–4.6	6.3–10.1	19–30
Atmospheric Nitrate [b]	1	1	1	1	4

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

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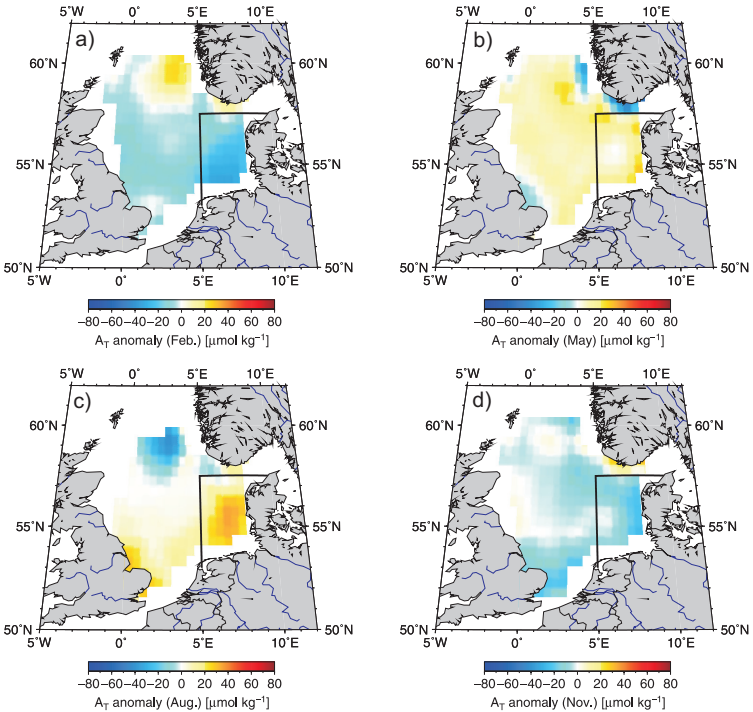

Fig. 1. Seasonality of Alkalinity. Seasonal anomalies of A_T, **(a)** winter (February), **(b)** spring (May), **(c)** summer (August/September) and **(d)** autumn (November). The box borders the southeastern bight (see methods for details). The color scale is identical in all panels (a)–(d). The surface 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.

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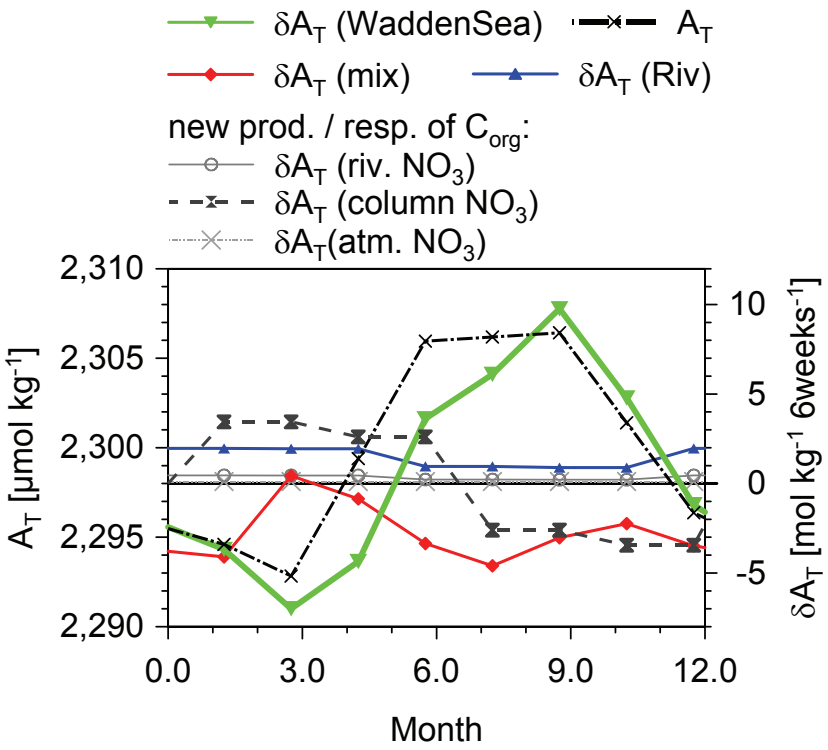

Fig. 2. Processes controlling the seasonal variability of A_T in the southeastern bight of the North Sea according to Eq. (1). The seasonal cycle of A_T (black line and symbols), as well as the seasonal cycle of the Wadden Sea A_T input (δA_T(WaddenSea), green line and symbols), riverine A_T inputs (δA_T(Riv), blue line and symbols) as well as the A_T release to the central North Sea (δA_T(mix) , red lines and symbols). 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 (δA_T(atm. NO_3).

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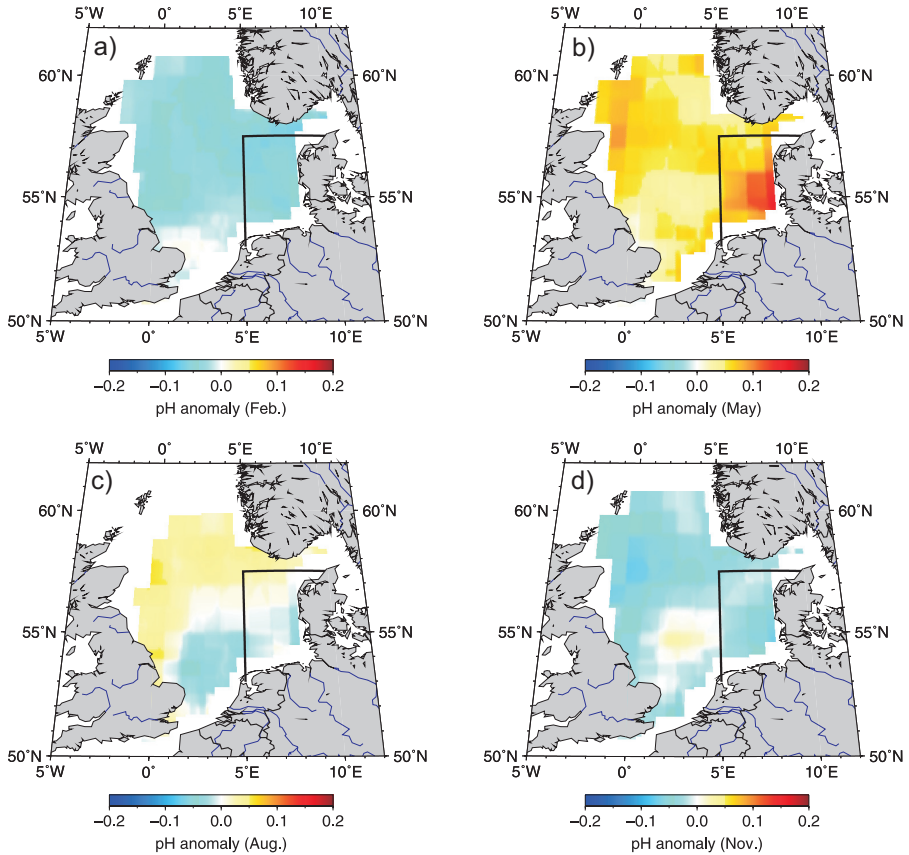

Fig. 3. Seasonality of pH. Seasonal anomalies of pH, **(a)** winter (February), **(b)** spring (May), **(c)** summer (August/September) and **(d)** autumn (November). The box borders the southeastern bight (see methods for details). The color scale is identical in all panels (a–d).

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