We would like to thank for the constructive review of our manuscript. We answered your questions and followed your advices whenever possible. In the following lines we copied your text as bold and gave our remarks in detail.

Review of the paper "Interannual sedimentary effluxes of alkalinity in the southern North Sea: Model results compared with summer observations" by J. Pätsch et al., submitted for possible publication to Biogeosciences.

The paper by Pätsch and coworkers deals with an important topic, namely on how coastal systems respond to increased nutrients input. Hitherto the focus of this discussion has largely been on the interaction between primary production, aerobic respiration and oxygen conditions with respect to changes of the overall CO2 pool. In recent times this focus has been broadened to further consider anaerobic metabolic pathways for the respiration of organic matter, which in turn affect both the overall CO2 and and also alkalinity pools. The paper by Pätsch et al. analyses this issue for the shallow waters of the North Sea and provides compelling evidence for the dependency of metabolic alkalinity generation on nutrient runoff/input. Overall I think the paper is publishable, as it constitutes a major step forward in this field. I do have some remarks for consideration to improve the paper.

Specific remarks:

Figures: All figures should be designed that each panel does clearly reveal the property, its unit and magnitude, such the the reader can read the panel without referring back to the caption. In the present form, only Fig. 9 has been designed accordingly. The other figures are not usable without the caption, which makes it very difficult to follow the text, and might be in part even misleading, such as in Fig. 7, where the property (N) is given, but points to different species of the N cycle. I think this point is also important if any colleagues might use such a figure for a talk or teaching. The only way to prevent misunderstandings is to carry the information in each panel as well (even if redundant).

done

Page 2, line 4: loss of reduced sulfate products: this (mainly?) refers to burial of sulfides (FeS, FeS2). If so, please be specific.

We specified the products.

Page 8, section 3.2, and related figures. While technically correct, it appears during the first and second read confusing to attribute aerobic degradation an alkalinity gain, and then separately name nitrification to a reduction of alkalinity. As this route is o pursued throughout the paper, please explicitly explain this here. Also a consideration might be to lump them together, if these processes always occur together. In other words, are there situations in this modelling study, where these two processes are not strictly coupled, which in turn would justify the need to treat them separately?

We introduced a sentence in section 2.3.3. By definition x mol TA is produced by incomplete aerobic degradation to ammonium and 2x mol TA are consumed by nitrification. Fig. 4b shows that TA

generation and consumption by these two processes is about equal in the sediment. This clearly shows that the two processes are not strictly coupled.

Page 9 lines 212-218. Calcium carbonate. To me the calcium carbonate discussion reads a bit like a closed loop argument, since apparently all hinges on the prescribed POC:PIC ratio. I have problems to see the need and justification for this discussion as it appears to be arbitrarily(!) controlled by the choice to the POC:PIC constant. I' d recommended to tone down this discussion, and focus it on the point where it might be necessary, namely when attempting to explain the difference outcomes of observational (summertime) studies, and year-round modeling studies, the latter ones possibly closing the CaCO3 budget. Alternatively, an attempt could be made to adjust/establish that ratio to improve the pCO2 fields, as for example provided by Thomas et al. 2004. Another weakness of the fixed POC:PIC ratio is that CaCO3 production is reported to occur sporadically, and not necessarily in tandem with primary production, which in turn would diminish or vanish the assumed advantage over the observational records.

We toned done the discussion and gave the hint to the possibility of sporadically occurring calcite production.

Page 11, lines 282-284: I think this statement could be strengthened by looking into coherence or lag-times between changes in NO3-runoff and extent of denitrification. The data are there, so an analysis in that direction should be easy to be carried out.

Thank you for this advice. We calculated the correlation coefficient for different monthly time shifts. And indeed a shift of 2-3 months gave the best (and significant) correlation. We added corresponding text in section 4.1.

Page 11. lines 285-300.

I think this discussion needs to be rewritten to some degree, as I see major arguments missing, or not fully considered.

Why attempting to relate a 9-month accumulation to an in-situ observation of a seasonally varying property? While I can can see the reason for this, yet it has to be considered:

A: the residence time of the water at any given location. If the residence time is on average much shorter than the 9-month integration, the latter one does not make sense and should be shortened.

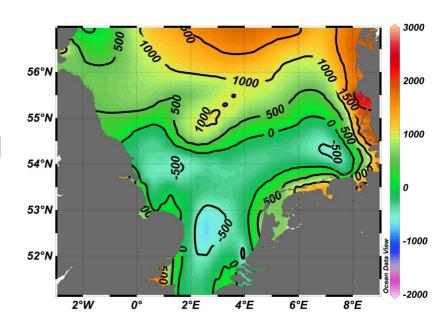
B: the entire concept only applies to vertically mixed regions. In stratified regions the zone of AT production is separate from the surface, thus if there is any impact it can be only visible, once, stratification breaks down in autumn (if at all). Also there are regions in the North Sea, which are permanently stratified. See for example Burt et al. 2014 (GBC) and observations of shortlived Ra isotopes in North Sea surface waters.

C: for the more Northern regions: what about transport times scales and amounts? Is any of that alkalinity produced in the southern surface sediments transported northward and might have an

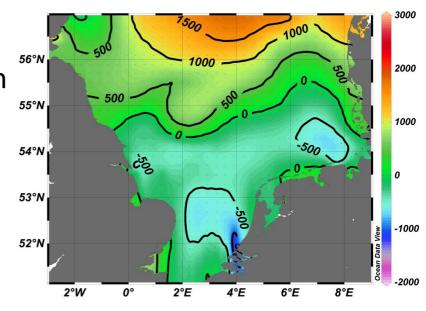
effect on the pCO2 there? I am not sure whether this plays a role, but it might be more likely to occur than the vertical impact mentioned under B. (See Burt et al., 2016 L&O)

We understand that our approach has several shortcomings. One of them is the arbitrariness of choosing the 15^{th} of September. Therefore we recalculated the pCO2 as September mean. Another shortcoming is the fact that for some places the alkalinity effluxes have no impact on local pCO2, neither for September nor for any other time. To overcome this we analyzed the temporal cumulated air-sea flux of CO2 from the beginning of the year until mid of September which at least weakens the argument related to flushing times. The attached figure shows horizontal distributions of the cumulated fluxes for both model runs. The patter resembles the Δ pCO2 distributions in September (Fig. 9). Northern areas with greater water depths show hardly any change. Small differences can be seen in the southern open sea areas and high differences occur near the continental coast where also the differences due to altered primary production were found. We added corresponding text in section 4.2.

Reference run
Cumulative ASF until
mid of September
(mmol m⁻²)



Pristine condition run Cumulative ASF until mid of September (mmol m⁻²)



Thank you for the constructive review of our manuscript. We answered your questions and followed your advices whenever possible. In the following lines we copied your text as bold and gave our remarks in detail.

GENERIC COMMENT the paper presents an interesting implementation of a vertically structured benthic model to estimate the alkalinity fluxes from the Southern North Sea sediments. This is a challenging topic that needs to be addressed and authors are commended for this. The methods are generally sound, with some clarification needed and some suggestions for improvements provided. The results are presented clearly, the discussion could benefit of some more in-depth analysis, particularly on the role of pelagic primary productivity and on the relevance of the alkalinity fluxes for the entire ecosystems.

Thank you for the hints regarding primary production and the role of alkalinity fluxes. During revising the text and answering your specific comments primary production was highlighted. One example is the positive feedback of pelagic production when enhanced nitrogen effluxes occur. In our model the direct effect of alkalinity effluxes on the whole ecosystem is restricted to the pelagic carbonate system and the air-sea flux of CO2. The indirect effect of connected effluxes of nutrients and oxygen is discussed now in a more comprehensive manner.

SPECIFIC COMMENTS: section 2.2.5 and table 1: why I appreciate that turnover rate for deep ocean would not be suitable for shelf seas, authors did not specify how they define the new values, if via calibration (against which observations?) or with literature (which references?).

As for the North Sea the annual budget of carbon export into the sediment and the efflux of DIC is nearly in balance, the changes of the reaction rates aimed at this target. In a first step we replaced the spatial uniform porosity used in the open ocean sediment module (0.85 first layer) to observation-based values for the southern North Sea (between 0.3 - 0.51). Additionally, the constant diffusion rate was replaced by a porosity, temperature and substrate dependent formulation. These changes made it necessary to adjust the turnover rates. As shelf areas are hardly resolved in the coarse resolution of the global model seasonality of organic matter fluxes and DIC effluxes were no tuning criteria. We changed the text in section 2.3.5 accordingly.

Lines 144-146: authors assumed that in advective sediments the coefficient for diffusion is increased tenfold. They state that this has been determined by several sensitivity analysis, but they did not state what were the criteria of the sensitivity analysis (stability? calibration? Something else?) more details are needed

As said before the target was to achieve a more or less equal annual DIC efflux and POC influx. Furthermore, the seasonality of the DIC efflux should resemble the known temporal evolution. An upper constraint for the diffusion coefficients was the penetration depth of significant oxygen concentrations. Below 1 cm depth almost no oxygen should be detected. We changed the text accordingly.

lines 175-178: authors claims that a reduction of 10% of riverine input of nitrogen corresponds to a "pristine" scenario without anthropogenic influence. Authors cite a paper to corroborate this

assumption. However it seems to me that 10% is a bit of an underestimation for such and industrialised area.

This is a misunderstanding. We reduced the riverine input to 10 % of the anthropogenic value.

Line 179-183: do the rates in the "plate run" scenario are comparable with those of table 1? I appreciate that the equation will be different and therefore the value of the parameter, but reporting these for a comparison would help in understanding how much of the difference is due to model structure and how much to simple parameter values

The carbon degradation rate of the plate run is defined as a time constant (2.8E-2/d), whereas the aerobic rate of the reference run is an oxygen dependent rate (r1 = 2 E-10 m3/(mmol [O2] s). For an off-shore station (54.4 °N, 7.4 °E) with a typical oxygen concentration of 100 mmol/m3 r1 results in a comparable rate (1.7 E-3 /d). In contrast to the plate run where nearly all POC is dissolved over one year POC concentrations in the upper most sediment level of about 0.35 E6 mmol C/m3 in winter and 0.48 E6 mmol C/m3 in summer are found in the reference run. This results in a winter flux of 1.2 mmol C/(d m2) and a summer flux of 1.6 mmol C/(d m2). The corresponding fluxes of the plate run were 0.36 mmol C/(d m2) in winter and 2.3 mmol C/(d m2) in summer. We added some text in section 4.4 accordingly.

line 220 and following. I'm not sure that providing a point-to-point comparison on a single day is the more effective way to assess the model. Small shift in phenology (not rare in coupled biogeochemical models) could result in a significant error that could not be related to the benthic model rather to error in the physics or in the forcing. I would suggest to compare the observations with a longer temporal means (monthly?) and to discuss the uncertainty. Also, while visual comparison can be appealing, they are not much informative: I suggest to provide also measures of the actual fit. For example, in relative error term, I'm not sure figure 6 shows a much better fit.

We switched from the analysis of 15 September to September means. But this did not change much because especially in September no big changes were expected (compare Fig 11b). We added an error analysis (definition in section 2.6).

Section 4.2: authors seem to suggest that the strong undersaturation of pCO2 in the German bight is driven by the strong alkalinity fluxes from benthos. I'm not entirely sure that the simple colocation of the two is enough to establish a causal link. For instance what's the role of pelagic primary production (PP)? A high PP could explain both the strong undersaturation (DIC is fixed into plankton) and the alkalinity fluxes (due to strong POM settling and associated processes in the benthic environment). Have the author tested to turn off the benthic fluxes of TA and check the consequences in the delta pCO2 signal?

This was a very helpful hint: in a further sensitivity run we switched off the benthic TA fluxes in the reference run. Consequently the pCO2 values increased. But the coastal low pCO2 did not fully vanish. We concluded that both the primary production and the benthic TA effluxes were responsible for the near-coast low pCO2 values. We added some text accordingly.

Section 4.3: authors said that it's astonishing that the model simulates higher benthic pelagic fluxes under higher porosity, when the diffusion coefficient is lower. Do authors have any suggestion on what are the mechanisms driving this?

To understand this contra-intuitive dynamics we compared the model results of the high porosity run (HP with 0.51) with the low porosity run (LP with 0.3) in the first and second spinup year. At the beginning of the first spinup year all conditions are the same. Until spring the flux of oxygen into the sediment was lower in HP because there the effective diffusivity was lower than in LP. The lower oxygen content in HP stimulated the benthic anaerobic processes. At the end of the first year this resulted into a higher efflux of NH4 from the sediment in the HP scenario. The higher NH4 efflux of the HP scenario was not compensated by the higher NO3 flux into the sediment. At the end of the year more DIN was in the pelagic water column in the HP scenario than in the LP scenario. In the second year this surplus of DIN stimulated higher primary production for the HP scenario. The corresponding enhanced particle export additionally increased the benthic-pelagic fluxes. The loss of N2 due to enhanced denitrification was compensated by the larger NH4 efflux. These deviating dynamics are even stronger at stations with lower pelagic DIN concentrations. We added some text accordingly.

Section 4.4: this section is important to understand the need for detailed model. However authors simply state the difference between the two models, without trying to tease out the reason behind that, particularly in regard to the difference in the seasonal signal

There are several reasons for the deviating seasonal cycle of DIC efflux. In general the less pronounced cycle comes about

- the structure of the 3d-sediment model which leads to a combination of multiple time scales acting on the reaction rates due to diffusive processes between the layers,
- the fact that the remineralization fluxes do not produce immediately effluxes. In case of the 3d-sediment model the dissolved compounds have to be transferred via diffusion into the pelagic system,
- the reservoir effect in the 3d-sediment model: Whereas the 2d-plate model more or less all POC is degraded after winter, in the 3d-sediment model a relative high POC concentration remains.

We added text accordingly.

technical comment: please translate "gedankenexperiment" in English.

done

Interannual sedimentary effluxes of alkalinity in the southern North Sea: Model results compared with summer observations

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Abstract

For the sediments of the central and southern North Sea different sources of alkalinity generation are quantified by a regional modelling system for the period 2000 - 2014. For this purpose a formerly global ocean sediment model coupled with a pelagic ecosystem model is adopted to shelf sea dynamics where much larger turnover rates than in the open and deep ocean occurs. To track alkalinity changes due to different nitrogen-related processes the open ocean sediment model was extended by the state variables particulate organic nitrogen (PON) and ammonium. Directly measured and from Ra isotope flux observation derived alkalinity fluxes from the sediment into the pelagic are reproduced by the model system but calcite building and calcite dissolution are underestimated. Both fluxes cancel out in terms of alkalinity generation and consumption. Other simulated processes altering alkalinity in the sediment like net sulfate reduction, denitrification, nitrification and aerobic degradation are quantified and compare well with corresponding fluxes derived from observations. Most of these fluxes exhibit a strong positive gradient from the open North Sea to the coast where large rivers drain nutrients and organic matter. Atmospheric nitrogen deposition shows also a positive gradient from the open sea towards land and supports alkalinity generation in the sediments. An additional source of spatial variability is introduced by the use of a 3D-heterogenous porosity field. Due to realistic porosity variations (0.3 - 0.5) the alkalinity fluxes vary by about 4 %. The strongest impact on interannual variations of alkalinity fluxes exhibit the temporal varying nitrogen inputs from large rivers directly governing the nitrate concentrations in the coastal bottom water, thus, provide nitrate necessary for benthic denitrification. Over the time investigated the alkalinity effluxes decrease due to the decrease of the nitrogen supply by the rivers.

1. Introduction

- 2 Alkalinity generation from anaerobic degradation in coastal sediments favors the marine uptake
- 3 capacity for atmospheric CO₂. This is because these paths of organic matter degradation include

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irreversible processes like N2 production and loss of reduced sulfate products like pyrite and hydrogen sulfide. In September 2011 and June 2012 Brenner et al. (2016) measured alkalinity fluxes from the North Sea sediment using several sediment cores. For the southern North Sea they found a mean flux of 6.3 $mmol \, m^{-2} \, d^{-1}$. Alkalinity effluxes into the pelagic system could partly determine the relative high surface alkalinity concentrations (Fig. 1a) in the southern North Sea as observed by Thomas et al. (2009) in September 2001. Together with observed concentrations of dissolved inorganic carbon (DIC) (Bozec et al., 2006) these surface alkalinity concentrations can be translated into ΔpCO_2 values $(pCO_2^{ocean} - pCO_2^{atmosphere})$ which are mainly responsible for the air sea exchange of CO_2 between ocean and atmosphere (Fig. 1b). In the southern North Sea positive values indicate oversaturation and thus outgassing, whereas in the northern parts negative values result in an uptake of atmospheric CO_2 . When in a simple thought experiment the observed alkalinity fluxes by Brenner et al. (2016) would be reduced by 50 % from the beginning of the year, the alkalinity concentrations especially in the shallow southern North Sea would be reduced (Fig. 1c) and the corresponding ΔpCO_2 values would exhibit much stronger oversaturation (Fig. 1d). This simple experiment focuses only on the reduced alkalinity flux without embedding such a situation into a corresponding environment. Furthermore it ignores the seasonality of the alkalinity fluxes and the fact that DIC fluxes would vary in concert. In this paper we investigate the variability of alkalinity generation and the efflux to the pelagic zone by means of a regional biogeochemical model. The second chapter presents methods concerning the model setup, particular with regard to the adaptation of the former open ocean sediment model (Heinze et al., 1999) to shelf sea conditions. Within the third chapter model results are compared with observational data. In the fourth chapter we show the results of several scenarios demonstrating the sensitivity of the total model dynamics on environmental settings due to changing alkalinity fluxes. One of these scenarios picks up the thought experiment mentioned above. It demonstrates the strong impact of reduced alkalinity fluxes on the pCO_2 (see Chapter 4.2).

o 2. Methods

The simulations were performed with the ecosystem model ECOHAM (Pätsch and Kühn, 2008) using the nesting method focussing on the central and southern North Sea (50.88° to 57.28°N, 3.42°W to 9.25°E) (Pätsch et al., 2010). The model system includes the hydrodynamic model HAMSOM (Backhaus, 1985; Pohlmann, 1996; Pätsch et al., 2017) and the vertically resolved sed-iment model originally developed for the deep open ocean (Heinze et al., 1999). The latter model has been adopted to shelf sea dynamics, details are discussed below. The 3D fields of temperature (T), salinity (S), advective flow and vertical turbulent mixing coefficients calculated by HAMSOM are used as forcing for ECOHAM. The time step of ECOHAM is 5 minutes.

2.1. The hydrodynamic Model The 3D fields of temperature,

The 3D fields of temperature, salinity, advective flow and vertical turbulent mixing coefficients calculated by the hydrodynamic model HAMSOM are used as forcing for the pelagic biogeochemical model ECOHAM. HAMSOM is a baroclinic, primitive equation model using the hydrostatic and Boussinesq approximations. The current velocities are calculated using a first order component-upstream scheme. The horizontal is discretized on a staggered Arakawa C-grid (Arakawa and Lamb, 1977) with a resolution of $\Delta\lambda = 1/3^{\circ}$ and $\Delta\phi = 1/5^{\circ}$. In a first step the model was applied on a larger area including the Northwest European Shelf (15.250°W - 14.083°E, 47.583°N - 63.983°N) (Lorkowski et al., 2012). For this large-domain run sea surface elevations of the semi-diurnal lunar tide M2 were prescribed at the open boundaries (Backhaus, 1985). The corresponding results of temperature, salinity and surface elevation were stored on the boundaries of the smaller model domain used in this study (black lines in Fig. 2). These data were used as boundary conditions for the hydrodynamic model HAMSOM implemented on the smaller domain with a vertical resolution of 5 m in the upper 50 m and increasing resolution below. The M2-tide is thus induced implicitely by the prescribed surface elevation at the boundaries. Details of the nesting procedure can be found in Schwichtenberg (2013).

55 2.2. The pelagic biogeochemical Module

In the same way as for the hydrodynamic model in a first step the biogeochemical model ran on the larger model domain and provided boundary conditions for the model on the smaller grid (Fig. 2). The pelagic biogeochemical model includes 4 nutrients (nitrate, ammonium, phosphate, silicate), two phytoplankton groups (diatoms and flagellates), two zooplankton groups (micro- and mesozooplankton), bacteria, two fractions of detritus (fast and slowly sinking), labile dissolved organic matter, semi-labile organic carbon, oxygen, calcite, dissolved inorganic carbon, and total alkalinity. Only for phytoplankton growth and exudation a Q_{10} value of 1.5 is defined. All other processes are temperature independent. Calcite formation is performed by flagellates, only. The molar ratio of soft tissue production to calcite production is 10:1. Opal is built by diatoms only and the ratio of carbon to opal production is 1.74:1. The model differentiates between normal exudation by phytoplankton, the result of which is labile dissolved organic matter with Redfield composition corresponding to the Redfield production, and an excess exudation of semi-labile organic carbon. The pelagic module is described in detail in Lorkowski et al. (2012). For this study we included the prognostic alkalinity calculation from Schwichtenberg (2013). The different processes (Fi) and their influence on alkalinity are:

• F01 - calcite dissolution

- F02 calcite formation
- F03 nitrification
- F04 uptake of nitrate
- F05 release of ammonium
- F06 uptake of ammonium
- F07 atmospheric deposition of ammonium
- F08 atmospheric deposition of nitrate
- F09 uptake of phosphate
- F10 release of phosphate
- These fluxes determine the change of alkalinity:

$$\frac{\partial TA}{\partial t} = 2(F01 - F02 - F03) + F04 + F05 - F06 + F07 - F08 + F09 - F10 \tag{1}$$

Together with the dynamic sediment module which exchanges TA and DIC with the pelagic system

86 it was possible to simulate the full carbonate system prognostically.

87 2.3. The Sediment Module

88 2.3.1. The open ocean sediment model

The original sediment model was developed by Heinze et al. (1999) for the global ocean. This model simulated accumulation, degradation and burial of particulate organic and shell material and a diffusive pore water exchange with the overlaying ocean. It was applied mainly for the deep ocean with its low amounts of incoming particulate matter compared to the shallow shelf sea export. The corresponding time scales of flux variations were rather large (annual to decadal) and showed no seasonal signal. This model included the solid components particulate organic matter (POM), calcite, opal and silt exported from the pelagic and the dissolved components phosphate (PO₄), dissolved inorganic carbon (DIC), alkalinity (TA), silicate (Si(OH)₄), nitrate (NO₃), oxygen (O₂), and dinitrogen (N₂).

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2.3.2. The vertical resolution

The upper 156 mm of the sediment are resolved by 12 layers with increasing thickness (2 - 24 mm). Below the deepest layer a dimensionless burial layer is implemented. 10:

2.3.3. New Components

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As the pelagic model delivers sinking particulate material with freely varying stoichiometry, we 104 differentiated benthic POM into the state variables particulate organic carbon (POC), nitrogen 105 (PON) and phosphorus (POP). Additionally we added ammonium (NH₄) as product of the in-106 complete aerobic degradation which can be oxidised by nitrification when oxygen is available 107 (Paulmier et al., 2009). The release of ammonium by aerobic degradation increases alkalinity. This ammonium can be nitrified locally which in turn leads to the combined effect of an alkalinity 109 decrease. Still it is possible that this ammonium is released or oxidised elsewhere. Nitrite is not 110 explicitly included. The model combines the effect of sulfate reduction and reoxidation of reduced 11: sulfate compounds as net sulfate reduction (i.e., sulfate reduction minus reoxidation). The differ-112 ent reaction equations including the alkalinity generation are listed in the appendix.

2.3.4. Varying Porosity

The effectivity of several sediment reactions depends on the porosity, i.e., the portion of pore 116 water in a given sediment volume. While the global ocean sediment model was implemented with a horizontally uniform porosity of 0.85 (Heinze et al., 1999), in the presented shelf application 118 varying porosities were taken into account. The main parts of the North Sea sediments consist of 119 sand, but there are also muddy areas and even rocky areas exist. The different sediment classes 120 are defined by the composition of grains with different diameters. W. Puls kindly delivered us a North Sea wide map of such grain compositions (pers. comm.). As the sediment model uses porosity values (P), the different grain size distributions have to be mapped to porosity values. 123 We used the median grain size (D50) to calculate the porosity (pers. comm. W. Puls):

$$P_{surf} = min(1, max(0.3, 0.2603 \cdot 1.20325^{D50}))$$
(2)

$$D50 = -\log_2 d \tag{3}$$

were d is the grain diameter in mm.

The resulting porosity values P_{surf} fall in the range [0.3,1]. Only for rocky sediments the porosity is defined as zero (Fig. 2). According to Heinze et al. (1999) porosities P(z) in deeper layers were defined in relation to the top layer:

Process	Turnover Rates	Open Ocean	Shelf	unit	Eqn. No
aerobic degradation	r1	$1.160 \cdot 10^{-13}$	$2.000 \cdot 10^{-10}$	$\frac{m^3}{mmol O_2 \cdot s}$	(7)
denitrification	r2	$1.157 \cdot 10^{-7}$	$1.736 \cdot 10^{-3}$	$\frac{1}{s}$	(8)
sulfate reduction	r3	$1.157 \cdot 10^{-9}$	$3.472 \cdot 10^{-9}$	$\frac{1}{s}$	(9)
calcite dissolution	r4	$1.000 \cdot 10^{-13}$	$1.000 \cdot 10^{-8}$	$\frac{m^3}{mmol\ CO_3^{2-} \cdot s}$	(10)
opal dissolution	r5	$1.000 \cdot 10^{-12}$	$1.000 \cdot 10^{-11}$	$\frac{m^3}{mmol SiO_2 \cdot s}$	(11)
nitrification	r6		$1.157 \cdot 10^{-4}$	$\frac{1}{s}$	(12)

Table 1: Comparison of open ocean (Heinze et al., 1999) and shelf (this study) turnover rates.

$$P(z) = P_{surf} \cdot e^{k_0 \cdot z(m)} \tag{4}$$

For $k_0 = 2.12$ and $P_{surf} = 0.3$ the deepest layer at $z_{k=12} = -0.144 \, m$ obtains a value of $P(z_{k=12}) = 0.22$.

2.3.5. Turnover Rates

The reaction equations and the chosen stoichiometries are described in detail in the Appendix.

These equations use turnover rates which were modified in comparison to the original open ocean
sediment model (see Table 1). One typical feature for the North Sea is that particulate organic
carbon fluxes and DIC effluxes are nearly balanced (de Haas et al., 2002). To achieve this we had
to increase the rates. Another criterion to alter the rates was to adapt the seasonality of oxygen
fluxes into the sediment to observations (Friedrich et al., 2015).

2.3.6. Temperature Dependency

As the shallow water column in the North Sea exhibits strong seasonal temperature variations ($\Delta T > 15^{o}$ C) a temperature dependency of both, the turnover rates (see Appendix) and the vertical diffusion was implemented.

A Q_{10} value of 1.2 for aerobic degradation, denitrification, nitrification, sulfate reduction and the dissolution of calcite and opal was chosen (see Appendix).

The vertical diffusion coefficient for all pore water tracers in the original open ocean model was constant ($dv = 10^{-9} \frac{m^2}{s}$). In the shelf model the coefficients were defined as temperature (T) and porosity (P) dependent (Gypens et al., 2008):

$$dv = \left\{ \begin{array}{rcl} (d_0 + a \cdot T) \cdot P & : & P < 0.4 \\ \\ (d_0 + a \cdot T) \cdot P^2 & : & P \geq 0.4 \end{array} \right. \label{eq:dv}$$

The parameters d_0 and a are defined in Gypens et al. (2008) (their Table 2) for different groups of pore water tracers: The lowest coefficient is defined for phosphate $(dv_{pho}(T_{10}) = 5.4 \cdot P \cdot 10^{-10} \frac{m^2}{s})$

a medium coefficient $(dv_{tra}(T_{10}) = 1.4 \cdot P \cdot 10^{-9} \frac{m^2}{s})$ is valid for the biogeochemical tracers DIC, nitrate, ammonium, alkalinity and silicate. The highest coefficient was defined for the gases oxygen and dinitrogen $(dv_{nit}(T_{10}) = 1.6 \cdot P \cdot 10^{-9} \frac{m^2}{s})$, all at $T_{10} = 10^{\circ}$ C and a porosity P < 0.4, which 15: is typical for sandy ground. In order to take into account advective exchange of pore water with 152 the pelagic system the coefficients for the uppermost layer were increased by a factor of 10. This factor was determined by several sensitivity runs to balance the exchange between the sediment 154 and the pelagic. An upper constraint for this factor was the limitation of the aerobic zone to the upper 1 cm of the sediment. The same factor is used by Neumann et al. (2017) to switch between 156 diffusive and advective nitrate exchange between sediment and pelagic in the German Bight. The 157 temperature of the sediment was defined as the temperature of the lowest pelagic layer. The vertical diffusion coefficient for DIC compares well with the corresponding coefficient given 159 by Burdige and Komada (2013) (their Table 3) for $T = 5^{\circ}$ C and P = 0.36.

2.4. External Data 162

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The meteorological forcing (Kalnay et al., 1996) and the river loads of carbon, alkalinity, nutrients 163 and organic compounds have been implemented according to Lorkowski et al. (2012). To treat 164 these tracers more realistically in this study also daily freshwater discharge of the rivers was used (Pätsch et al., 2016). In this way the input of tracers from the rivers (mmol d⁻¹) can be an 166 effective source or sink depending on the concentrations of the tracers in the river water. For 2011 167 the total N river input was $34.4 \text{ Gmol N yr}^{-1}$. 168 169

The calculated shortwave incoming radiation has been reduced by 10% as it has been shown that the sea surface temperature (SST) would otherwise be overestimated (compare Fig. 3 in Lorkowski et al. (2012)). 17:

The atmospheric nitrogen deposition was derived following Große et al. (2016), using annual data from the EMEP (Cooperative program for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) model. As our simulation period exceeds the period of data 174 available from EMEP a long-term trend according to Schöpp et al. (2003) was applied in addition. Atmospheric deposition is implemented as inputs of nitrate and ammonium. For 2011 the total N 176 deposition was $16.8 \text{ Gmol N yr}^{-1}$. 177

2.5. The Experiments

For each experiment described below the biogeochemical simulation in the central and southern North Sea area spun up over 20 years repeating the year 2000 until all processes were in equlibrium and did not change from year to year. After this procedure the years 2000 to 2014 were simulated 18 consecutively. 182

- Different experiments or scenarios were performed:
- The **reference run** with the new sediment module provides a basis with realistic boundary conditions and horizontally varying porosities.
 - In order to reproduce a situation without anthropogenic influence, we reduced the inorganic and organic river input of nitrogen and phosphorus to 10 % of the reference run. Additionally the atmospheric deposition of nitrogen was reduced to 28 %. This run more or less reproduced the "pristine conditions" Serna et al. (2010) established.
 - To analyse the impact of the new sediment module on the pelagic system we compare the results of the reference run with results of the scenario "plate run". In this scenario a simple sediment module was used, which collects, remineralises and releases the sunken particulate organic material on a two dimensional plate (Pätsch and Kühn, 2008).
- In the reference run horizontally varying porosities were used $(P_{min} = 0.3, P_{max} = 0.51)$.

 To study the influence of this feature we conducted two additional model runs with basin wide uniform porosities: One with the minimum porosity P_{min} and one with the maximum porosity P_{max} .

2.6. Error estimates

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To compare simulated results with observations a normalised error estimate was conducted. We used the following formula:

$$rms = \frac{\sqrt{\sum_{i=1}^{n} (obs_i - sim_i)^2}}{\sum_{i=1}^{n} \frac{obs_i + sim_i}{2}}$$
 (5)

Where n are the numbers of observations, obs_i and sim_i are the corresponding values of the observations and simulations taken from the same location. As simulation results we used the corresponding monthly means.

3. Comparison with Observations

To get confidence into the adapted sediment model we compared simulated and observed fluxes between sediment and pelagic. Additionally, simulated pore water profiles were compared with observed profiles.

3.1. Oxygen Fluxes

Brenner et al. (2016) measured the total oxygen consumption of sediment cores which can be 210 compared with simulated oxygen fluxes into the sediment. The corresponding available data and 21: their positions are shown in Fig. 3 (rectangles). The underlying map of simulated oxygen fluxes 212 at the time when observations were taken show reasonable values (rms = 0.312). Only in the 213 German Bight the model underestimates the measurements. An explanation for this effect is that 214 particulate organics (POM) imported by the rivers are considered as slowly sinking detritus. As 215 consequence the horizontal export of POM out of the German Bight is overestimated and the local 216 flux into the sediment is underestimated. 217

218 3.2. Alkalinity Fluxes

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Fig. 4 shows the comparison of fieldwide averaged alkalinity effluxes and the contributions from 219 aerobic degradation, denitrification, net sulfate reduction, nitrification and calcite dissolution from observations in September 2011 (Brenner et al., 2016) and from our model results for September 22: 2011. For the observational data only the spatial standard deviation of alkalinity efflux is given (see 222 grey error bar in Fig. 4a). The temporal standard deviation of the simulated daily values within 223 September 2011 is for all fluxes very small and not shown ($< 0.003 \,\mathrm{mmol}\,\mathrm{m}^{-2}\,\mathrm{d}^{-1}$). The spatial 224 standard deviation of the simulated September fluxes are shown as error bars in Fig. 4b. Even 22! though the simulated efflux lies within the high spatial variability of the observed alkalinity efflux, 226 the model rather underestimates all contributions. Only the simulated contribution from aerobic degradation is larger than the corresponding observation. The main deviation can be attributed 228 to the low simulated calcite dissolution within the sediment. The rms error of alkalinity generation is 0.655. 230 In comparison to other models (Ridgwell et al., 2007; Lorkowski et al., 2012) the ratio of simulated 23: 232

particulate organic carbon to particulate inorganic carbon (POC:PIC) DELETED: or the .. is relatively low meaning high calcite production in relation to organic carbon production. Nonetheless our model still leads to an underestimation of the calcite dissolution in the sediment compared to the analysis of Brenner et al. (2016). DELETED: (The mean simulated ..) Calcite production is reported to occur sporadically, which in turn would characterize the observations not necessarily representative for the southern and central North Sea.

Fig. 5 shows the corresponding simulated alkalinity fluxes to the pelagic system for DELETED:
15September 2011. The alkalinity efflux is strongest in the German Bight near the mouth of River
Elbe. The flux decreases with distance from the continental coast. Elevated values can be seen
off the Danish coast. Similar features can be observed for the contributors aerobic degradation,

denitrification, net sulfate reduction, and calcite dissolution. The distribution of the negative
fluxes due to nitrification shows also elevated values in the German Bight.

When ignoring the sedimentary calcite dissolution in both the simulation and the observed data,
the remaining alkalinity generation compares better with the observations (Fig. 6). The rms
error reduces to 0.447. DELETED: The colors within the four rectangles identify the strength
of the observational data whereas the horizontal distribution shown by the colored map stands
for simulations. Only in the inner German Bight the simulated flux appears far too low. An
explanation for this effect is the same as for oxygen fluxes: The export of POM out of the German
Bight is overestimated and thus local remineralization underestimated.

252 3.3. Profiles

During the cruise He-308 in May 2009 several sediment cores in the German Exclusive Economic Zone (EEZ) were taken and investigated. The nitrate data are published by Neumann et al. 254 (2017), all data are archived in Pangaea (2017). We compare our results of the reference run 255 with observed data of oxygen, nitrate, phosphate and ammonium (Fig. 7). To understand the model sensitivity, also the corresponding profiles of the "pristine conditions" run are shown. The 257 position of the chosen core is between the German coast and the island Helgoland (54° 5'N, 8° 258 E). This area is strongly affected by high nutrient loads from the continental rivers and high atmospheric nitrogen deposition (Pätsch et al., 2010) resulting in significant differences in the simulated 260 porewater concentrations of the reference run and the scenario "pristine conditions" (solid and dashed black lines). The simulated oxygen penetration depth (concentration $< 10 \,\mathrm{mmol}\,\mathrm{O}_2\,\mathrm{m}^{-3}$) 262 is about 0.5 cm which fits to the observations (Fig. 7a). It is about 0.8 cm in the scenario "pristine 263 conditions". In the upper 0.4 cm the model underestimates in both scenarios the observed oxygen 264 concentrations. Fig. 7b shows the profiles of observed NO_x including nitrate and nitrite and the 26 profiles of simulated nitrate. This seems to be a proper comparison as observed nitrite concentrations are low ($< 0.8 \,\mathrm{mmol}\,\mathrm{N}\,\mathrm{m}^{-3}$, not shown). Observed NO_x concentrations are detectable only 26 in the upper 2 cm. Due to uncalibrated measurements deeper values appear discriminable from 268 zero concentration, but they should be interpreted as zero concentration (pers. comm. Andreas Neumann). The simulated concentrations (reference run) reach very low values already at 1 cm 270 depth, the "pristine conditions" scenario shows very low concentrations already at 0.5 cm depth. 27: Observed phosphate concentrations in Fig. 7c indicate two mixing regimes: In the upper 9 cm the sediment core shows concentrations slightly increasing with depth, below a stronger gradient can 273 be seen. The upper part appears well-mixed while in the lower part mixing decreases. This effect might be caused by bioturbation and bioirrigation in the upper 9 cm. As the latter processes are 275 not included in the model we got a more homogenous picture of the phosphate profiles. The model (reference run) overestimates the observational values in the upper part while it underestimates

them in the lower part. A similar pattern can be seen for ammonium (Fig. 7d), where again the observational concentrations indicate an upper and a lower mixing zone. The simulated values increase between the surface and the 5 cm horizon, below they are more or less constant. The values of the reference run are too high in the upper 13 cm. These high simulated ammonium values might be caused by neglecting the process of anammox in the model. This process transforms reactive nitrogen compounds (ammonium and nitrite) into inert molecular nitrogen. Similar high ammonium concentrations can be found in Luff and Moll (2004) within their Fig. 9.

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4. Results

37 4.1. Temporal Variations

The temporal development of monthly alkalinity effluxes (2000 - 2014) without calcite dissolution of a near coast station (54° N, 8° E) shows an overall decreasing trend (Fig. 8). To understand this feature the sources of alkalinity generation and the annual loads of nitrate by the River Elbe (Radach and Pätsch, 2007; Pätsch et al., 2016) in the German Bight (53.9° N, 8.9° E) are shown (see Fig. 1a). Calcite dissolution is very variable and exhibits a decrease over the simulation period. Because of its high variability which would overwrite the nitrogen-related signals calcite dissolution is not shown.

Aerobic degradation with a distinct annual cycle appears quite constant over the years. Sulfate reduction is more or less constant, while nitrification (as negative contribution) shows a positive trend in opposite to the negative trend of denitrification. The dark blue line represents the nitrate discharge of the nearby River Elbe. With strong seasonal peaks it exhibits a negative trend which can explain a similar trend in denitrification.

300 Strong nitrate discharge events are followed some months later by local maxima in denitrification.

An anylysis of the correlation of these two time series showed highest and significant coefficients (r > 0.65) for 2-3 months time shift. This can be seen in 2003 and 2011. Over several successional winter months in 2007/2008 high nitrate loads lead to strong denitrification in 2008. In all these years the TA efflux was elevated. This is reflected by high lag correlations (r > 0.63) of the time series Elbe nitrate and TA generation for time shifts of 4-5 months.

306 4.2. Alkalinity Generation and pCO₂

As already demonstrated in the thought experiment in the introduction the alkalinity release from the sediment has a significant impact on the carbonate system and thus on the ΔpCO_2 regulating the exchange of CO_2 between the atmosphere and the sea.

Using the simulated timeseries 2000 - 2014 (reference run) we analysed the cumulative alkalinity efflux out of the sediment from the beginning of the year 2011 to mid September 2011 (Fig. 9a).

Near the Danish coast we found a flux of about $1000 \text{ } mmol \text{ } m^{-2}$ for this period. For the inner German Bight even higher values can be found. These maxima result in corresponding areas of 313 strong undersaturation in respect of ΔpCO_2 for DELETED: 15 September (Fig. 9b). The interior 314 and the northwestern part are slightly oversaturated. Near coastal areas of strong undersaturation 315 are also affected by high primary production, which in addition to the alkalinity efflux from the sediment lowers the ΔpCO_2 . This could be shown in an additional experiment where these effluxes 317 were artificially switched off. 318 Fig. 9c shows the alkalinity flux of the "pristine conditions" run until mid September. The 319 flux reduction (compare with Fig. 9a) is strongest ($\approx 20\%$) in areas where the generation of 320 alkalinity was strongest. Areas of oversaturation of ΔpCO_2 (Fig. 9d) increase and especially in 32: the shallow areas with high sediment impact the previously undersaturated situations turn into 322 oversaturation (or light undersaturation). Because of the distance to the rivers the situation is more or less unchanged in the central part. 324 As the effect of alkalinity generation until mid of September on the mean September ΔpCO_2 325 distributions is not straight forward we analyzed additionally the horizontal distributions of the temporal cumulated air-sea flux of CO_2 until mid of September (not shown). Similar as for the 32 ΔpCO_2 distributions in September more or less no differences between the reference run and the 328 "pristing conditions" run can be seen in the deeper water of the northern areas. Small differences 329

can be found in the southern open sea areas, but high differences occur near the continental coast

where also the differences due to altered primary production exist.

332 4.3. Sensitivity on different porosities

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To investigate the effect of spatially varying porosities we conducted two additional simulations 333 which were spun up separately: One with a basin wide uniform porosity with the minimum value 334 of the reference run except for rocks $(P_{\min} = 0.3)$ and one with the maximum value $(P_{\max} = 0.51)$. 335 For the different annual fluxes between the sediment and the pelagic at 54° 5′N, 8° E the relative 336 deviations (%) of these two runs are analysed for 2011 (Fig. 10). 33 Switching over from the P_{min} to the P_{max} run the diffusive flux of DIC, alkalinity and phosphate out of the pore water of the sediment increases by about 4%. The flux of silicate from the 339 sediment increases by 16%. Also the import of oxygen and nitrate increase. This overall increase is astonishing as the effective diffusivity decreases when the porosity passes over the limit of 0.4 34: (see section 2.3.6). Of interest are also the deviations of the five contributors to the alkalinity flux, 342 i.e., the alkalinity flux due to the aerobic degradation (+7%), the calcite dissolution (+3.4%), the denitrification (+1.5%), the sulfate reduction (-7.8%) and the (negative) nitrification (-0.5%). Sulfate reduction decreases as the amount of POC reaching the deeper sediment layers decreases due to the enhanced aerobic remineralisation.

Due to positive feedback mechanisms on the nutrients in the water column the sinking fluxes of particulate organic matter (POC, PON, POP) increase. The largest increase in solids entering the sediment can be found for opal (+5.6%) corresponding with the large silicate efflux from the 349 sediment into the pelagic. Calcite export slightly decreases as the silicon shell building diatoms 350 are favored by the increased silicate availability. To understand this contra-intuitive dynamics we compared the model results of the high porosity 352 run with the low porosity run in the first and second spinup year. At the beginning of the first spinup year all conditions are the same. Until spring the flux of oxygen into the sediment was lower 354 in the high porosity run because there the effective diffusivity was lower than in low porosity run. 35! The lower oxygen content in the high porosity run stimulated the benthic anaerobic processes. At the end of the first year this resulted into a higher efflux of ammonium (+5.8%) from the 357 sediment in the high porosity scenario. The higher ammonium efflux of the high porosity scenario was not compensated by the higher nitrate flux into the sediment (+1.6%). At the end of the year 359 more DIN was in the pelagic water column in the high porosity scenario than in the low porosity 360 scenario. In the second year this surplus of DIN stimulated higher primary production for the high porosity scenario. The corresponding enhanced particle export additionally increased the benthic-362 pelagic fluxes. The loss of molecular nitrogen due to enhanced denitrification was compensated by 363 the larger ammonium efflux. These deviating dynamics are even stronger at stations with lower 364 pelagic DIN concentrations in off-shore areas.

4.4. Comparison of the vertical resolved and the plate sediment module

In former model versions (Pätsch and Kühn, 2008; Lorkowski et al., 2012; Große et al., 2016) the 367 sediment was represented by a two-dimensional plate without depth resolution. The sinking material was gathered and remineralised on the surface of this plate. The remineralisation rates had been adjusted so that the particulate organic material from the last year was more or less dissolved 370 and released until February/March of the following year.

The temporal development of carbon exchange between sediment and pelagic in 2011 at 54° 5′N, 372 8° E is shown in Fig. 11a for the "plate run". The time in the year when half of the exported 373 particulate material is returned as DIC ("half time") is indicated by the black arrow on the x-axis. 374 For the "plate run" this is day 230. 375

Fig. 11b shows the corresponding carbon fluxes of the reference run. While the shape of the curve representing the particulate export is similar to that of Fig. 11a, the remineralisation flux shows 37 less temporal variation. Due to the high remineralisation flux in winter the "half time" is reached earlier (day 207). 379

The different carbon remineralisation rates in the sediment and the simulated concentrations of

particulate organic carbon and oxygen of the reference run and the "plate run" resulted in comparable effluxes of carbon.

There are several reasons for the deviating seasonal cycle of DIC efflux. In general the less pronounced cycle comes about

- the structure of the 3d-sediment model in which the fastest reaction occurs in the very thin upper layer. Lower layers act more slowly,
- the fact that the remineralization fluxes do not produce immediately effluxes. In case of the 3d-sediment model the dissolved compounds have to be transferred via diffusion into the pelagic system,
 - the high concentration of POC in the 3d-sediment model: Whereas in the 2d-plate model nearly all POC is dissovled after winter, in the 3d-sediment model still a relative high standing stock of POC remains.

5. Discussion

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96 5.1. Nitrogen related processes

After calcite dissolution benthic denitrification is the second largest positive contribution to alkalinity generation (Fig. 4). Near-bottom nitrate concentration which is correlated with near bottom oxygen saturation governs the direction of nitrate exchange across the pelagic - sediment interface (Neubacher et al., 2011). In case of the invasion of pelagic nitrate into the sediment benthic den-400 itrification is stimulated. The other source of benthic nitrate is the benthic nitrification which is 40 driven by oxygen within the sediment. At 54° N, 8° E, however 86 % of oxygen are consumed by 402 aerobic degradation and only 14 % by benthic nitrification. For shelf seas Seitzinger and Giblin 403 (1996) estimated the local benthic denitrification rate (DNR) to be about 2% of the local primary 404 production (PP). This estimate, of course, can be influenced by parameters like water depth, ad-405 vection, and near bottom oxygen consumption. Indeed the evaluation of our reference run shows that the relation r=DNR/PP was about 2% in regions with water depth of about 30 m and an 407 annual Redfield production (see 2.2) of about 150 $g C m^{-2} y r^{-1}$, which can be found some tens of 408 kilometers off the mouths of the big rivers. According to our simulations r is only larger than $2\,\%$ near the mouth of River Elbe. For all other regions r ranges between 1.1% and 1.4%. 410

In the case of the ammonium profile (Fig. 7d) the "pristine conditions" simulation matches the observation better than the reference run. This might have to do with the absence of the process

anammox within the model which would consume ammonium under presence of nitrite.

The comparison of the reference run and the "pristine conditions" run exhibits a deeper penetration of oxygen into the sediment for the pristine more nutrient depleted scenario (Fig. 7a). This is in accordance with the findings of Neubacher et al. (2011) who differentiated a realistic and a rich hypoxic situation, the latter with lower penetration depths.

420 5.2. Sources of Alkalinity

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An effective tracer of North Sea total alkalinity is the naturally occurring radium isotope ²²⁸Ra 42 (Burt et al., 2014). These authors estimated a coastal alkalinity input of 3.4 - 23.6 $mmol \, m^{-2} \, d^{-1}$ into the southern North Sea (A=190.765 km²) in September 2011. This input was assumed to come 423 mainly from the Wadden Sea. The amount of this input lies in the same range Brenner et al. (2016) 424 estimated as total input from the sediments into the pelagic southern North Sea (Fig. 4). This 425 estimate is valid for a late summer situation and includes the large effect of calcite dissolution. For 426 the southern North Sea calcite dissolution and production is roughly balanced on an annual basis. The estimate by Burt et al. (2014) and the measurements by Brenner et al. (2016) appear high 428 in comparison to the value given by Thomas et al. (2009) who estimated an alkalinity input from 429 the Wadden Sea of 1 $mmol m^{-2} d^{-1}$ into the south-eastern North Sea over the year. This value was calculated using an alkalinity budget which does not differentiate input from autochthonous 43: sediment and from the adjacent Wadden Sea and, additionally, does not take into account calcite production and dissolution. 433 Together with our simulation results the following picture can be given: The relative high flux 434 esimates by Burt et al. (2014) and Brenner et al. (2016) can be explained by the inclusion of calcite dissolution and the time in the year when measurements were taken. When calcite dissolution is 436 excluded our annual estimate for the total model region $(0.4 \, mmol \, m^{-2} \, d^{-1})$ can be compared with 43 the estimate by Thomas et al. (2009) for the south-eastern North Sea with higher productivity than the average of the model region.

440 6. Conclusion

Even though our model may slightly underestimate benthic denitrification in the southern North
Sea it reveals this process as the largest net contribution to alkalinity generation in this area.
This compares well with the estimates by Brenner et al. (2016) when the dissolution of calcite is
not taken into account, because the observational data might miss the calcite production signal
which then would cancel out the effect on alkalinity. Estimates of other alkalinity fluxes like
alkalinity generation in the Wadden Sea are not taken into account as their estimates appear

not well constrained. A direct modelling approach of such sources of alkalinity appears necessary (Schwichtenberg, 2013), but is beyond the scope of this study.

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8. Figure Caption

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Fig. 1 a) Surface alkalinity concentrations (mmol kg $^{-1}$) measured in September 2001, b) corresponding ΔpCO_2 (ppm), the difference of partial pressure of ocean and atmospheric pCO₂, c) reduced alkalinity concentrations due to a reduction of 50 % of the estimated alkalinity flux by Brenner et al. (2016), d) ΔpCO_2 corresponding to the reduced alkalinity in c).

Fig. 2 Porosity field according to W. Puls (pers. comm.). Blue areas indicate rocky sediments, red areas indicate muddy sediments with low grain diameters and green areas indicate sandy ground.

The black lines indicate the model boundaries.

Fig. 3 Simulated and observed oxygen fluxes (mmol O_2 m⁻² d⁻¹) for DELETED: 15 September 2011. The observations by Brenner et al. (2016) are indicated by the colored rectangles.

Fig. 4a): Mean observed alkalinity flux for the southern North Sea in September 2011. Additionally the derived mean alkalinity generation due to aerobic degradation, dentrification, net sulfate reduction and calcite dissolution are shown. A sink for alkalinity is nitrification. All fluxes in mmol m⁻² d⁻¹ (Brenner et al., 2016). b): Simulated alkalinity flux for the southern North Sea in DELETED: 15 September 2011. Additionally the alkalinity generation and reduction due to aerobic degradation, dentrification, net sulfate reduction, nitrification and calcite dissolution are shown. The grey error bars indicate the spatial standard deviation.

Fig. 5 a) Simulated net alkalinity generation and corresponding sources and sinks due to b) aerobic degradation, c) denitrification, d) net sulfate reduction, e) nitrification, f) calcite dissolution in September 2011. All fluxes in mmol m^{-2} d⁻¹. The scale of a) - d) is identical.

Fig. 6 Simulated and observed alkalinity generation (mmol m⁻² d⁻¹) without calcite dissolution for DELETED: 15 September 2011. The observations are indicated by the colored rectangles.

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Fig. 7 Profiles of porewater concentrations of a) oxygen, b) nitrate, c) phosphate and d) ammonium at 54° 5′N, 8° E in May 2009. Nitrate data were published by Neumann et al. (2017). The black solid line indicates the reference run, the dashed black line represents the results of the "pristine conditions" scenario and the different blue lines are derived from observations during the cruise He-308. In the figures b-d repeated observational profiles are shown. Notice the different profile depths.

Fig. 8 Simulated monthly values of alkalinity efflux from the sediment without calcite dissolution at 54° N, 8° E, the corresponding sources and sinks due to aerobic degradation, denitrification, net sulfate reduction, nitrification and the annual loads of nitrate from River Elbe (Radach and Pätsch, 2007; Pätsch et al., 2016). Note: nitrification has a negative contribution to the alkalinity generation.

Fig. 9 a) Simulated cumulative alkalinity generation in 2011 until mid September (mmol m⁻²) for the reference run b) the corresponding ΔpCO_2 in September, c) cumulative alkalinity generation until mid September with reduced river input (10%) and only 28 % atmospheric nitrogen deposition ("pristine conditions"), d) ΔpCO_2 in September ("pristine conditions").

Fig. 10 Deviations between the "high" and the "low" porosity run. Shown is the relative change of annual fluxes (%) between the sediment and the pelagic for a station at 54° 5′N, 8° E in 2011. DIC, TA, PO₄, SiO₄, N₂, NH₄ indicate the diffusive fluxes of dissolved matter from the sediment into the pelagic. Ox and NO₃ are corresponding fluxes from the pelagic into the sediment. aeralk, cacalk, dnralk, suralk and nitalk indicate the partitioning of the alkalinity flux according to its sources aerobic degradation, calcite dissolution, denitrification, sulfate reduction and nitrification, respectively. The fluxes of solids from the pelagic into the sediment are POC, PON, POP, OPAL and CaCO3.

Fig. 11 Temporal development of carbon fluxes between the pelagic and the sediment at 54° 5′N,
8° E in 2011 for a) the "plate run" and b) the reference run. The time in the year when half of the
deposited particulate material is returned as DIC is indicated by the black arrow on the x-axis.

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597 10. Appendix

⁵⁹⁸ 10.1. Equations for solid and dissolved sediment components

Dissolved Matter: exchange with the pelagic ecosystem model ECOHAM

600
$$(DIC(i=1), TA(i=2), PO_4(i=3), NO_3(i=4), NH_4(i=5), N_2(i=6), SiO_4(i=7),$$

601 $O_2(i=8))$

$$\frac{\partial C_i}{\partial t} = dv_i \frac{\partial^2 C_i}{\partial x^2} + \frac{R_j}{P} \qquad j = 1,..,6$$
 (6)

 $R_j: [mmol \, m^{-3} \, s^{-1}]$ are reaction terms for the dissolved matter. P: Porosity

 $_{603}$ dv_i are the vertical diffusion coefficients described in section 2.3.6.

Solids: input from the pelagic ecosystem model ECOHAM

 $(POM(C/N/P), CaCO_3, SiO_2 \text{ (Opal)}, Silt \text{ (with predefined constant input)})$

$$\frac{\partial S_j}{\partial t} = D \frac{\partial (w S_j)}{\partial z} - \frac{R_j}{1 - P} \qquad j = 1, ..., 5$$
 (7)

 $w: \ vertical \ advection \ (downward) \qquad \quad R_j: \ [mmol \ m^{-3} \ s^{-1}]$

607 10.2. Reaction Terms R_j

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• Degradation of POM

- aerobic degradation (j=1)

$$R_{POC}^{AD} = r_1 \cdot T_{fac}(T) \cdot [POC] \cdot [O_2]$$
(8)

$$r_1: \left[rac{m^3}{mmol \, O_2 \cdot s}
ight]$$

$$R_{PON}^{AD} = R_{POC}^{AD} \cdot \frac{rnit}{rcar}$$

$$R_{POP}^{AD} = R_{POC}^{AD} \cdot \frac{1}{rcar}$$

- anaerobic degradation

* DNR (denitrification) (j=2)

$$R_{POC}^{DNR} = r_2 \cdot T_{fac}(T) \cdot \left(1 - \frac{[O_2]}{[O_2^{half}] + [O_2]}\right) \cdot \min\left(\frac{\frac{1}{2}[NO_3^-]}{nitdem}; [POC]\right)$$
(9)

 $r_2: \lceil rac{1}{r}
ceil$

* SR (sulfate reduction) (j=3)

$$R_{POCs}^{SR} = r_3 \cdot T_{fac}(T) \cdot \min(\frac{[TA]}{rnit}; [POC])$$

$$r_3 : \left[\frac{1}{s}\right]$$
(10)

• $CaCO_3$ dissolution (j = 4)

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$$R_{CaCO_3} = r_4 \cdot T_{fac}(T) \cdot [CaCO_3] \cdot (\max([CO_3^{2-}]^{sat} - [CO_3^{2-}]; 0))$$

$$r_4 : \left[\frac{m^3}{mmol\ CO_3^{2-} \cdot s}\right]$$
(11)

 $r_4: \lfloor \frac{m}{mmol\,CO_3^{2-}\cdot s}
brace$ 620 $[CO_3^{2-}]^{sat} = \frac{ksp}{Ca}$

ksp: apparent pressure corrected solubility product of calcite

 $_{622}$ Ca = 10.3 [mol m⁻³]: Calcium concentration

• SiO_2 (Opal Dissolution) (j=5)

$$R_{SiO_2} = [SiO_2] \cdot r_5 \cdot T_{fac}(T) \cdot ([Si(OH)_4]^{sat} - [Si(OH)_4])$$
(12)

$$r_5: \left[\frac{m^3}{mmol\,Si(OH)_4\cdot s}\right]$$

$$\left[Si(OH)_4\right]^{sat} = 1\,mol\,m^{-3}$$

• NH_4 (Nitrification) (j=6)

$$R_{NH_4}^{NO_3} = r_6 \cdot T_{fac}(T) \cdot [NH_4] \tag{13}$$

 $r_6: \left[\frac{1}{s}\right]$

with
$$T_{fac}(T) = 1.2^{\frac{T-T_0}{T_0}}$$
 with $T_0 = 10^{\circ} C$ (14)

- 629 10.3. Reaction Equations and Stoichiometry
- All stoichiometric factors are based on $R_0 = rcar + \frac{1}{4}z$ with rcar = C/P
- and z: H-excess for the notation of organic matter: $C_x (H_2 O)_w (NH_3)_y H_z H_3 PO_4$
- 1) Incomplete Aerobic Remineralisation (after Paulmier et al., 2009)

$$C_a H_b O_c N_d P + \underbrace{\left(a + \frac{1}{4}b - \frac{1}{2}c - \frac{3}{4}d + \frac{5}{4}\right)}_{=ro2ut} \cdot O_2$$

$$\longrightarrow a \cdot CO_2 + d \cdot NH_3 + H_3PO_4 + (\frac{1}{2}b - \frac{3}{2}d - \frac{3}{2})H_2O$$

with
$$R_0 = a + \frac{1}{4}b - \frac{1}{2}c - \frac{3}{4}d + \frac{5}{4} \implies ro2ut = R_0$$

with
$$a = rcar = C/P$$

$$b = H/P$$

$$c = O/P$$

$$d = rnit = N/P$$

2) Complete Denitrification (after Paulmier et al., 2009)

$$C_a H_b O_c N_d P + (\underbrace{\frac{4}{5}a + \frac{1}{5}b - \frac{2}{5}c + 1}_{=nitdem}) \cdot HNO_5$$

$$C_{a} H_{b} O_{c} N_{d} P + (\underbrace{\frac{4}{5}a + \frac{1}{5}b - \frac{2}{5}c + 1}_{=nitdem}) \cdot HNO_{3}$$

$$\longrightarrow a \cdot CO_{2} + H_{3}PO_{4} + (\underbrace{\frac{2}{5}a + \frac{3}{5}b - \frac{1}{5}c - 1}_{=1}) \cdot H_{2}O + (\underbrace{\frac{2}{5}a + \frac{1}{10}b - \frac{1}{5}c + \frac{1}{2}d + \frac{1}{2}}_{n2prod}) \cdot N_{2}$$

with
$$R_0 = a + \frac{1}{4}b - \frac{1}{2}c + \frac{5}{4} \implies n2prod = \frac{2}{5}R_0 + \frac{4}{5}d = \frac{1}{2}(nitdem + d)$$

$$nitdem = \frac{4}{5}R_0 + \frac{3}{5}d$$

- ₆₄₅ 3) Sulfate Reduction
- for $O_2 < 1\mu M$ and $NO_3 < 1\mu M$:

$$C_{a} H_{b} O_{c} N_{d} P + (\underbrace{\frac{1}{2}a + \frac{1}{8}b - \frac{1}{4}c - \frac{3}{8}d + \frac{5}{8}}_{=R_{0}/2}) \cdot H_{2} SO_{4}$$

$$\longrightarrow a \cdot CO_{2} + d \cdot NH_{3} + H_{3} PO_{4} + (\frac{1}{2}b - \frac{3}{2}d - \frac{3}{2}) \cdot H_{2} O$$

$$1 \quad 1 \quad 1 \quad 3 \quad 5$$

$$+(\underbrace{\frac{1}{2}a + \frac{1}{8}b - \frac{1}{4}c - \frac{3}{8}d + \frac{5}{8}}_{=R_0/2}) \cdot H_2S$$

- 4) Nitrification of ammonia to nitrate
- for $O_2 > 1 \mu M$
- $NH_3 + 2 \cdot O_2 \longrightarrow HNO_3 + H_2O$
- 653 10.4. Alkalinity Generation
- $R_{TA} = rnit \cdot R_{POC}^{AD} + nitdem \cdot R_{POC}^{DNR} + rnit \cdot R_{POCs}^{SR} + 2 \cdot (R_{CaCO_3} R_{NH_4}^{NO_3})$