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**Biogeochemistry in  
deeper coastal  
sediments**

J. M. Holstein and  
K. W. Wirz

# On the origin of highly active biogeochemistry in deeper coastal sediments – inverse model studies

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## Abstract

In coastal sediments, zones with highly active diagenesis may be situated below the usually studied first decimeters. Pore water profiles from a backbarrier tidal flat in the German Wadden Sea display a  $\text{SO}_4$  minimum zone associated with a distinct  $\text{NH}_4$  peak at a sediment depth of around 1.5 m. Such evidence for significant degradation of organic matter (OM) is challenging our understanding of tidal flat biogeochemistry as little is known about processes that rapidly transfer reactive OM into layers far distant from the sediment-water interface. We here test and compare two different scenarios for OM transfer: scenario A assumes rapid sedimentation and burial of OM, scenario B assumes lateral advection of suspended POM. A diagenetic model is adapted to describe both hypotheses. Uncertain process parameters, in particular those connected to OM degradation and (vertical or lateral) transport are systematically calibrated using existing data.

We found that both scenarios, advection and sedimentation, have solutions consistent with the observed pore water profiles. Constrained process parameters are within the range of reported values. Solutions to scenario B describing advective transport of particulate material are, however, rather improbable due to highly specific assumptions on the OM source and flow geometry. In the alternative deposition set-up, model simulations suggest that the source OM was deposited about 60 yrs earlier (1945). A mean sedimentation rate of approximately  $2 \text{ cm yr}^{-1}$  indicates substantial changes in near coast sediment morphology, since sea level rise is at a much lower pace. High sedimentation rates most probably reflect the progradation of flats within the study area. These or similar morphodynamic features also occur in other coastal areas so that regional values for OM remineralization rates may often be much higher than predicted from surface biogeochemistry.

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## 1 Introduction

Coastal sediments are critical for marine life. Anthropogenic factors such as eutrophication, coastal constructions, and accelerated sea level rise endanger the functioning of coastal habitats as breeding areas for fish, resting areas for birds, and for water quality restoration, with relevant impacts on neighboring ecosystems (Postma, 1983; De Jong et al., 1993; Lozán et al., 1994; Jentoft and McCay, 1995). Beyond, coastal sediments have a global footprint due to intensive nutrient remineralization and the release of greenhouse gases (Bange, 2006) which emphasizes the need to understand the driving mechanisms that regulate coastal biogeochemical cycling.

Shallow coastal seas are known not only for their rapid biogeochemical cycling, but also for significant changes in morphology. In particular, tidal flats continuously grow or disappear, and they may connect and disconnect laterally. However, little is known about how morphodynamics, lateral pore water flow and biogeochemical cycles are related. How can signals in the vertical distribution of major geochemical species like Particulate Organic Matter (POM), ammonium ( $\text{NH}_4$ ) or sulphate ( $\text{SO}_4$ ) be indicative for morphological changes? Or, asked from the opposite site, to what extent is the effective remineralization potential of coastal systems shaped by vertical changes (loss and deposition of sediments) and horizontal subsurface transport?

Especially with respect to climate change and the inevitable rise of sea level, the sediment budget needs to be understood in order to assess consequences of shifts in morphodynamic balance (Voss and van Kesteren, 2000). Here, models are important tools to identify key processes, more completely assess collected data and predict future trends. Inverse modeling allows to constrain parameters that can only be measured with great difficulties (Usbeck et al., 2003; Holstein and Wirtz, 2009).

In this paper, we study the origin of the unusual high reactivity at the rim of a tidal flat using a modelling approach. In particular, we test two hypotheses regarding the most probable transport mechanism of labile POC in deeper tidal sediments: lateral transport by advection and burial by rapid sedimentation. This way, we aim to elucidate the

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quantitative effect of both processes on the vertical distribution of major biogeochemical species. Biogeochemical parameters could be constrained as well as relevant estimates for local deposition.

### 1.1 The transgressive barrier island depositional system

5 The Wadden Sea at the southeastern edge of the North Sea covers one of the world's largest tidal flat areas. Confined by a meso-tidal barrier island chain with intermittent estuaries of major river systems, the large siliciclastic back barrier tidal flats host a rather resilient ecosystem in the midst of a densely populated and highly industrialized region (Hertweck, 1994; Ducrotoy and Elliott, 1997; Kock, 1998; Grimm et al., 1999).

10 The assembly of the modern Wadden Sea with tide-dominated barrier islands was induced 5000 years BP (Behre et al., 1979). During the last 1000 years coastal protection structures and land reclamation efforts stopped the transgression, establishing a new morphodynamic balance (Flemming, 1992). Nevertheless, in the course of future sea level rise the accretion space will narrow and the tidal flat depositional system will ultimately disappear (Flemming and Davis Jr., 1994; Flemming and Bartholomä, 1997).

15 The coastal morphology is in constant motion. Up to now, the rate of sedimentation easily keeps pace with rising sea-level (recently 1–2 mm/yr) and therefore the islands and the tidal flats accrete and migrate laterally with time maintaining hydro-morphometric balance (Eisma, 1993; Oost and De Boer, 1994). The gradual morphology reshape is recorded by the sediments if not eroded. While vertical seabed oscillation may add up to more than 500 mm of sediment deposited or eroded during a year by hydrodynamic forces (chiefly tides and storms), they are thought to be mostly event driven, short termed and local, thus having no significant impact on the regional sediment budget (Voss and van Kesteren, 2000; Tilch, 2003). In contrast, longer termed average sedimentation rates that deviate from the mean sealevel rise and changed flat progradation rates indicate morphodynamic evolution of the tidal flats (Yang et al., 2001, 2006).

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## 1.2 The fate of organic matter

Decay of organic matter (OM) largely differs between surface and deeper sediments. Bioirrigating and bioturbating organisms considerably affect biogeochemical cycling and transport in the upper 10–20 cm of the sediment (Aller and Aller, 1998; Berg et al., 2001; D'Andrea et al., 2004; Meysman et al., 2006). Moreover, at the top sediment layer of the sands and muddy sands of the backbarrier area, interactions of bottom water currents and sediment topography induce continuous flushing of the uppermost benthic layers (Roy et al., 2002; Precht and Huettel, 2004; Cook and Roy, 2006), leading to rapid exchange of solutes (Precht and Huettel, 2003; Precht et al., 2004) and to filtration of organic particles that are degraded on the spot (Rusch and Huettel, 2000; Huettel et al., 2003). Although, the actual contents of reactants may be low, high turnover rates in surface sediments are maintained by the constant supply of reactants and removal of metabolites (Huettel et al., 2006). Pore water advection induced by bottom-flow-topography interaction acts down to 10 cm deep into the sediment (Huettel et al., 1998). This flow regime, also named “skin-circulation” by Billerbeck et al. (2006), varies on scales of few centimetres and timescales of days in contrast to the “body-circulation”, that is a deep-reaching flow regime with small flow velocities driven by tidal pumping (Robinson et al., 2007; Gibbes et al., 2008). Large scale advection is a major contributor for geochemical cycling in meso-tidal coastal sediments (Whiting and Childers, 1989; Robinson et al., 2006) which has been specifically well documented for the Spiekeroog backbarrier tidal flats (Billerbeck et al., 2006; Beck et al., 2008; Roy et al., 2008). Subterranean aquifers are sparsely investigated contributors to coastal geochemical cycling, but may have major impact on budgets by connecting large areas and high flow velocities (Schlüter et al., 2004).

If the stratigraphic sequence is unaffected by gravity flows or other events that may dislocate significant amounts of sediment, deposits at greater depth usually are much less reactive than surface sediments. Aged autochthonous organic material is remineralized at notably reduced rates (Middelburg, 1989) and lower diffusion rates within the tighter

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pore space contribute to the general decrease of turnover rates with depth. Except for continental margin sediments, where gravity flows are a general feature (Hensen et al., 2000; Romero and Hensen, 2002) leaving visible marks in pore water profiles (Hensen et al., 2003), increasing OM reactivity with sediment depth has not been reported to our knowledge.

## 2 Materials and methods

### 2.1 Study area: sedimentary and geochemical records

Only at few places the connection between sediment-water interfaces and deeper sediments has been studied. An exception is the backbarrier area of Spiekeroog Island (Wadden Sea, southern North Sea) where a location close to the low water line at the northern edge of the Neuharlingersieler Nacken tidal flat (NN1: 53°43.270' N, 7°43.270' E) has been selected based on previous studies. 5 m cores were taken three times during the years 2002–2004 (Fig. 1). 40 m southward into the direction to the central area of the flat another core was recovered in 2005 (NN2: 53°43.270' N, 7°43.270' E). Sedimentological survey of the 5 m long cores by Tilch (2003); Chang et al. (2006b); Wilms et al. (2006b) revealed a trisection of the sediment column: the upper 1.7 m are composed of sands with intersections of silts (intertidal flat and channel deposits) followed by an approx. 0.7 m thick shell beds with massive sand interbedding (shell lag deposits). Organic carbon contents of the sand and shell layers is 0.3% on average, but may reach up to 1.2% in the silty layers. The base consists of greyish muds (saltmarsh and mudflat deposits) containing 1.2% POC on average. Sulfate depletion between 1 and 2 m depth at site NN1 is accompanied by a clear NH<sub>4</sub> peak, which both indicates rapid decay of OM (Wilms et al. (2007); Beck et al. (2009) Fig. 2). The sulfate and ammonium signals cannot be directly related to TOC-rich layers in the sediment. TOC peaks at 1.0 m and 1.5 m are both accompanied with increased fine (< 63 μm) lithoclastic material, which indicates that TOC measure-

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ments are less suited to identify active layers since fresh OM is may be obscured by refractory OM. High concentrations of acetate at 1.5 m, with 2.2 mmol/l making up nearly 50% of the DOC fraction, indicate active fermenting processes. Additionally, the  $\Delta^{13}\text{C}$  isotope ratio is elevated here (J. Köster, personal communication, 2008). Microbial investigations by Köpke et al. (2005) and Wilms et al. (2006a) found significantly enhanced activity at the edges of the sulfate free, methanogenic, zone. Though less pronounced, ongoing diagenesis is also visible at site NN2 in the sulfate profile –  $\text{NH}_4$  was not measured.

## 2.2 Modelling approach

Which process is able to fuel rapid OM remineralisation in deeper coastal sediments? Since age and reactivity of OM are well correlated (Middelburg, 1989), the question we need to answer is how fast OM has been relocated and by what transport mechanism. We here test two plausible scenarios, conceptualized in Fig. 3, of either sedimentation (scenario A) or advection (scenario B) being suitable for supplying labile OM to deeper sediment layers. In scenario A, OM of high or intermediate quality is deposited at the surface and transferred to depth by rapid sedimentation in order to compensate sediment deficits supposedly created by ramp propagation into the channel. In scenario B we assume a subterranean aquifer or advective zone in 1–2 m sediment depth that connects site NN2 to NN1 and transports intermediate OM from a hypothetical source upstream of NN2 to the study sites.

Both scenarios are represented as specific set-ups of the Integrated Sediment Model (ISM) (Wirtz, 2003; Holstein and Wirtz, 2009). For the model calibration in scenario A, we employ a Monte-Carlo parameter variation. From 84 model parameters 9 most critical parameters were chosen based on an extensive sensitivity study carried out by (Holstein and Wirtz, 2009). We obtain a standard calibration with minimal relative root mean squared error (relative RMSE) of  $\text{SO}_4$  and  $\text{NH}_4$  pore water profiles which also serves as base calibration for scenario B. This set-up is also implemented as a 1-D (one dimensional) vertical column (Fig. 4a). Horizontal advection is assessed by in-

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terpreting the geochemical transformation of the waterbody through time as a change through space along the advective (horizontal) flow-path, i.e., the reference system moves along with the water. This approach is justified if (i) the reaction rates are slow compared to the flow velocity so that horizontal concentration gradients are negligible compared to vertical gradients, and (ii) the sediment composition in terms of physicochemical properties is consistent along a horizontal flowpath. Both conditions are supposedly met. Additionally, a 2-D simulation with coarse spatial resolution was used to verify the results of the 1-D advective model setup. The intermediate POC decay constant served as the sole master variable. Advective flow velocities are calculated from the distance between NN1 and NN2 and the times needed by the  $\text{SO}_4$  pore water profile to develop from the initial state via NN2 to a state found at NN1.

### 2.3 Model structure

The ISM simulates transport and reactions of chemical species in porous media, particularly resolving carbon degradation. Specific to the ISM compared to many other diagenetic models (e.g., Berner, 1980; Boudreau, 1997) is that most redox reactions are carried out by competing microbial populations (defined according to their catabolic pathways). The decay of OM is calculated for different quality classes, differentiating between enzymatically enhanced hydrolyzation and quality related consumption of OM by heterotrophic bacteria. A sketch of the biochemical cycling scheme is depicted in Fig. 5. For a comprehensive description of the governing equations, the reader is referred to Holstein and Wirtz (2009). In this study, the model consists of a column of 50 boxes, each 10 cm thick, representing the sediment column from sediment surface to 5 m depth. In brief, the boxes consider the following processes and geochemical reactions: diffusive transport affects all aqueous species within the model area and also leads to import of solutes through the upper boundary during times of water coverage. The upper boundary represents the bottom water overlying the sediment and nutrient concentrations are set to monthly means of measurements of Liebezeit et al. (1996). For oxygen and sulfate, constant concentrations of 0.25 and 24.0 mmol/l respectively

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are assumed.

Bioturbation is implemented as diffusion acting on both solutes and solids. Bioirrigation is implemented as non-local exchange. Both rates decrease exponentially with depth to 5% of the full value at biomixing depth. Below, there is no mixing.

Hydrolysis of POC is assumed to depend on the reactive area of particulate material, which is assumed to scale with volumetric concentration with exponent 2/3

$$\frac{\partial}{\partial t} \text{POC}_j = -\frac{1-\phi}{\phi} r_j Q_{10}^{(T-TS)/10} \text{POC}_j^{2/3} (1+h \text{ BAC}) \quad (1)$$

5 where the index  $j$  denotes the quality class,  $\phi$  the porosity,  $h$  quantifies enzymatic enhancement of hydrolysis, BAC the active bacterial biomass (weighed by the functional group specific growth rates). The model includes the nonlinear  $Q_{10}$  temperature term after van't Hoff rule.  $T$  and  $TS$  denote ambient and standard temperature. Referring to Boudreau (1992), POC is divided in 3 quality classes that differ in their specific rate constant  $r_j$  ( $1/d$ ) and their Redfield composition according to which  $\text{NH}_4$  is released into the porewater upon POC destruction. Carbon from hydrolized POC is re-distributed among 3 DOC pools such that the highest quality POC class will also contribute most to the highest quality DOC class. POC class 3 is refractory and, in the model initialization, mainly confined to the gray mud layers below 2.5 m (Fig. 2) in concentrations of approximately 1.25% of bulk dry sediment. POC class 2 collects intermediate material. In scenario A, it is deposited at the top box with 2.5% dry mass concentration at simulation start, and is incorporated in the sediment body throughout subsequent sedimentation. In scenario B, a 30 cm thick layer (i.e. 3 boxes) around 1.5 m sediment depth was primed with 1.0% intermediate POC. POC class 1 is highly reactive and small contents are therefore confined to the uppermost layer. The composition of suspended particular matter in the overlying bottom water in terms of quality classes is assumed 1:5:200 (POC class 1:2:3).

20 Redox reactions comprise the primary reactions for OM degradation according to Froelich et al. (1979), denitrification and secondary redox reactions. These altogether

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20 reactions are mediated by bacteria. Additionally, monosulfide precipitation and re-oxidation and pyrite formation are thermodynamically controlled (Holstein and Wirtz, 2009).

Sedimentation (only scenario A) is implemented as a discontinuous process. At a supposed sedimentation rate of, e.g., 1 cm/yr, all boxes are shifted to the next deeper layer every 10 years. Contents of the lowest model box are lost and the uppermost box is filled with sediment and pore water according to surface conditions. Discontinuous deposition avoids numerical diffusion of solid species and prevents the loss of OM stratification and sediment characteristics. Compared to continuous sedimentation, we postulate a better reproduction of the sedimentation regime in the Wadden Sea where times of sediment deposition and resuspension vary on a daily, seasonal and annual scale (Chang et al., 2006a).

## 2.4 Parameters of interest

The extensive parameter variation approach is excellently suited to constrain parameters, provided parameters converge towards a value and the variation range was sensibly chosen. A total of approximately 34 000 simulations were run with randomly varied parameter values within reasonable limits as given in Table 1 to obtain the standard calibration for scenario A. The variation range for porosity was derived from mud content ( $< 63 \mu\text{m}$ ), since a significant relation exists between pore space and mud content (Flemming and Delafontaine, 2000). Bioturbation is highly variable and uncertain, so we used values from Tromp et al. (1995) for high to low sedimentation rate settings. The decay constant of the POC fraction of interest (intermediate quality) was varied within values just as high as the highly reactive fraction, which is short-lived and therefore exists only in the surface sediment, and just as low as the poorly reactive, refractory fraction.  $\text{NH}_4$  concentrations, specifically the extent of the peak value at 1.5 m sediment depth is very sensitive to the C:N ratio of the decomposing OM which was varied within limits typical for that area (Beck et al., 2008, and references therein). The bacterial yield on  $\text{SO}_4$  controls the growth of the sulfate reducers. It's value is relative to

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the yield on O<sub>2</sub> which is 1. Since the understanding of the reactivity of OM as well as metabolic constraints is fragmentary, bacterial metabolic efficiency may vary and the bacterial yield may significantly differ from the Gibbs free energy of the related reaction (Jørgensen, 1978; Berner, 1980). Introducing OM fractions of different reactivity and the acceleration of the hydrolization by the bacteria themselves is a step towards a more complete description (Rothman and Forney, 2007). Still, our simplified implementation of hydrolization is not verified and therefore a large spectrum of values are considered.

### 3 Results and discussion

In both scenarios, model runs with the calibrated parameter set are able to produce accurately fitting SO<sub>4</sub>, NH<sub>4</sub> and DOC pore water profiles for core NN1 as shown in Fig. 6. Calibrated parameters with an average relative standard deviation (%RSD) of less than 5% for SO<sub>4</sub> and NH<sub>4</sub> converge towards values given in Table 1. This model calibration for scenario A served as the base calibration for scenario B.

#### 3.1 Scenario A – rapid sedimentation

Given the very good reproduction of the pore water data, and the convergence of well fitting parameter values, the inverse modeling of the sulfate and ammonium profiles yields a robust estimate of recent sedimentation rates. Best model runs in terms of relative RMSE for SO<sub>4</sub> and NH<sub>4</sub> assume sedimentation rates of 1–4 cm yr<sup>-1</sup>. The top 140 cm of sandy intertidal flat and channel deposits most likely formed during the last 35–140 yrs.

For the simulation with standard calibration as given in Table 1, the decay of intermediate quality OM at  $8 \times 10^{-5} \text{ d}^{-1}$  (corresponding to a half-life of 24 yrs) provides the DOM used by sulfate reducers. Numerically, this can explain the developing sulfate gap in 1–2 m within 64 years. Weaker constraints regarding the sedimentation rate

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follow from the ammonium profile fitting, but at rates below  $1 \text{ cm yr}^{-1}$  the model error drastically increases. Hence, the sandy flat and channel deposits, which make up the upper section of the cores, must have been deposited at rates significantly higher than required just to keep up with sea level rise. The relative RMSEs of DOC and TOC (not shown) are largely insensitive to the sedimentation rate.

The best 145 model calibrations (composite  $\text{SO}_4$  and  $\text{NH}_4$  relative RMSE  $< 5\%$ ) represent the uncertainty of the calibrated values as well as the partial overlap of parameter functions. In general, parameters are less constrained than in a comparable study by Beck et al. (2009) which was expected because we vary more parameters here. The POC decay constant, the yield on  $\text{SO}_4$  and the specific enhancement of hydrolytic exoenzymes all affect the speed in which sulfate reducers degrade the organic matter. Due to a similarly accelerating effect these highly important parameters for OM degradation (Holstein and Wirtz, 2009) were only moderately constrained and best calibrations have relative standard deviations of 15–37%.

In contrast, porosity changes produce a rather unequivocal response, demonstrating the prominent role of sediment transport characteristics for the model results. Best fitting porosity of the deposited sediment was estimated to be 0.46 which is in good agreement with a range of 0.37–0.43 calculated from mud content by Flemming and Delafontaine (2000) for East Frisian Wadden Sea intertidal surface sediments.

The calibrated bioturbation coefficient accurately fits estimates for coastal systems with reported sedimentation rates of few  $\text{cm yr}^{-1}$  (Tromp et al., 1995, and references therein). Bioirrigation coefficients from literature are also remarkably close to our estimates. However, a bioturbation/irrigation depth of 54 cm is found to be most compatible with the observed convex or kink shape of the sulfate profile. This estimate clearly exceeds the usually reported values of 10–30 cm for bioturbation (Furukawa et al., 2000; Meile et al., 2001) and of 10–20 cm for bioirrigation (Boudreau, 1994, 1998; Sandnes et al., 2000; Crusius et al., 2004). The latter is the accepted burrow depth of the lugworm *Arenicola marina*, the most common burrowing macrofauna species of the study area, and *Heteromastus filiformis*. However, bioturbation may reach as deep as

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0.5 m in sediments overlying high-productivity areas (Wetzel, 1981) and some species (*Callianassa subterranean* and *Maxmuelleria lankesteri*, though undocumented in the investigated habitat, are known to have burrows reaching such depth (Koretsky et al., 2002). Another explanation for kink shape pore water profiles, previously pointed out by Hensen et al. (2003), is that sedimentation of the upper 0.5 m happened faster than relaxation of the concentration gradient. This scenario would require deposition during one or few events, which is in line with the sedimentation pattern proposed by Chang et al. (2006b) and explains the absence of bioturbation structures.

A Redfield ratio of C:N of 9.5 is able to explain the height of the ammonium peak around  $6 \text{ mmol l}^{-1}$  and the bell shape of the ammonium pore water profile. This calibrated value exceeds the standard Redfield C:N ratio of 6.6. But it is in the stoichiometric range of suspended particular organic matter (SPOM) in the open water column of the study area (around 7.8; Lunau et al., 2006) and comparable to an integrated value of 8.6 for the upper 3 m of sediment on a neighboring flat by Beck et al. (2008).

A (relative) bacterial yield of sulfate reducers on DOC of 0.08 means that sulfate reducers yield 8% the energy oxic heterotrophs would gain from a unit of DOC converted into growth. If just the Gibbs free energies of the corresponding reactions after Froelich et al. (1979) are considered, the yield of sulfate reducers should be around 0.12. Given the relatively high relative standard deviation of 28%, the calibrated value seems reasonable since reported bacterial growth efficiencies show a wide scatter (Payne and Wiebe, 1978; Russell and Cook, 1995).

In scenario A, the sulfate profile is reproduced best, while the peak in the ammonium profile could not be reproduced to the same extent. The initialized OM pulse is presumably too broad to generate such a distinct peak. In the model, the DOC peak between 1.5 and 2.0 m depth consists of intermediate DOC, which is situated above a layer of refractory compounds. This peak is narrower than empirical data suggest but broader than the distinct acetate peak at this site (not shown). It can hence be speculated that some of the DOC is refractory. The observed total organic carbon (TOC) profile is satisfactorily reproduced. An exception is the simulated soft peak in intermediate quality

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TOC below 1.5 m depth where the field data display a more complex picture with higher values at 1.0 and 1.5 m.

### 3.2 Scenario B – advection

Reasonable model-data fits were also found for scenario B. This is not surprising since both scenarios differ only in the mechanism which is used to transfer OM to depth. In both scenarios OM is subject to the same array of processes, with comparable results regarding degradation and pore water evolution. For core NN2, which is not used for the model calibration of scenario A, the sulfate fit is less satisfying due to the fact that the whole profile, including the sulfate minimum and the sulfate bulge below, is slightly elevated with respect to the core NN1 profile. Model error for sulfate and ammonium of core NN2 and NN1 become minimal at a degradation rate of  $0.7 \times 10^{-4} \text{ d}^{-1}$  (Fig. 8a). According to timing and geometry, this corresponds to a macroscopic flow velocity of  $1.4 \text{ myr}^{-1}$  (Fig. 8b). Assuming invariant aquifer dimensions and conditions, the OM source is then located 6 m upstream of core NN2 (Fig. 8c). That way, it takes approximately 10 years for the sulfate profile to develop the shape observed at core NN2 and another 60 years to develop the shape observed at core NN1 as depicted in Fig. 9.

At degradation rates below  $0.5 \times 10^{-4} \text{ d}^{-1}$ , sulfate reduction is too weak to produce a sulfate-free zone, which is reflected by increasing relative RMSE for core NN1 sulfate fits. At rates above  $1.0 \times 10^{-4} \text{ d}^{-1}$ , the OM source moves close to NN2, so that it can not be located at the surface anymore. In this case advection must be discarded as the process to relocate OM from surface to depth.

However, DOC pore water profiles of cores NN1 and NN2 document that the dissolved compound alone cannot be responsible for the observed sulfate reduction. Concentrations are simply not high enough and do not change from core NN2 to NN1. Therefore the supplied carbon has to arrive as suspended particles (that exceed  $1.2 \mu\text{m}$ , which was the filter size for pore water extraction by Beck et al., 2009). Retention of POM has not been considered in the model calculations. It would slow

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down carbon transport, delaying pore water evolution and, as a result, further decrease the distance from core NN1 to the hypothetical carbon source. Though the existence of an aquifer cannot be excluded from the investigations, the heavily curved flowpaths required for this scenario point to tidal pumping as the driving force for underground water flow. Macroscopic flow velocities projected by Wilson and Gardner (2006); Roy et al. (2008) are compatible with our model derived estimates.

The hypothesis yet appears implausible, since the geometric premises required for scenario B are highly specific and too contrived to sustain a reasonable probability at this site. Since tidal pumping affects the whole sediment body, advection would not be restricted to a certain layer unless obstructed by sediment properties for which there is no lithologic evidence. In case of unhindered flow, the carbon source needs to be very confined, ruling out water column SPOM as carbon source. For example, a macroalgae agglomerate buried in the surface sediment few meters upstream of core NN2 might create a confined SPOM plume to match observations. Given the constant reworking of the surface sediment by hydrodynamic forces, the carbon source is not likely to stay put for at least 60 yrs to cause effect at both sites NN2 and NN1.

#### 4 Conclusions

We compared the two most probable processes for the rapid transfer of reactive OM into deeper sediment layers. Both sedimentation and advection could in general explain the observed pore water profiles of  $\text{SO}_4$ ,  $\text{NH}_4$ , DOC and TOC.

However, discrepancies regarding requirements and observations of carbon source and flow geometry make the advection hypothesis rather improbable. But provided higher flow velocities, pore water advection principally may relocate reactive organic matter over much longer distances and deep into the sediment.

The sedimentation hypothesis implies the rapid compensation of a great sediment deficit, e.g., tidal flat progradation. Inversely modeled sedimentation and progradation rates are in the range of observations. The estimates for the Redfield ratio and the

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decay rate of the OM organic matter that was initially deposited in the surface sediment suggests that the POM composition was typical for the area, which is moderately nitrogen depleted and of intermediate reactivity.

Therefore, we suggest scenario A to be more probable. In morphodynamically very active areas like many coastal systems, this would have consequences for the biogeochemical fingerprint of the entire sediment body. If layers of high OM content become buried within few decades, estimates of, e.g., organic preservation efficiency, methane production, or nutrient remineralization will be much higher than extrapolated from studies of the surface layer or distant deeper sediments. In particular methane emissions from coastal areas will thus be higher than projected estimates that do not take into account larger amounts of buried but still relatively fresh OM in greater depth. Sedimentation rates of a few  $\text{cm yr}^{-1}$  over decades signal morphologic change. The assumed tidal flat progradation, as a manifestation of morphodynamics, is in accordance with nautical charts of the years 1866–2003 for our study area Tilch (2003). While most of the northern and northeastern parts of the tidal flats that form the southern and southwestern bank of the main tidal channel (Neuharlingersieler Nacken and Janssand) suffer from erosion following the general trend towards higher energies, the study area receives sediment. For 2 m of young sediment to deposit, it would require a flat progradation of a little less than 1 m/y into the channel at an inclination of  $2.3^\circ$  of tidal flat surface plane during 60 years. Since great channels may laterally relocate 25 to 30 m/y on average according to Lüders (1934) it seems a conceivable hypothesis.

We demonstrated that models can be indispensable for a sound interpretation of biogeochemical data. By using automated model calibration, we were in particular able to infer the average sedimentation rate during the last decades. On this timescale, sedimentation rates are rarely estimated for marine environments. Morphodynamic changes like flat progradation are not restricted to the study site. We therefore suggest that at many shallow coasts OM turnover (connected with significant production of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  or  $\text{CH}_4$ ) will be more intense than apparent from surface-restricted studies.

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**Table 1.** Parameter ranges for Monte Carlo parameter variation, standard calibration (Fig. 6), and relative standard deviation (%RSD) of parameters from 145 calibrations with average %RSD < 5% with respect to SO<sub>4</sub> and NH<sub>4</sub> (Fig. 7).

Parameter	Variation range	Standard calibration	%RSD
Porosity	0.4–0.6	0.47	8
Sedimentation rate (cm yr <sup>-1</sup> )	0.1–10	2.2	30
Bioturbation coefficient (cm <sup>2</sup> day <sup>-1</sup> )	0–3	0.1	31
Bioirrigation coefficient (d <sup>-1</sup> )	0–50	0.6	29
Biomixing depth (cm)	0–100	45	34
Intermediate POC decay constant (× 10 <sup>-4</sup> d <sup>-1</sup> )	0.1–5.0	0.8	37
C/N ratio of intermediate POC	3–15	9.5	14
Sulfate reducer yield on DOC	0.05–0.15	0.08	28
Effect of hydrolytic exoenzymes	1–100	21.5	15

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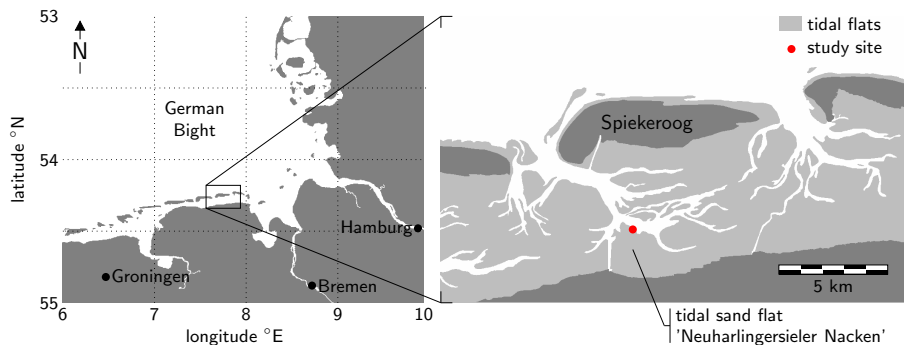
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**Fig. 1.** The study site in the backbarrier area of Spielerog Island, Wadden Sea, Germany is located at the northern rim of an intertidal sand flat (Neuharlingersieler Nacken).

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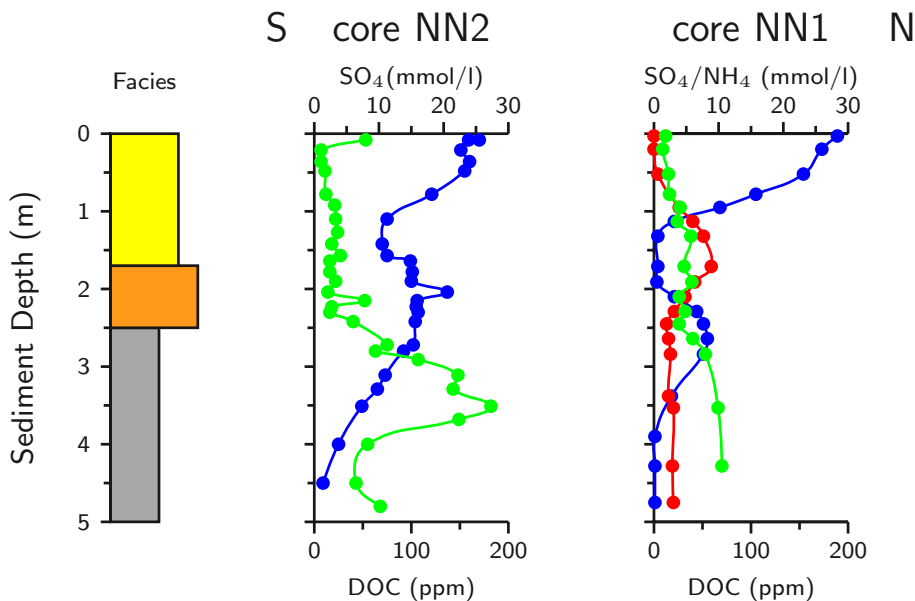
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**Fig. 2.** Lithology and geochemical inventory at the study site. The N-S oriented transect covers 40 m at the northern rim of the Neuaharlingersielener Nacken tidal flat. Facies association according to Chang et al. (2006b): sandy intertidal flat and channel deposits (yellow), shell lag deposits (orange), and saltmarsh/mudflat deposits (gray). Pore water data of DOC (green),  $\text{SO}_4$  (blue), and  $\text{NH}_4$  (red) show sulfate depletion between 1 and 2 m depth accompanied by a  $\text{NH}_4$  peak (NN1). Core NN1 shows pore water data from 2005 (one of three parallel cores).

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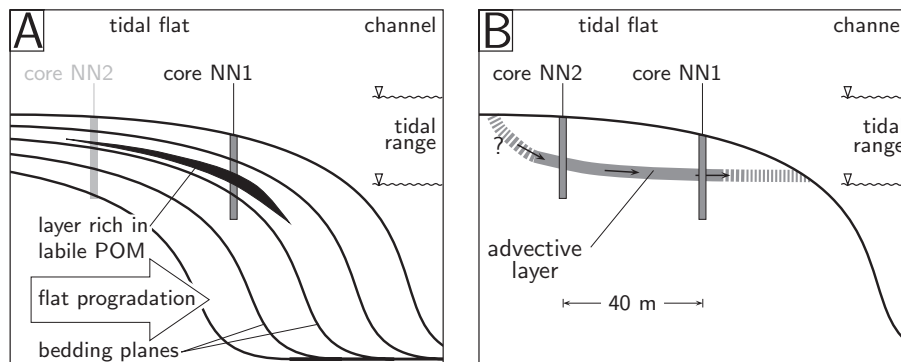
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**Fig. 3.** Alternative scenarios to explain fast OM degradation in deep sediment. **(A)** Scenario A: rapid sedimentation transfers POM to greater depth that was previously deposited at the surface. **(B)** Scenario B: an advective zone or subterranean aquifer in 1–2 m sediment depth connects core NN2 and core NN1 to a hypothetical SPOM source upstream of core NN2.

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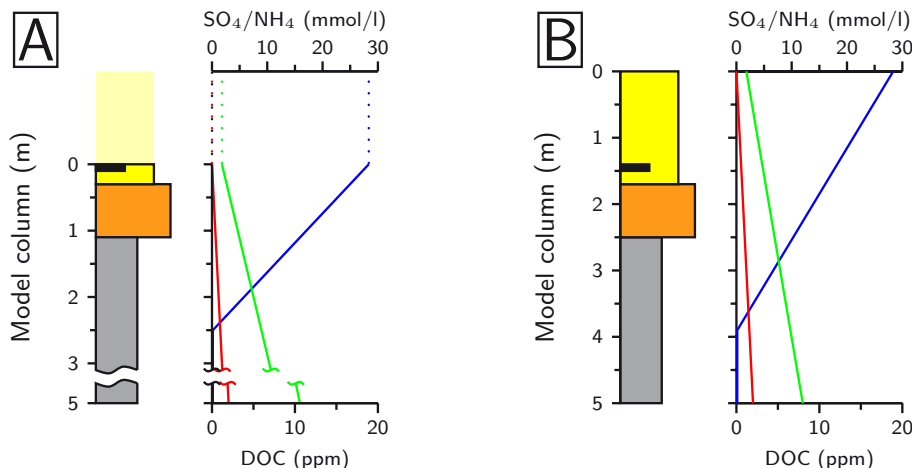
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**Fig. 4.** Model setups of scenario A and scenario B (cf. Fig. 3). Initial pore water profiles of DOC, SO<sub>4</sub>, and NH<sub>4</sub> in green, blue, and red. Respective POM and SPOM priming positions are shown in black. Corresponding to facies (cf. Fig. 2), variable sediment diffusivities are assumed:  $\phi = 0.5$ ,  $\theta = 2.4$  (yellow);  $\phi = 0.6$ ,  $\theta = 4.4$  (orange);  $\phi = 0.7$ ,  $\theta = 9.4$  (gray).

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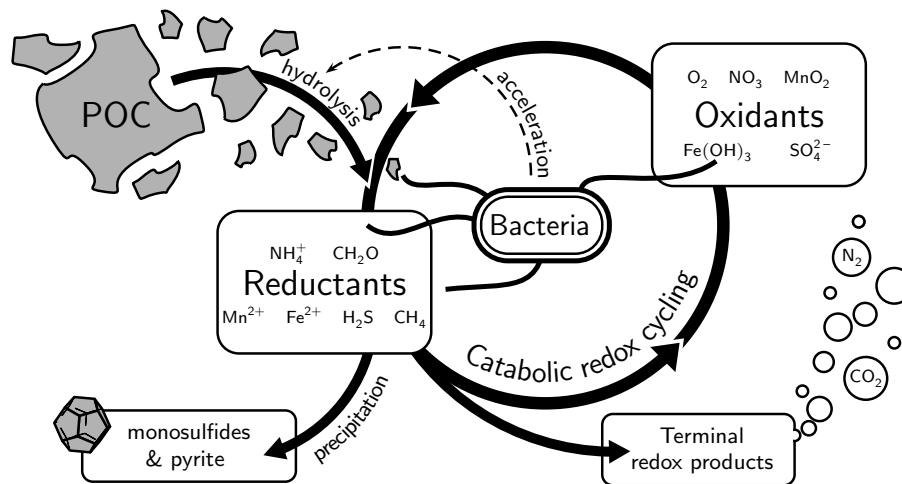
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**Fig. 5.** Sketch of the biochemical cycling scheme in each ISM model box: functional groups of heterotrophic and lithotrophic bacteria conduct the irreversible redox reactions. Educts may participate in subsequent redox reactions. Heterotrophic bacteria accelerate POC hydrolysis.

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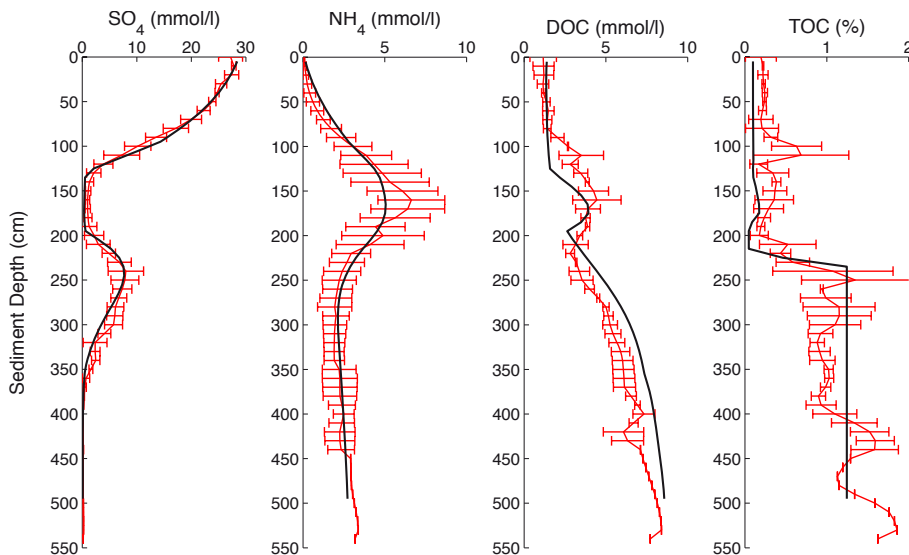
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**Fig. 6.** Scenario A: model results for sulfate, ammonium, DOC and TOC for a sedimentation rate of 2.2 cm/y after 44 years. Error bars (red) indicate standard deviation of three parallel cores. Similar fits are obtained with scenario B.

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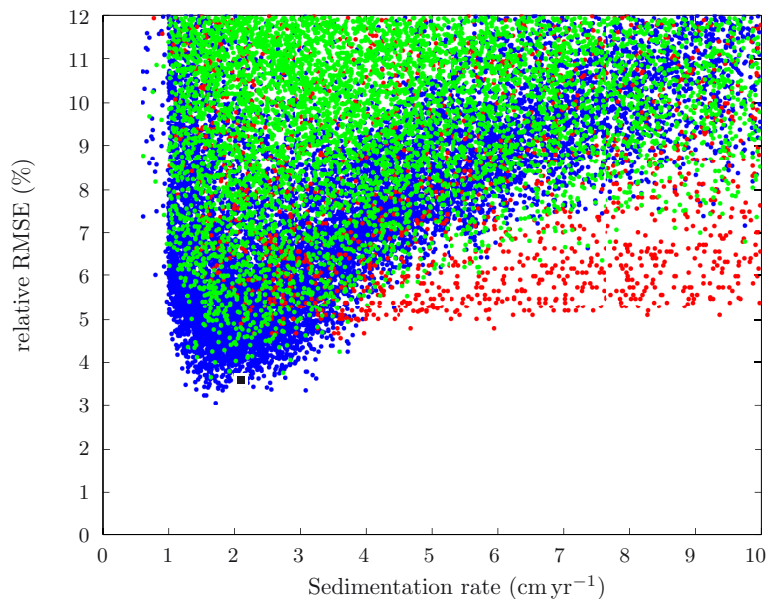
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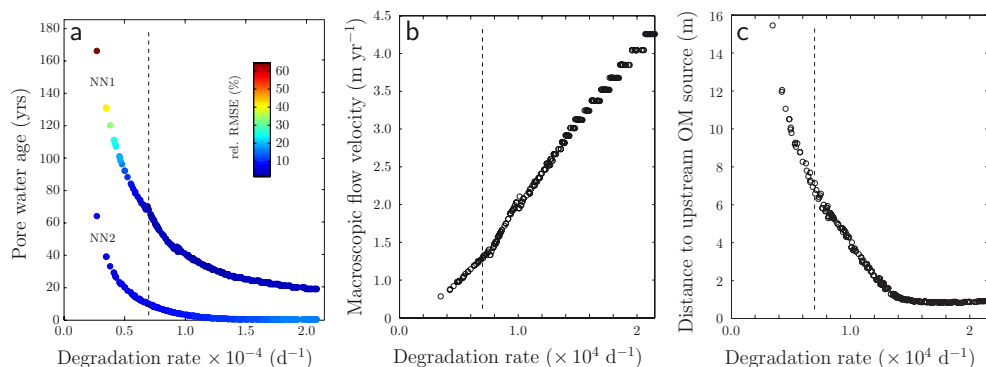


**Fig. 7.** Model error in a Monte Carlo parameter variation, projected to the effect of variations in the sedimentation rate. The dots show the relative root mean squared error (relative RMSE) of the pore water profile of SO<sub>4</sub> (blue), NH<sub>4</sub> (red), and composite of both profiles (green). The black square denotes the best fitting run (standard calibration) given in Table 1 and shown in Fig. 6.

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**Fig. 8.** Flow parameters of scenario B and their relation to intermediate POC decay constant. **(a)** Age of pore water at core NN2 and NN1 according to pore water sulfate evolution. Relative root mean square errors (relative RMSE) of a particular best fit are indicated by color. Minimal relative RMSE is attained at  $0.7 \times 10^{-4} d^{-1}$  (dashed line). **(b)** Macroscopic flow velocity required to cover the distance of 40 m between core NN2 and NN1 in the length of time between the best fits of sulfate pore water profiles at respective locations. **(c)** Distance of core NN2 to the hypothetical source of OM.

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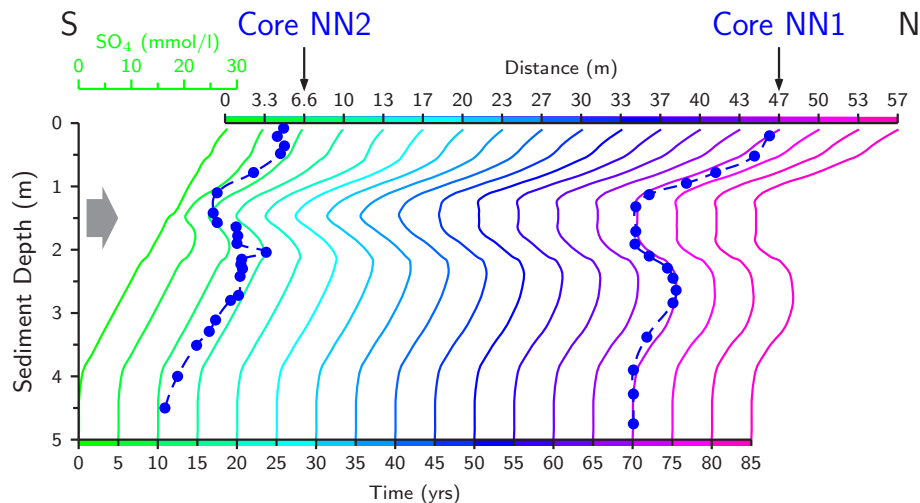
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**Fig. 9.** Model pore water  $\text{SO}_4$  evolution (varicolored) along the flow path with a degradation rate of intermediate POC of  $0.7 \times 10^{-4} \text{ d}^{-1}$  yielding best fits (minimal RMSE) for field data  $\text{SO}_4$  pore water profile (blue). Pore water reaches NN2 after 10 years, approximately 7 m from POC source, and for NN1 after another 60 years, 40 m downstream of NN2.

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