Exploring nitrogen dynamics in coastal sediments: A study of permeable sands in the southern North Sea

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Abstract

Coastal systems are immensely impacted by mobile ground touching fisheries, global change related effects (e.g. increasing water temperatures, sea level rise and ocean acidification) and other human induced pressures (e.g. pollution and sand extractions). These stressors contribute to a worsening of the environmental status of the southern North Sea. To prevent further degradation, three marine protected areas have been established in the German Exclusive Economic Zone (EEZ). This thesis investigates benthic biogeochemical processes, with a focus on benthic oxygen and nitrogen dynamics in permeable sands of the southern North Sea and explores potential effects of the exclusion of mobile ground touching fisheries.

First (chapter 2), various sediment characteristics (e.g. chlorophyll-a, phaeophytin-a, total organic carbon and mud content) and their application as proxies for benthic oxygen consumption and nitrogen turnover are explored. A parameterization framework is developed within this context to predict both net (oxygen, ammonium and nitrate) and gross (ammonium and nitrate) benthic reaction rates based on sedimentary predictor variables. The findings indicate that mud content and phaeophytin-a concentrations are among the most suitable proxies for assessing sediment reactivity.

The following chapter (chapter 3) builds on a previously established pore water advection model and the parameterization framework introduced in chapter 2 to develop a process-driven biogeochemical model for permeable sands. This model utilizes the previously identified proxies to predict benthic fluxes of oxygen, ammonium, nitrate and dinitrogen. It examines how the vertical distribution of substrates within the sediment affects the magnitude of these fluxes, revealing that this vertical substrate distribution has minimal impact on the modeled benthic fluxes in permeable advection controlled sands.

The fourth chapter extends the application of the benthic biogeochemical model to calculate total fluxes within the Natura 2000 MPAs of the German Bight. This forms the basis for integrating the sediment into a digital twin, enabling the exploration of "what-if" scenarios, such as the effects of excluding mobile bottom-contact fishing on the sedimentary organic matter inventory and sediment reactivity. The results show that excluding bottom trawling results in only slight increases in sedimentary total organic carbon content, leading to minor changes in the benthic fluxes of oxygen and nitrogen.

Overall, this study provides a foundational understanding of sediment reactivity in coastal systems and provides crucial insights for refining management strategies to protect and sustain the southern North Sea.

Zusammenfassung

Küstensysteme werden durch mobile grundberührende Fischerei, Effekte des Klimawandels (z.B. steigende Wassertemperaturen, Meeresspiegelanstieg und Ozeanversauerung) und anderen menschlich bedingten Belastungen (z.B. Verschmutzung und Sandentnahme) strapaziert. Diese Stressoren tragen zu einer Verschlechterung des Umweltzustands der südlichen Nordsee bei. Um eine weitere Verschlechterung zu verhindern, wurden drei Meeresschutzgebiete in der deutschen Ausschließlichen Wirtschaftszone (AWZ) eingerichtet. Die vorliegende Arbeit untersucht benthische biogeochemische Prozesse mit einem Schwerpunkt auf benthischem Sauerstoff- und Stickstoffkreislauf in permeablen Sanden der südlichen Nordsee und erforscht potenzielle Auswirkungen des Ausschlusses von mobilen, grundberührenden Fischereien.

Zuerst (Kapitel 2) werden verschiedene Sedimenteigenschaften (z.B. Chlorophyll-a, Phaeophytin-a, organischer Kohlenstoff und Feinkorngehalt) und deren Anwendung als Indikatoren für benthische Sauerstoffzehrung und Stickstoffumsatz untersucht. In diesem Zusammenhang wird eine Parametrisierung entwickelt, um sowohl benthische Netto- (Sauerstoff, Ammonium und Nitrat) als auch Brutto- (Ammonium und Nitrat) Reaktionsraten basierend auf sedimentären Prädiktorvariablen vorherzusagen. Die Ergebnisse zeigen, dass Feinkorngehalt und Phaeophytin-a-Konzentrationen zu den am besten geeigneten Indikatoren für die Bewertung der Sedimentreaktivität gehören.

Das darauffolgende Kapitel (Kapitel 3) baut auf einem zuvor etablierten Porenwasser-Advektionsmodell und auf der in Kapitel 2 eingeführten Parametrisierung, um ein prozessgesteuertes biogeochemisches Modell für permeable Sande zu entwickeln. Dieses Modell nutzt die zuvor identifizierten Indikatoren, um benthische Flüsse von Sauerstoff, Ammonium, Nitrat und Distickstoff vorherzusagen. Es untersucht, wie die vertikale Verteilung der Substrate innerhalb des Sediments die Flüsse beeinflusst und zeigt, dass diese vertikale Substratverteilung nur minimale Auswirkungen auf die modellierten benthischen Flüsse in permeablen, advektionskontrollierten Sanden hat.

Das vierte Kapitel erweitert die Anwendung des benthischen biogeochemischen Modells, um die Gesamtflüsse innerhalb der Natura 2000 Schutzgebiete der deutschen Bucht zu berechnen. Dies bildet die Grundlage für die Integration des Sediments in einen digitalen Zwilling, der die

Erkundung von „Was-wäre-wenn“-Szenarien ermöglicht, wie die Auswirkungen des Ausschlusses von mobilen, grundberührenden Fischereien auf den Bestandes von sedimentären organischen Kohlenstoff und die Sedimentreaktivität. Die Ergebnisse zeigen, dass der Ausschluss von mobiler grundberührender Fischerei nur zu geringfügigen Erhöhungen des sedimentären Gesamtgehalts an organischem Kohlenstoff führt, was wiederum nur zu geringfügigen Änderungen der benthischen Flüsse von Sauerstoff und Stickstoff führt.

Insgesamt bietet diese Studie ein grundlegendes Verständnis der Sedimentreaktivität in Küstensystemen und liefert wichtige Erkenntnisse zur Verbesserung von Managementstrategien zum Schutz und zur Erhaltung der südlichen Nordsee.

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1 Introduction

1.1 The role of coastal systems in nutrient biogeochemistry

Coastal ecosystems are intricate and dynamic interfaces where terrestrial and marine influences converge, creating habitats of immense ecological importance. Despite only covering a small fraction of the ocean's surface (<9%; Jahnke 2010; Jorgensen 1983; Bratek et al., 2020), continental shelves disproportionately contribute to marine primary production and provide valuable habitats and ecosystem services (Bratek et al., 2020; He and Silliman, 2019; Neumann et al., 2021; Van Oostende et al., 2018; Ward et al., 2020). The sediments in these systems may be described as coastal nitrogen filters, play a crucial role in global nutrient cycling, carbon mineralization and owing to their shallow depth are tightly linked to biogeochemical processes in the water column (Ahmerkamp et al., 2017; Albert et al., 2021; Bartl et al 2019; Hellemann et al., 2020). These services are important for chemical water quality, fisheries and nutrient management. Given the crucial roles coastal ecosystems play in ecological and biogeochemical cycles, it becomes imperative to understand the underlying mechanisms that regulate their functionality. Central to this understanding are benthic fluxes - dynamic processes through which oxygen and nutrients are exchanged between the sediments and the overlying water column. These fluxes are influenced by diverse factors ranging from physical sediment characteristics to biological activity and anthropogenic impacts. In the following, I will address these controlling factors and explore how they intertwine to shape the nutrient pathways and ecological outcomes in coastal environments.

In coastal systems, much of the organic matter from the water column accumulates and sinks to the seafloor (Alldredge and Silver, 1988). During sinking, heterotrophic microbes drive remineralization processes of organic material. However, since the shallow water depth limits the time for gravitational settling of particles, water column remineralization is less important than sedimentary remineralization (Malone et al., 1983). Compared to the overlying water column, organic matter in sediments is exposed to increased bacterial abundances and exo-enzyme concentrations, leading to accelerated degradation (Ahmerkamp 2016). Once settled, labile organic matter serves as a primary food source for benthic microorganisms and is a key driver of biogeochemical processes in sediments by stimulating microbial activity. This microbial activity not only transforms organic matter but also implicates continental shelf sediments as sinks for atmospheric carbon dioxide (CO_2), storing large amounts of organic carbon (Diesing et al., 2021; Graves et al., 2022; Laruelle et al., 2018; Van Dam et al., 2022). Additionally, these coastal sediments play a crucial role as nitrogen sinks, accounting for up to 80% of the total benthic N_2 production in regions like the southern North Sea, which is particularly important for permeable sediments (Bratek et al., 2020).

Permeability, the resistance to flow of water through the sediment, overall controls the exchange of solutes and particles within the sediment (Neumann et al., 2017a). The transport mechanisms of solutes such as oxygen and nutrients, are predominantly categorized into two types: diffusion-controlled and advection-controlled sediments. In diffusion-controlled environments, the movement of solutes is primarily governed by molecular diffusion, a process driven by the concentration gradients across the sediment-water interface (Boudreau, 1997). This mechanism typically dominates in finer, less permeable sediments where pore water flow is minimal (Huettel et al., 2004). Conversely, in advection-controlled sediments, fluid flow induced by physical forces such as wave actions and tidal currents enhances the transport of solutes (Bartl et al., 2019; Cook et al., 2007; Gao et al., 2012; Huettel et al., 1998, 2004, 2014; Marchant et al., 2018). This advective transport is significant in coarser, more permeable sediments, facilitating a faster exchange of solutes between the sediment and overlying water (Huettel et al., 2014). Sandy, more permeable sediments are typically characterized by lower organic carbon concentrations compared to the muddier, less permeable sediments, which contributed to their historical characterization as biogeochemical deserts throughout much of the 20th century (Anschutz et al., 2009; Boudreau et al., 2001; De Beer et al., 2005). However, the role of sandy sediments in the organic matter cycle has gained recognition only in recent decades. This shift in understanding underscores the crucial influence of sediment permeability on biogeochemical processes. Generally, sediments are considered permeable once the permeability exceeds 10^{-2} m^2 (Huettel et al., 2014). These sediments are composed of sand or gravel and cover approximately 50% of the continental shelf area (Huettel et al., 2014).

Along with pore water transport mechanisms in the sediment, resuspension events exert a major control on sediment dynamics in coastal systems. Such events are primarily driven by surface gravity waves, including tidal and wind-generated waves, which cause regular turbulence and lead to the resuspension of sediments. This process results in sediment sorting, where finer sediment fractions are transported to areas with weaker hydrodynamic forces (De Jonge and Van Beusekom, 1995; George and Hill, 2008; Guillen and Hoekstra, 1997; Guillén and Hoekstra, 1996; Rios-Yunes et al., 2023). Moreover, the frequency and intensity of these resuspension events are expected to increase in the future, influenced by the climate change-driven intensification of extreme weather conditions such as storms. In addition to these natural forces, mobile ground touching fisheries (e.g. bottom trawling) significantly contributes to sediment disturbance and resuspension, further altering sediment composition and impacting benthic habitats. This anthropogenic factor exacerbates the natural sediment dynamics, contributing to a more pronounced disturbance in coastal ecosystems (Rios-Yunes et al., 2023; Morin and Morse, 1999; Dounas et al., 2007; Tiano et al., 2021).

Macrofauna is another control factor of water movement and benthic fluxes in sediments. It alters the transport of organic matter within the sediment, changing its vertical distribution (de Beer et al., 2005; Kristensen et al., 2012, Neumann et al., 2021). These organisms engage in bioturbation, actively reworking the sediment and thereby enhancing the diffusion of gases and solutes across sediment layers. This activity increases the depth of aerobic layers and influences the rates of organic matter decomposition and nutrient cycling. Additionally, macrofauna performs bioirrigation, pumping water through their burrows, which modifies the chemical environment by introducing oxygen and flushing out metabolites, further affecting microbial and chemical reactions. Through feeding and excretion, macrofauna directly alters nutrient dynamics, mobilizing nutrients such as ammonium that are critical for microbial processes. The cumulative impact of these activities not only changes the physical structure of sediments but also shapes the microbial communities within, affecting the overall biogeochemical processes in marine ecosystems.

1.2 Benthic nitrogen cycling

Nitrogen (N) is a key compound in marine biogeochemistry, which is a crucial nutrient for biological productivity and is therefore tightly coupled to the elemental cycle of carbon (C). It forms an integral component of many molecules, including amino acids, nucleic acids and photosynthetic pigments such as chlorophyll-*a* (Veuger et al., 2012).

Nitrogen exists in multiple chemical forms and oxidation states, which allows for a multitude of microbially mediated biogeochemical transformation reactions (Fig. 1.1). The most abundant form of nitrogen is dinitrogen gas (N_2), which makes up ~78 % of the earth´s atmosphere but is not bioavailable for most organisms. N_2 can only be converted to bioavailable "reactive" nitrogen by specialized N-fixing microbes during microbial nitrogen fixation. Bioavailable forms of nitrogen are organic nitrogen and dissolved inorganic nitrogen (DIN), including ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) (Gruber et al., 2008).

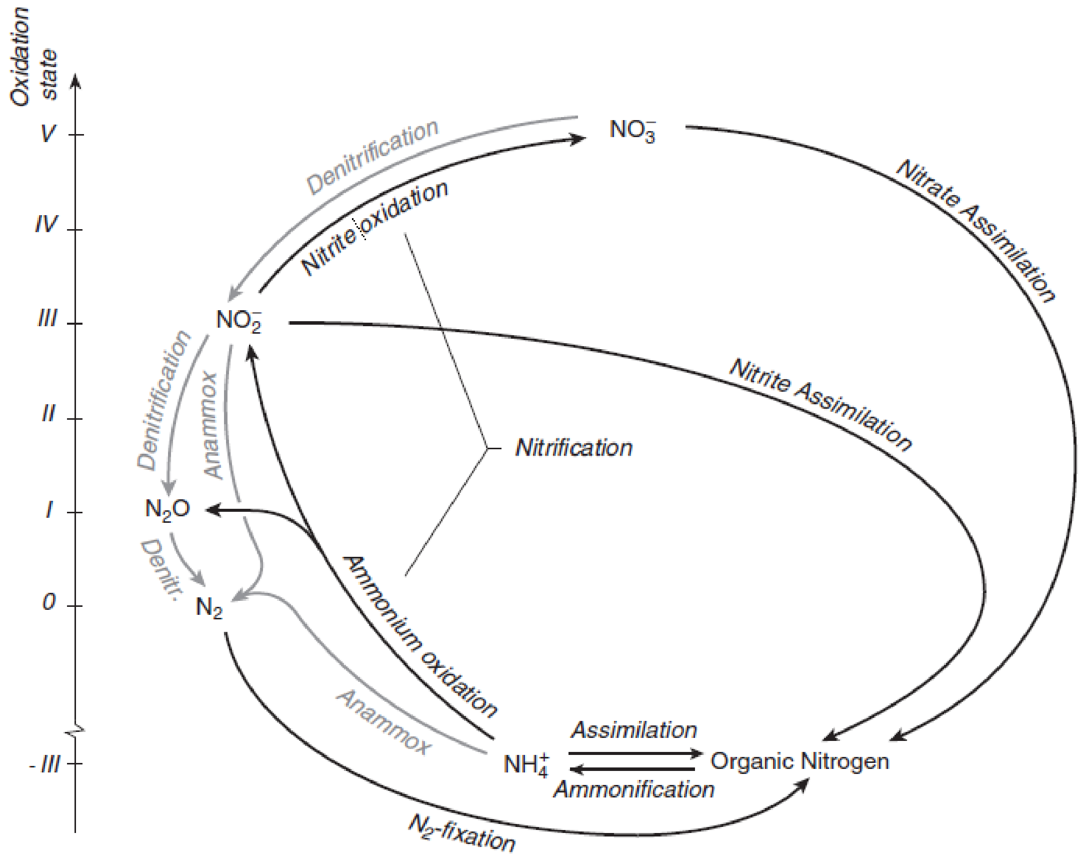

Figure 1.1: Simplified overview of the marine nitrogen cycle, with major chemical forms (plotted against their oxidation state) and pathways of nitrogen. Gruber et al. (2008).

As labile organic nitrogen is microbially broken down, NH_4^+ is released by heterotrophic bacteria. This so-called ammonification essentially is the return pathway of ammonium assimilation, which integrates ammonium into organic molecules. During assimilation, phytoplankton preferably take up NH_4^+ and convert it to biomass (Fig. 1.1). The uptake of NO_2^- and NO_3^- is more energy consuming and therefore less favorable (Dortch 1990; Kirchman 1994; Gruber et al 2008). NH_4^+ is oxidized aerobically during nitrification to NO_2^-, followed by the subsequent NO_2^- oxidation to NO_3^- (Fig. 1.1). These processes transform DIN compounds and keep reactive N within the system.

The excessive enrichment of water bodies with reactive N is one of the main drivers for eutrophication, leading to severe ecological and economic damages including the overgrowth of algae and harmful algae blooms (Anderson et al., 2002; Brockmann et al., 2003; Heisler et al., 2008) and the subsequent depletion of oxygen (Diaz and Rosenberg 2008). Denitrification plays a crucial role in the removal of reactive N from the system, mitigating negative eutrophication consequences. Denitrification is the dissimilatory microbial reduction of NO_3^-, with intermediate products, to N_2 and generally occurs within suboxic and anoxic sediment layers (Dodds et al., 2017).

Understanding and quantifying these nitrogen transformations is critical for managing and enhancing ecosystem services, particularly in combating eutrophication and supporting sustainable marine environments. Other nitrogen pathways include anaerobic ammonium oxidation (anammox) which utilizes NH_4^+ and NO_2^- to produce N_2 (Bale et al., 2014) and dissimilatory nitrate reduction to ammonium (DNRA) (Aalto et al., 2021; Villa et al., 2019). The latter two processes however seem to play minor roles in benthic biogeochemical N-turnover in the North Sea (Villa et al., 2019).

In sediments, the diversity and composition of benthic microbial communities determines the rates at which nitrogen turnover processes (e.g. ammonification, nitrification, denitrification) occur. Each microbial group brings specialized enzymatic capabilities that facilitate specific reactions in the nitrogen cycle, directly impacting the efficiency of nutrient recycling. Their vertical distribution within sediments is dictated by redox conditions. Aerobic microbes dominate the surface sediment where they consume oxygen. With increasing sediment depth and decreasing oxygen concentrations, they are replaced by anaerobes that utilize different electron acceptors. Generally, these electron acceptors are utilized in order of decreasing energy yield. Oxygen is thermodynamically the most favorable, followed by nitrate, manganese (IV), iron (III), , sulfate and carbon dioxide (Ahmerkamp 2016; Bonthond et al., 2023).

1.3 Working area: the southern North Sea

The southern North Sea is a semi-enclosed area surrounded by densely populated and industrialized countries. It is subject to conflicting usage and a variety of anthropogenic disturbances, including nutrient inputs from the major European rivers, fisheries, sand extraction and offshore windfarms (Bratek et al., 2020; Dutkiewicz et al., 2015; Heinatz and Scheffold 2023; Neumann et al., 2017b; Tebaldi et al., 2021). These accelerating anthropogenic pressures lead to habitat destruction and reduced biodiversity, ultimately resulting in the aggravation of the environmental status of the German Bight, as defined in the European Marine Strategy Framework (MSFD 2008). To counteract these negative pressures, three marine protected areas (MPA´s) have been established within the European Natura 2000 program (Fig. 1.2): Borkum Riffgrund, Doggerbank and Sylter Außenriff. However, recent assessments suggest that anthropogenic disturbances are too high to achieve good environmental status (OSPAR 2023) with current management strategies, highlighting the ongoing challenge posed by high anthropogenic impacts. Management strategies in these MPAs focus on minimizing human impacts. Restrictions on commercial fishing, particularly bottom trawling, aim to protect benthic habitats. These measures seek to restore the ecological balance, enhancing biodiversity and maintaining sustainable fish populations. Therefore, in parts of these MPA´s, fisheries with bottom contact gears shall be excluded.

In the dynamic southern North Sea, the cycling of nutrients is essential for sustaining primary productivity. Photosynthetic organisms depend on these nutrients, largely supplied and regulated by microbial-mediated biogeochemical cycles, to support diverse marine life from zooplankton to mammals. The efficiency of these fluxes influences ecosystem productivity and stability, while biodiversity within these cycles ensures resilience, enabling adaptation to environmental changes. Biogeochemical fluxes also provide crucial ecosystem services: they improve water quality by processing pollutants, support vital fisheries for food security and livelihoods and enhance recreational and cultural activities. Understanding these complex processes is critical for maintaining ecological balance and supporting biodiversity in coastal ecosystems. Additionally, the southern North Sea acts as an excellent study area due to its outstanding data availability (e.g. sedimentary TOC).

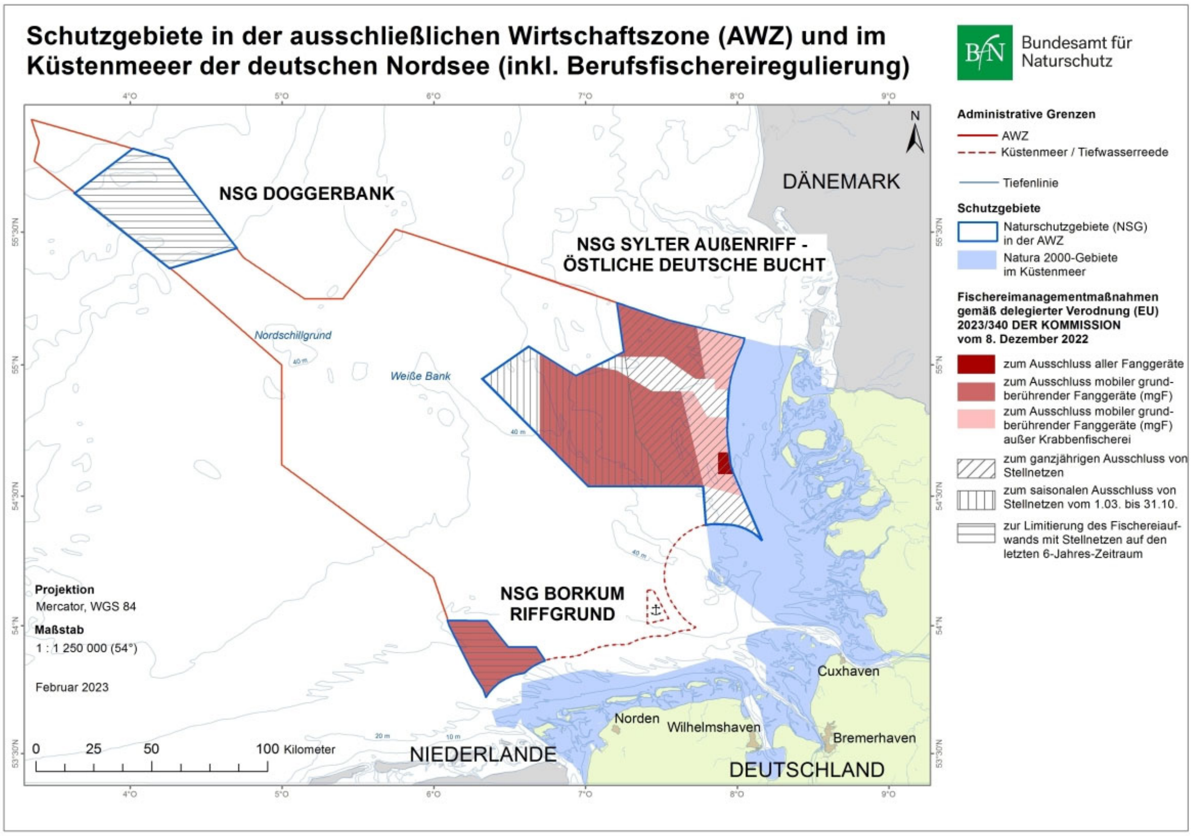

Figure 1.2: MPA´s within the german Exclusive Economic zone (EEZ) and in the coastal sea of the german North Sea (BfN)

1.4 Project and thesis outline

The doctoral thesis presented here is part of the DAM-MGF Nordsee project that provides an ecosystem baseline description of the three German Natura 2000 MPA´s (Borkum Riffgrund, Dogger Bank, Sylter Außenriff) within the German Bight, in terms of their physical, biological and biogeochemical parameters and processes. As mobile bottom-contact fisheries are to be excluded in parts of these areas, potential future changes shall be investigated to assess the long-term effects of management measures in a before-after-control impact (BACI) approach. Specifically, this study investigates biogeochemical processes, with a focus on benthic oxygen and nitrogen dynamics. The implementation of a process-driven biogeochemical model for permeable sands, based on the pore water advection model of Elliott and Brooks (1997), allows for the prediction of benthic fluxes of O_2, NH_4^+, NO^{3-} and N_2, which are imperative for most functions and food webs (Amo-Seco et al., 2021, Griffiths et al., 2017, Hopkinson and Wetzel, 1982).

The main part of this thesis consists of three chapters that are either published, submitted, or intended for publication to a peer reviewed scientific journal (chapters 2-4).

Chapter 2: "Sedimentary mud and phaeophytin-a are reliable predictors of oxygen consumption and nitrogen turnover in the southern North Sea"

Fabrizio Minutolo, Kirstin Dähnke, Marc Metzke, Moritz Holtappels and Andreas Neumann, Continental Shelf Research, 272, 105161, https://doi.org/10.1016/j.csr.2023.105161, 2024

Chapter 2 investigates several sediment characteristics and their possible application as proxies for sediment reactivity, with a focus on benthic oxygen consumption and reaction rates of reactive nitrogen. Within this context, a parametrization framework has been established to predict net (O_2, NH_4^+ and NO^{3-}) and gross (NH_4^+ and NO^{3-}) benthic reaction rates, using sedimentary values/data of predictor variables. The data suggest that mud content and phaeophytin-a concentrations could serve as appropriate proxies for sediment reactivity.

Chapter 3: "Benthic processes in advective sediments are insensitive to vertical substrate distribution"

Fabrizio Minutolo, Kirstin Dähnke, Marc Metzke and Andreas Neumann, Continental Shelf Research (submitted)

Based on the pore water advection model of Elliott and Brooks (1997) and the parametrization framework of chapter 2, chapter 3 implements a process-driven biogeochemical model for permeable sands. The model uses previously evaluated proxies and allows for the prediction of benthic fluxes of O_2, NH_4^+, NO^{3-} and N_2. It explores the influence of vertical substrate distribution within the sediment on the magnitude of these fluxes and reveals that the vertical distribution of substrates has almost no effects on modelled benthic fluxes in permeable sands.

Chapter 4: "Application of a benthic model for the implementation of management scenarios"

Andreas Neumann, Fabrizio Minutolo and Kirstin Dähnke, in preparation for publication

Chapter 4 spatially applies the benthic biogeochemical model to calculate total fluxes and nutrients in the Natura 2000 MPA´s of the German Bight. This lays the foundation for implementing the sediment in a digital twin, which is then used for "what-if" scenarios, exploring the effects of mobile bottom-contact fishing exclusion on the sedimentary inventory of organic matter and sediment reactivity. More specifically, the balance between nutrient recycling and the removal of reactive nitrogen (i.e. denitrification) is investigated. Our results indicate that the exclusion of bottom trawling leads to only marginal increases in sedimentary total organic carbon (TOC) content, which in turn causes minor alterations in the benthic fluxes of oxygen and nitrogen.

In a final section (chapter 5), the results of these studies are summarized towards an overarching conclusion of the work and to address possible future scientific and management perspectives in the light of the insights gained in this dissertation.

2 Sedimentary mud and phaeophytin-a are reliable predictors of oxygen consumption and nitrogen turnover in the southern North Sea

MINUTOLO, F., DÄHNKE, K., METZKE, M., HOLTAPPELS, M. & NEUMANN, A. 2024. Sedimentary mud and phaeophytin-a are reliable predictors of oxygen consumption and nitrogen turnover in the southern North Sea. *Continental Shelf Research,* 272.

Abstract

Coastal systems are exposed to variable human uses and anthropogenic pressures, yet they provide valuable ecosystem services. Understanding the benthic processes in these systems is crucial for their effective management and conservation. This study investigates sediment characteristics as proxies for oxygen and nitrogen turnover in coastal, sandy, permeable sediments. We incubated sediment samples to quantify the turnover of ammonium and nitrate and analyzed various sediment properties to determine the most suitable predictors of sediment reactivity. Oxygen consumption rates and rates of ammonium and nitrate turnover strongly correlate with mud content and phaeophytin-a, which are identified as the best proxies for sediment reactivity. Ultimately, our data show that sediment nutrient recycling and turnover is intimately linked to spring primary production in the water column. In order to deduce reaction rates of oxygen, ammonium and nitrate from sediment properties, we provide linear regression coefficients and their uncertainties, enabling access to previous observations that would otherwise remain inaccessible due to missing data. This study provides insights for the development of benthic models that ultimately can be used to assess the impact of anthropogenic pressures on coastal systems. The findings have implications for nutrient management and monitoring in the German Bight, as an improved understanding of sediment reactivity allows for more appropriate and sustainable management and monitoring policies to be implemented.

2.1 Introduction

Coastal systems cover only a small area of the ocean's surface, but disproportionally contribute to global marine primary production and provide valuable habitats and ecosystem services (Bratek et al., 2020; He and Silliman, 2019; Neumann et al., 2021; Van Oostende et al., 2018; Ward et al., 2020). Such ecosystem services include nutrient transformation, retention and removal through biogeochemical processes (Asmala et al., 2017), which in turn are important for fisheries, for chemical water quality, and for nutrient management. Owing to their shallow water depth, coastal systems commonly exhibit a tight benthic-pelagic coupling and play a key role in ocean biogeochemical cycling. (Bratek et al., 2020; Hellemann et al., 2020). In addition to effects of global change (e.g. ocean acidification, increasing water temperatures, and rising sea levels), the coastal southern North Sea is further stressed by multiple anthropogenic pressures such as fisheries, sand extraction, offshore windfarms, and discharge of riverine nutrients and pollutants (Bratek et al., 2020; Dutkiewicz et al., 2015; Heinatz and Scheffold, 2023; Neumann et al., 2017b; Tebaldi et al., 2021). These competing interests in nature conservation/restoration and economic exploitation require a comprehensive management of the coastal waters. Recently, models ('digital twins') emerge as tools to implement management measures in silico first to assess the results of planned interventions in a complex system (Pillai et al., 2022; Skakala et al., 2023). One obvious prerequisite for such models of the coastal North Sea is a validated parameterization of the benthic processes. First steps towards a comprehensive, process-driven model of benthic processes have been made (Ahmerkamp et al., 2017; Zhang et al., 2021), focusing on benthic oxygen and TOC dynamics. A comprehensive benthic model requires an optimized set of suitable environmental parameters to deduce e.g. reaction rates. The optimum here relies on at least two dimensions: predictive power and availability. The parameters used in the model have to be sufficiently correlated with the target parameters for viable predictions, but also have to be sufficiently available in terms of seasonal and spatial coverage from previous observations. Plausible choices of sediment parameters as reactivity proxies are TOC, grain size and mud content (<63 µm fraction), as these are frequently measured and are already available with high spatial resolution in the North Sea. Moreover, these basic sediment characteristics further enable deduction of additional parameters such as permeability (Neumann et al., 2017a) and bedform dimensions, which are necessary for estimates of pore water exchange (Ahmerkamp et al., 2017) and thereby contribute to a compact set of proxies. However, these basic sediment parameters are only indirectly linked to microbial activities, whereas other parameters like pigment content, carbohydrates, or TOC provide a more direct link to microbial turnover. Unfortunately, the latter parameters are less frequently measured, and the data availability in the North Sea is much lower. In this study, we examine a range of sediment characteristics as proxies for the sedimentary turnover of oxygen and nitrogen in permeable sands, with an emphasis on ammonium and nitrate. We expect higher concentrations of organic material and more intense oxygen and nitrogen turnover in shallower waters, where light availability is higher. We incubated permeable coastal sediment, quantified the turnover of ammonium and nitrate, and analyzed sedimentary properties that serve as most suitable predictors of sediment reactivity, in order to establish the linkage between predictor and process rate. Additionally, we provide equations for conversions among these parameters to open up previous observations. In the future, such proxies will be used to implement benthic models in order to analyze e.g. the response of benthic N-transformations to changing anthropogenic pressures, using various scenarios of, for example, bottom trawling fishing pressure. These improved prediction capabilities facilitate a more comprehensive understanding of sediment reactivity and nutrient dynamics, empowering decision makers with data-driven insights, supporting the development of sustainable policies for the management and monitoring of the German Bight.

2.2 Methods

2.2.1 Study site

Investigations took place in the southern North Sea, a semi-enclosed area surrounded by densely populated and industrialized countries, and subject to large anthropogenic nutrient inputs from the major European rivers Elbe, Rhine, Ems and Weser (Fig. 2.1). The sampling was performed in August and September 2021 during R/V *Heincke* cruise HE582 (Holtappels et al., 2021). Samples were taken from four sites, NOAH-I West (NIW), NOAH-I East (NIE), Sylter Außenriff (SAR) and Amrum Bank (AB) (Tab. 2.1).

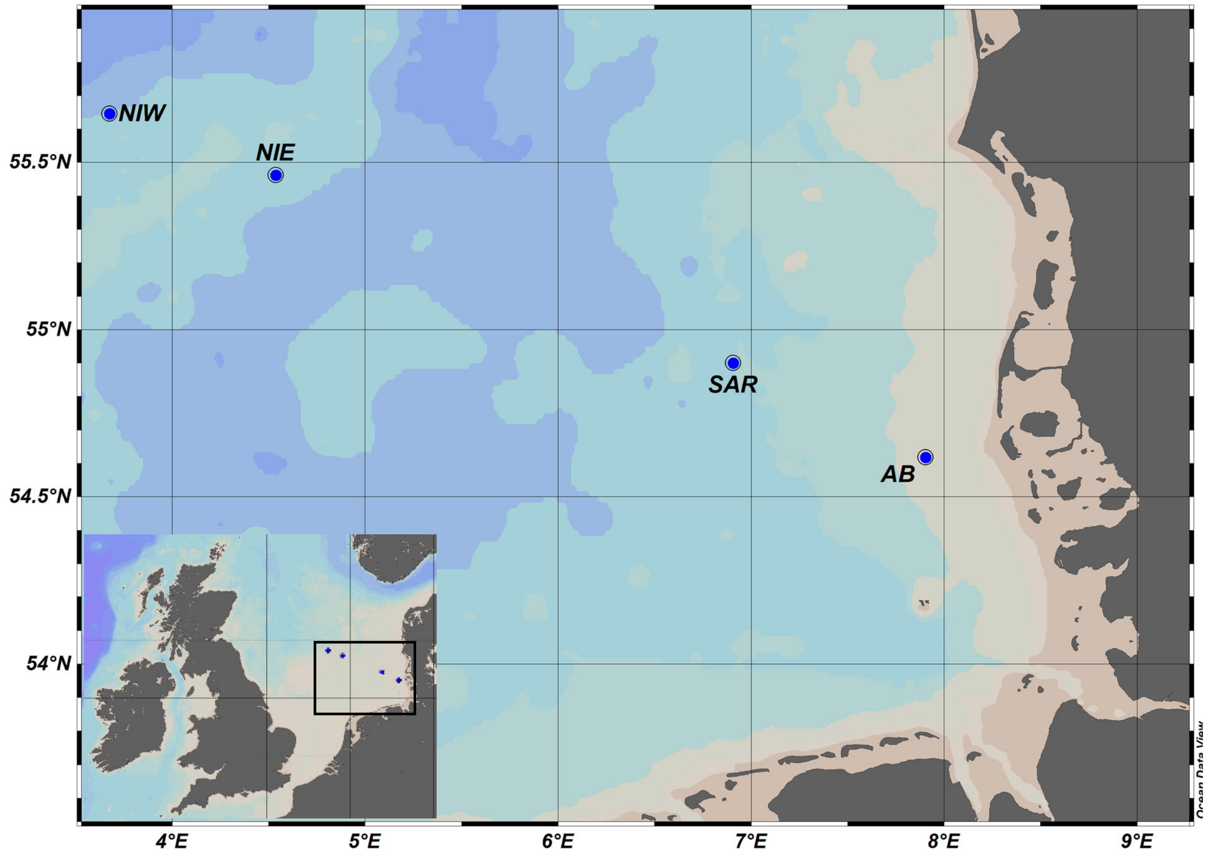

Figure 2.1: Sampling stations in the southern North Sea during the HE582 cruise.

Table 2.1: Coordinates, sampling date and water depth at the sampled stations in the southeastern North Sea.

Station	Latitude	Longitude	Date	Depth
	(deg)			(m)
NIW	55.645269	3.675083	28.08.2021	36.0
NIE	55.462272	4.537492	30.08.2021	28.2
SAR	54.899801	6.906302	31.08.2021	24.7
AB	54.618351	7.904198	02.09.2021	10.1

2.2.2 Sediment and water sampling

At each station, we took bottom water and sediment samples. Bottom water samples were taken at ~2 m above the sea floor with 6 L Niskin bottles attached to a CTD and kept at in situ temperature. Water samples then were filtered (polyethersulfone membrane, Whatman, 0.2 µm) and air was injected using aquarium pumps, to ensure air saturated oxygen concentrations. Surface sediment (<3 cm) was taken from Van Veen grab samples and sieved through a 1 mm mesh to exclude macrofauna from the sediment, as we were interested in process rates as intrinsic properties of the sediment. Permeable sands naturally are subjected to disturbances (e.g. tides and storm events), leading to bedform migration, ultimately resulting in a changing seabed topography (Ahmerkamp et al., 2015). Undisturbed sediments commonly refer to finer sediments with smaller grainsizes, where diffusion dominates transport processes. Therefore, the manipulation through sieving likely had minimal impacts on intrinsic sediment properties. Furthermore, this ensures a homogenous sediment distribution in the flow-through-reactors (FTRs). Fig. 2.2 shows the sediment depth profiles of pigments of the same stations three weeks earlier during the HE581 cruise, with values for pigments of the FTR sediment used in this study as reference. Pigments measured in our FTR sediment approximately are of the same order of magnitude than previously measured depth profiles (with the exception of station SAR). For further information on sediment profiles and benthic macrofauna within similar sites of the southern North Sea, cf. Neumann et al. (2021); Zhang et al. (2019).

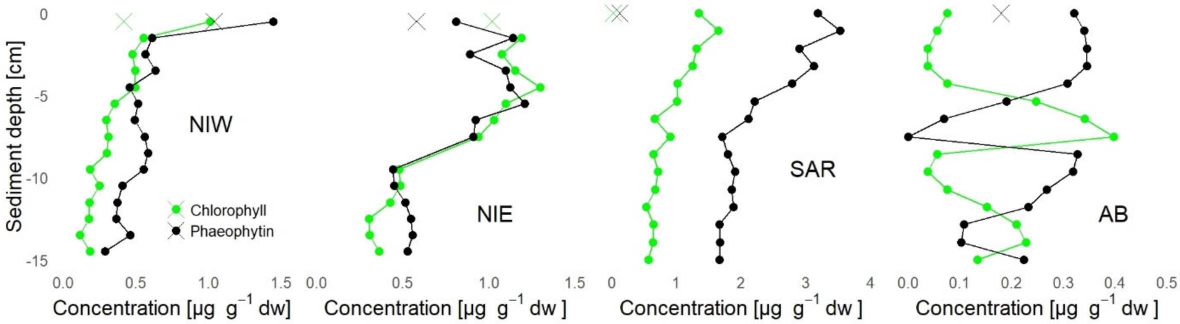

Figure 2.2: Sediment depth profiles of pigment data from other cruises (HE581 for NIW, NIE and SAR, and HE588 for AB) at the same stations. Crosses represent pigment values of the FTR sediment from this study. Note: No FTR chlorophyll-a value for station AB.

2.2.3 Flow-through-reactor incubations

We used the FTRs described in Ahmerkamp et al. (2017). In a temperature-controlled laboratory, four FTRs per site were carefully filled with sieved sediment and incubated in the ship's laboratory at in situ temperature (~15°C). To exclude trapping of potential air bubbles within the FTRs, the filling step was done underwater with the previously filtered station bottom water. Upon closure of all FTRs, two filtered and air saturated water reservoirs were amended with $^{15}NH_4$ and $^{15}NO_3$ (98 at%, Isotec) and pumped through FTRs 1–2 and 3–4, for an assessment of gross ammonium and gross nitrate production, respectively (Fig. 2.3). NH_4^+ and NO_3^- concentrations of the added tracer solutions were adjusted to bottom water concentrations, previously measured spectrophotometrically on site, and incubations were carried out at tracer level to prevent alterations of benthic turnover rates (Bratek et al., 2020). The tracer addition was calculated and a maximum isotopic enrichment of 5000‰ in substrates was aimed for. As an example, at station NIW, the addition of 128 µL 1 mM $^{15}NO_3$ solution to the 10 L water reservoir raised the nitrate concentration from initial 7.00 µmol L^{-1} NO_3^- to a final NO_3^- concentration of 7.13 µmol L^{-1} and yet resulted in the desired isotope enrichment. When ammonium or nitrate concentrations were low (<10 µmol L^{-1}), ammonium standard solution or an internal nitrate standard was added to the water reservoir supplying the FTRs, respectively. This was done, to ensure proper tracer addition, allowing accurate isotopic measurements. Flowrates were chosen to mimic natural pore water flow. Oxygen concentrations at the FTR in- and outlets were measured continuously with flow-through optodes (PyroScience, Germany). Incubations were run for approximately 20 h. Once steady state (ss) was reached, samples for nutrients (FTR 1–4) and stable isotopes of NH_4 (FTR 1–2), NO_3 (FTR 3–4) for three sampling points (ss1, ss2 and ss3) were taken consecutively. Samples of the water reservoirs supplying the FTRs, were taken before the start of the incubation (res1) and at the end of the incubation, when all steady state samples had been taken (res2). Incubation water samples were filtered with a syringe filter (cellulose acetate, Sartorius, 0.45 µm) and frozen in polypropylene tubes (15 mL) at -20°C for later nutrient and isotope analyses. After the incubation, additional sediment samples were taken for sediment characteristics (TOC, chlorophyll-a, phaeophytin-a, carbohydrates, grain size and mud content) and frozen in polypropylene cups.

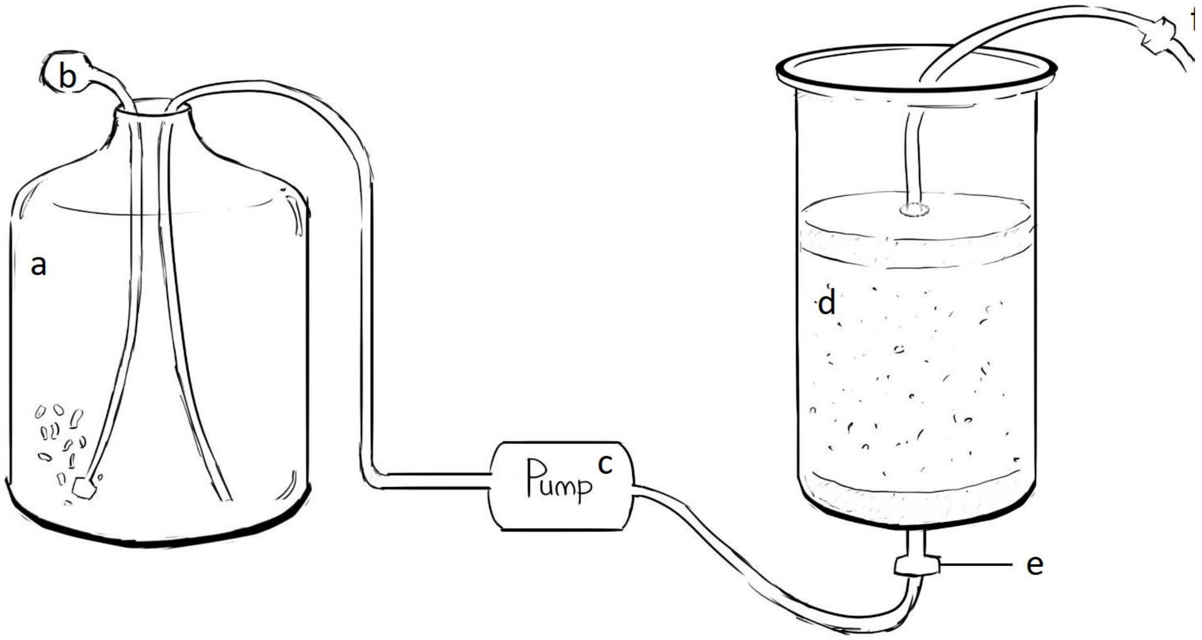

Figure 2.3: FTR incubation setup. a: water reservoir. b: aquarium pump aerating the FTR water reservoir. c: peristaltic pump, pumping water from the reservoir through the FTRs. d: FTR containing homogenized sand. e: inlet sampling and flow through optode, measuring oxygen concentrations. f: : outlet sampling and flow through optode, measuring oxygen concentrations. Pump direction: →

2.2.4 Analyses

2.2.4.1 Dissolved inorganic nitrogen concentrations

Concentrations of NO_x, NO_2^- , NH_4^+ and SiO_4^{4-} in water samples were determined in duplicate with a continuous flow analyzer (AA3, Seal Analytical, Germany) following standard colorimetric techniques (NO_x and NO_2^- : (Grasshoff et al., 1999); NH_4^+ (Kerouel and Aminot, 1997):). The difference between NO_x and NO_2^- was used to calculate NO_3^- concentrations. Based on duplicates, measurement precision for NO_x was better than 0.12 μmol L^{-1} and better than 0.05 μmol L^{-1} for NO_2^- and NH_4^+.

2.2.4.2 Sediment characteristics

All sediment samples were freeze-dried. Chlorophyll-a and phaeophytin-a were extracted with 90% acetone and concentrations were measured spectrophotometrically (Hach-Lange DR-6000) according to Lorenzen (1967). Subsamples of the freeze-dried sediment were taken for grain size distribution analyses and treated with potassium pyrophosphate solution (7,5%) to make a slurry prior to the analysis. Samples were then measured with a laser-diffraction particle sizer (Fritsch Analysette 22). Sediment subsamples of the dry sediment were ground, homogenized and analyzed for total carbon and total nitrogen contents with an elemental analyzer (Euro EA, HEKAtech). After removal of inorganic carbon using 1 M hydrochloric acid (HCl), the total organic carbon content was analyzed. The revised anthrone method (Frolund et al., 1996) was applied to spectrophotometrically (Hach-Lange DR-6000) determine carbohydrate contents.

2.2.4.3 Isotope measurements

The nitrogen isotope ratios of nitrate were determined according to the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), which is based on the mass spectrophotometric measurement of isotopic ratios of N_2O produced by the bacterium *Pseudomonas aureofaciens*. Two international standards (IAEA NO_3^- $\delta^{15}N = +4.7‰$, USGS34 $\delta^{15}N = -1.8‰$) were used for a regression-based correction of isotope values. For further quality assurance, an internal standard was measured with each batch of samples. For isotopic determination of ammonium, nitrite was removed by reduction with sulfamic acid (Granger and Sigman, 2009), then ammonium was chemically oxidized to nitrite by hypobromite at pH ~ 12 before reduction to N_2O using sodium azide (Zhang et al., 2007). For calibration purposes we used three international standards (IAEA N1 $\delta^{15}N = +0.4‰$, USGS25 $\delta^{15}N = -30.4‰$ and USGS26 $\delta^{15}N = +53.7‰$). N_2O produced by either method was analyzed with a Gas-Bench II, coupled to an isotope ratio mass spectrophotometer (Delta Plus XP, Thermo Fisher Scientific).

2.2.5 Benthic volumetric rates

Volumetric rates of oxygen consumption, net dissolved inorganic nitrogen (DIN = $NO_3^- + NO_2^- + NH_4^+$) and silicate (SiO_4^{4-}) turnover were calculated based on the concentration difference between FTR inlet (C_{in}) and outlet (C_{out}) during steady state. This approach provides an estimate of the overall change over a specific period. It considers the net effect of all processes that contribute to nutrient/oxygen cycling. Net rates provide a measure of the overall gain or loss of nutrients/O_2 in the system but may not capture the specific processes responsible for these changes. Benthic reaction rates can be calculated by using the retention time rt = Lc/u with u as the bulk porewater velocity/flowrate and Lc as the length of the FTR (Ahmerkamp et al., 2020):

$$R = \left(\frac{C_{out} - C_{in}}{r_t}\right) [\mu\text{mol } L^{-1} h^{-1}] \tag{2.1}$$

2.2.6 Gross rates of ammonium and nitrate production

Gross rates of ammonium and nitrate turnover were calculated according to the ^{15}N dilution method (Norton and Stark, 2011), based on $^{15}NH_4^+$ and $^{15}NO_3^-$ additions, respectively:

$$R = \left(\frac{C_{in} - C_{out}}{r_t}\right) * \frac{\log\left(\frac{C_{in}}{C_{out}}\right)}{\log\left(\frac{I_{in}}{I_{out}}\right)} [\mu\text{mol } L^{-1} h^{-1}] \tag{2.2}$$

Where C is the nutrient concentration, rt is the retention time and I is the ^{15}N atom % excess. Incubations were done in duplicate. This method allows for the direct measurement of specific ammonium and nitrate transformation processes, such as microbial oxidation. By introducing a known quantity of a stable isotope-labeled ammonium or nitrate compound, the transformation rates can be measured by tracking the isotope label over time. Gross rates provide a more detailed understanding of the individual processes contributing to ammonium and nitrate turnover and can help identify the specific drivers behind the observed net changes in ammonium/nitrate concentrations.

For comparability, and for future investigations across different seasons, gross and net rates were adjusted to 10°C according to the Q_{10} coefficient, relating biological processes to temperature dependence (Mundim et al., 2020):

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10K}{T_2 - T_1}} \tag{2.3}$$

Where k_2 is the measured rate at the measured temperature (T_2) during the incubation and k1 is the calculated rate at the desired temperature of 10°C (T_1). The value for Q_{10} was always set to 2, which is representative for biological reactions (Aisami et al., 2017).

2.3 Results

2.3.1 Sediment characteristics

At all sampled stations, sediment was sandy with highest median grain sizes for AB and lowest for NIW and NIE. The collected sediment consists of fine to coarse sands with median grain sizes of 218–619 µm and mud contents of 0.18–3.73 %. The mud and carbohydrate content were highest at station NIW and lowest at stations SAR and AB. A similar pattern with highest concentrations at NIW and lowest at SAR and AB can be observed for TOC and phaeophytin-a concentrations (Table 2.2).

Table 2.2: Sediment characteristics at the sampled stations in the southeastern North Sea. Note: TOC = total organic carbon of the homogenized sediment. Mud = mud content and Phaeo-a = phaeophytin-a concentration. Values represent the average per station. Bdl = below detection limit

Station	Phaeo-a	Chl-a	Mud	TOC	Grain size	Carbs
	µg g dw^{-1}		(%)		µg g dw^{-1}	mg g dw^{-1}
NIW	1.04 ± 0.11	0.42 ± 0.09	3.73 ± 0.47	0.06 ± 0.00	218 ± 8.10	0.09 ± 0.01
NIE	0.58 ± 0.05	1.02 ± 0.06	1.80 ± 0.16	0.05 ± 0.00	227 ± 2.90	0.09 ± 0.02
SAR	0.12 ± 0.05	0.02 ± 0.05	0.28 ± 0.05	0.03 ± 0.01	448 ± 8.54	0.04 ± 0.00
AB	0.18 ± 0.07	bdl	0.18 ± 0.10	0.02 ± 0.00	619 ± 26.56	0.05 ± 0.02

2.3.2 Benthic volumetric rates

We measured specific volumetric rates, rather than fluxes across interfaces. These rates are defined as the turnover of oxygen/nutrient per sediment volume and time, and may be regarded as an intrinsic sediment characteristic (Neumann et al., 2019). Whenever concentrations at the FTR outlets were at or below the detection limit (only for NH_4^+ at stations NIE FTR 2 and 3, SAR FTR 1), rates were not calculated and left out of the results (graphs and correlation analysis). If concentrations at the FTR inlets were below the detection limit (only for NH_4^+ at station SAR FTR 3 and 4), concentrations were set to zero. Specific O_2 consumption rates (Table 2.3) were lowest at stations AB and SAR, with 10.2 and 10.7 µmol L^{-1} h^{-1}, respectively and highest for NIW with 25.6 µmol L^{-1} h^{-1}. At stations AB and SAR there was a small release of ammonium with rates of 0.01 and 0.02 µmol L^{-1} h^{-1}, respectively. At stations NIW and NIE ammonium was taken up by the sediment with rates of -0.33 and -0.08 µmol L^{-1} h^{-1}, respectively. Turnover (of dissolved inorganic nutrients), in the following, refers to negative net reaction rates as well as positive ones. Net nitrate release was highest at station NIW (1.11 µmol L^{-1} h^{-1}). The same applies for net silicate release, showing lowest rates at station AB (0.32 µmol L^{-1} h^{-1}) and highest rates at NIW (2.57 µmol L^{-1} h^{-1}). Similarly, gross rates for ammonium and nitrate turnover are highest at station NIW (0.73 and 5.44 µmol L^{-1} h^{-1}, respectively) and lowest at station AB (0.01 and 1.11 µmol L^{-1} h^{-1}, respectively).

Table 2.3: Volumetric rates for O_2 consumption, net and gross dissolved inorganic nutrient turnover rates at the sampled stations in the southeastern North Sea. Note: Net turnover includes negative NH_4^+ rates. Values represent the average per station.

Station	**O_2 consumption**	**NH_4^+ turnover**		**NO_3^- turnover**		**SiO_4^{4-} turnover**
		Net	**Gross**	**Net**	**Gross**	
$\mu mol\ L^{-1}\ h^{-1}$						
NIW	25.6 ± 5.4	-0.33 ± 0.04	0.73 ± 0.10	1.11 ± 0.27	5.44 ± 0.01	2.57 ± 0.40
NIE	16.7 ± 1.3	-0.08 ± 0.04	0.20 ± 0.14	0.48 ± 0.08	1.55 ± 0.21	0.66 ± 0.02
SAR	10.7 ± 1.3	0.03 ± 0.02	0.06 ± 0.08	0.49 ± 0.03	2.55 ± 1.15	0.36 ± 0.01
AB	10.2 ± 0.5	0.01 ± 0.01	0.01 ± 0.01	0.23 ± 0.02	1.11 ± 0.1	0.32 ± 0.06

2.3.3 Correlation analyses

Generally, for the correlation analyses, all four values per station (4 FTRs per station) were used. However, at stations NIE and SAR, two and one of the four values for ammonium turnover, respectively, were left out because NH_4^+ concentrations at the FTR outlets were below the detection limit. Across all four sampling stations, a correlation analysis (Table 2.4) reveals that net ammonium turnover significantly correlates ($p < 0.001$) with mud content ($R = -0.96$), phaeophytin-a ($R = -0.95$) and specific O_2 consumption rate ($R = -0.94$) (Fig. 2.4). We also find that net NO_3^- turnover significantly ($p < 0.001$) correlates with the same parameters (mud content, $R = 0.85$, phaeophytin-a, $R = 0.81$, and specific O_2 consumption rate, $R = 0.93$). Both process rates also scale with and significantly ($p < 0.001$) correlate with sedimentary silicate release (Table 2.4). Similarly to net rates, gross rates (Fig. 2.5) for ammonium and nitrate turnover also correlate best with mud content ($R = 0.93$, $p < 0.001$ for ammonium and $R = 0.80$, $p < 0.1$ for nitrate) and phaeophytin-a ($R = 0.92$, $p < 0.01$ for ammonium and $R = 0.76$, $p < 0.1$ for nitrate). Gross rate measurements were done in duplicate. Across all measured parameters, we calculated linear regression equations and residual standard errors of conversions between these (Table 2.5).

Table 2.4: Pearson correlation coefficients of rates of O_2 consumption, net dissolved inorganic nutrient turnover (NH_4^+, NO_3^- and and SiO_4^{4--}) and sediment characteristics. Coefficients in bold and bold/large represent statistical significance and correspond to p-values of 0.01 and 0.001, respectively. Note: O_2 con. = O_2 consumption. For net NH_4^+ turnover, instead of four data points per station, there are only two data points for station NIE and three data points for station SAR.

O_2 con.	**-0,94**	**0,93**	**0,94**	**0,91**	0,47	**0,93**	**-0,77**	**0,79**	**0,67**
	NH_4^+	**-0,92**	**-0,98**	**-0,95**	-0,44	**-0,96**	**0,78**	**-0,80**	**-0,80**
		NO_3^-	**0,95**	**0,81**	0,23	**0,85**	**-0,69**	**0,72**	0,50
			SiO_4^{4-}	**0,90**	0,22	**0,92**	**-0,65**	**0,73**	0,58
				Phaeo-a	0,52	**0,98**	**-0,81**	**0,86**	**0,77**
					Chl-a	0,51	**-0,79**	**0,66**	**0,74**
						Mud	**-0,83**	**0,85**	**0,80**
							Grain size	**-0,91**	**-0,77**
								TOC	**0,73**
									Carbs

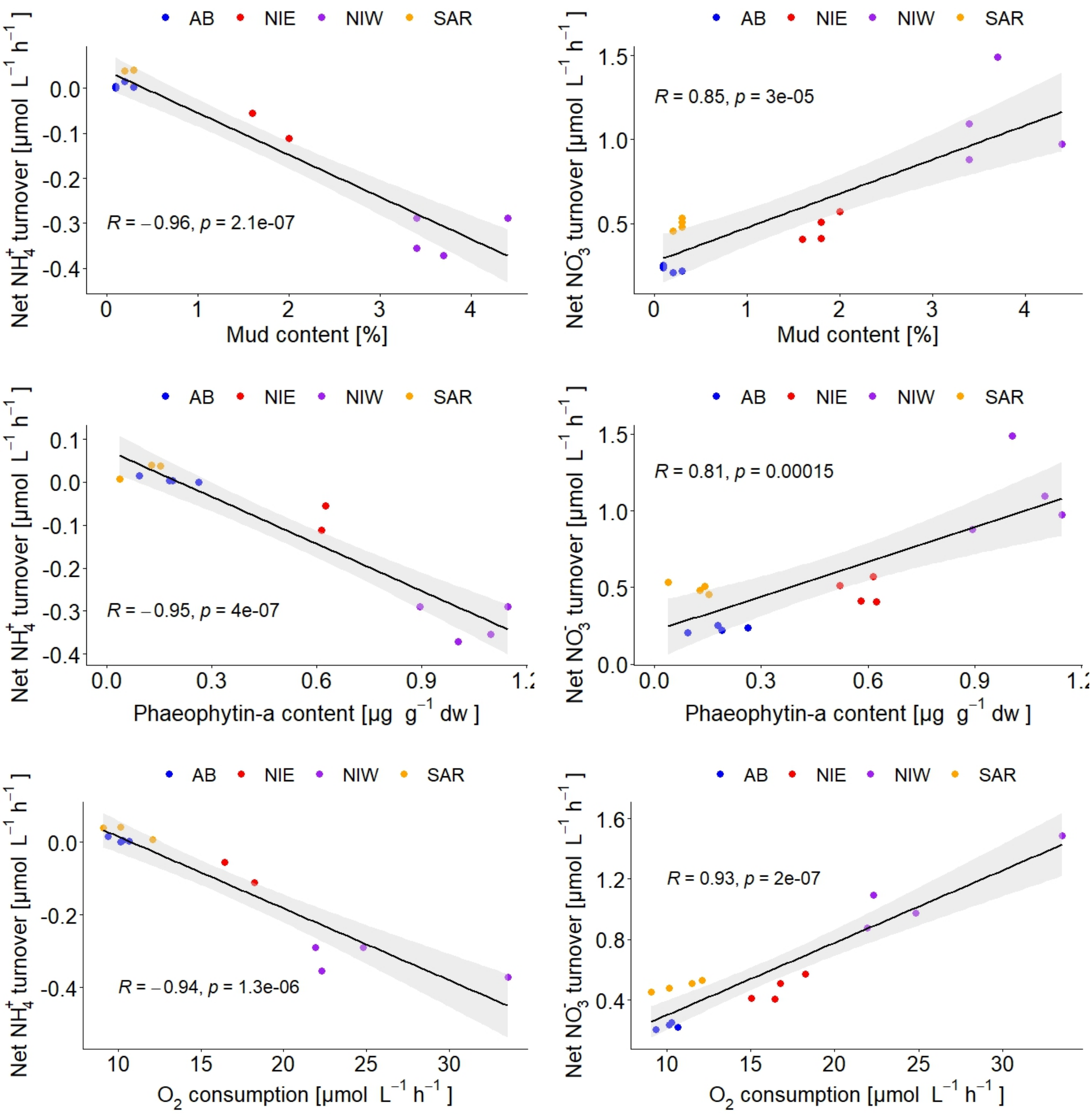

Figure 2.4: Pearson correlation of net NH_4^+ (left) and NO_3^- (right) turnover rates with mud (top), phaeophytin-a content (middle) and O_2 consumption (bottom). Note: Net turnover includes negative NH_4^+ turnover rates. The solid lines indicate the linear regression. Grey bands indicate confidence intervals. For net NH_4^+ turnover, instead of four data points per station, there are only two data points for station NIE and three data points for station SAR.

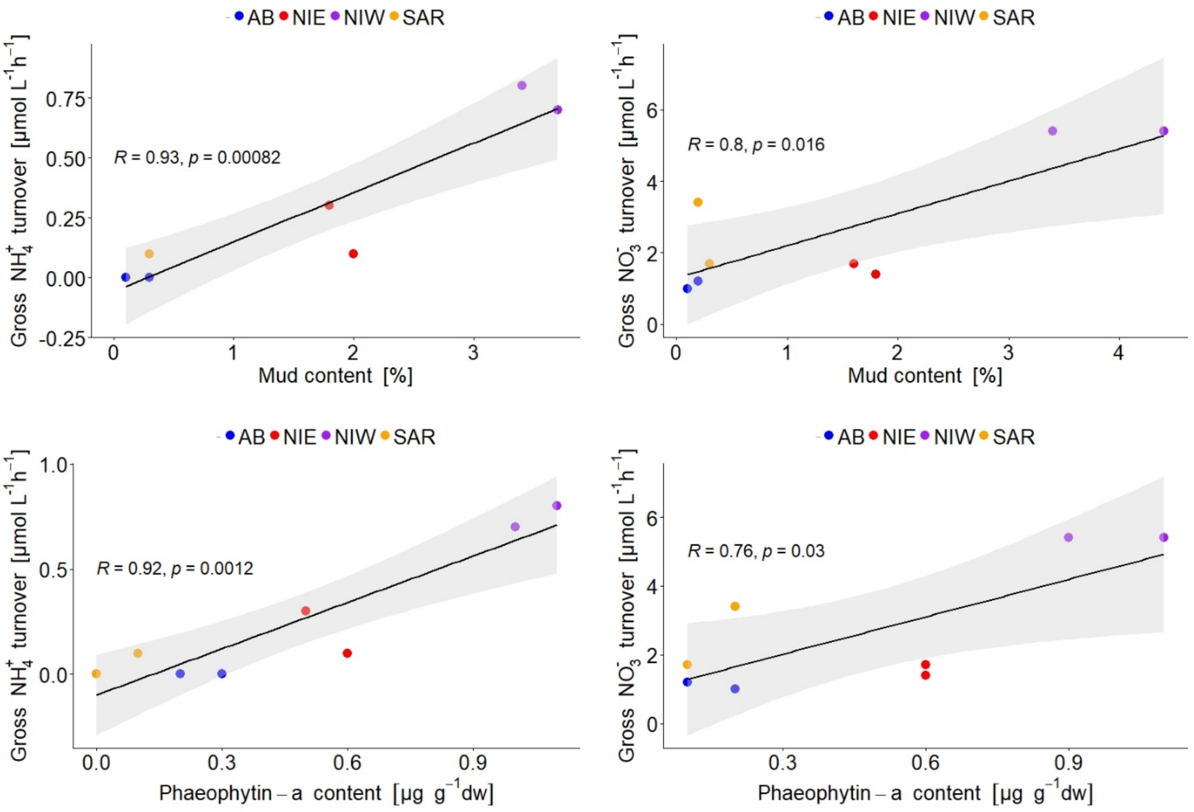

Figure 2.5: Pearson correlations of gross NH_4^+ (left) and NO_3^- (right) turnover rates with mud (top) and phaeophytin-a (bottom) content. Note: The solid lines indicate the linear regression. Grey bands indicate confidence intervals. Duplicate measurements per station.

Table 2.5: Conversion table with values for the intercept (b0), slope (b1) and residual standard errors (e) of linear regression line to calculate benthic O_2 consumption, net and gross benthic reaction rates of dissolved inorganic nutrient turnover from sediment parameters, using the linear regression formula y = b0 + b1 * x + e.

				Net turnover									**Gross turnover**					
	Respiration			**NH_4^+**			**NO_3^-**			**Si**			**NH_4^+**			**NO_3^-**		
	b0	**b1**	**e**	**b0**	**b1**	**e**	**b0**	**b1**	**e**	**b0**	**b1**	**e**	**b0**	**b1**	**e**	**b0**	**b1**	**e**
Mud content	9.36	4.29	2.64	0.04	-0.09	0.05	0.27	0.20	0.20	0.09	0.60	0.40	-0.05	0.20	0.13	1.29	0.91	1.18
Phaeophytin-a	7.93	16.29	3.05	0.08	-0.37	0.05	0.22	0.75	0.22	-0.11	2.29	0.43	-0.11	0.73	0.13	1.01	3.49	1.33
Grain size	27.44	-0.03	4.61	-0.38	0.00	0.10	1.12	0.00	0.27	2.37	0.00	0.77	0.71	0.00	0.24	4.97	-0.01	1.65
TOC	3.20	313.43	4.44	0.17	-6.90	0.10	0.02	14.78	0.26	-0.66	40.95	0.69	-0.34	15.19	0.18	0.50	52.30	1.72
Carbohydrates	3.81	171.59	5.31	0.23	-4.96	0.10	0.12	6.52	0.32	-0.48	20.95	0.82	-0.13	5.65	0.28	-0.72	47.11	1.60
Chlorophyll-a	13.02	7.54	6.36	-0.05	-0.19	0.15	0.51	0.19	0.36	0.80	0.50	0.99	0.18	0.19	0.33	2.68	-0.03	2.01

2.4. Discussion

2.4.1. Processes in the sediment

Overall, volumetric O_2 consumption rates (up to 25.6 µmol L^{-1} h^{-1}) were mostly within the range of recently published values for continental shelf areas (Ahmerkamp et al., 2017, 2020; Marchant et al., 2016), especially for rates obtained within the same season (Ahmerkamp et al., 2017, 2020). However, Marchant et al. (2014) found O_2 consumption rates to be an order of magnitude higher. They focused on the Janssand, a tide dominated intertidal sand flat in the Wadden Sea, where chlorophyll-a concentrations in the upper 5 cm of the sediment are more than an order of magnitude higher than at our sites (Billerbeck et al., 2006). This increased substrate availability likely resulted in comparatively high O_2 consumption rates. Furthermore, they did not exclude macrofauna, which may have further increased oxygen consumption. Our net rates for nitrogen turnover (Table 2.3), generally are below previously published data in the same area (Ahmerkamp et al., 2020; Marchant et al., 2016), but gross rates for nitrate production (Fig. 2.5) compare well with Marchant et al. (2014). Ammonium may be rapidly incorporated in various processes (e.g. uptake by microphytobenthos or ammonium oxidation), so that net rates for NH_4^+ turnover sometimes are poor predictors of overall NH_4^+ turnover. This variability of the intensity of NH_4^+ consumption in sediments, due to different ammonium reaction pathways, may explain differences between various studies that investigated sedimentary ammonium turnover (Seitzinger and Giblin, 1996). We find that the rate of O_2 consumption is highest at the highest water depth (Tables 2.1 and 2.3). This is surprising, because in shallow coastal areas, large fractions of particulate material from e.g. phytoplankton blooms are commonly believed to reach the sediment surface, where it is remineralized, resulting in an increased oxygen consumption (Enoksson, 1993). However, in our data, highest O_2 consumption coincides with smallest grain sizes. Our interpretation is, that fine organic and mineral particles as the main constituents of mud are frequently resuspended in the shallower coastal North Sea by tidal currents and wave turbulence, thereby transported along the residual current, and eventually deposited in areas with less near-bottom turbulence. Additionally, the large grain surface area per volume of fine-grained sediment results in an increased availability for microbial activity, ultimately leading to increased degradation and O_2 consumption (Ahmerkamp et al., 2020). All process rates clearly scale with silicate release (Tables 2.3 and 2.4). This further corroborates the hypothesis that summer nutrient regeneration directly depends on spring primary production, as our data show that nutrient cycling depends on benthic processing rates and likely, turnover and decomposition of phytoplankton biomass in sediments. As can be seen from Table 2.3, the release of silicate from the sediment is substantial. This release of silicate depends on temperature, pH and silicate saturation in the porewater, but it also is indicative of diatom presence (Marron et al., 2013). Diatoms have biogenic opal structures and the chemical dissolution of these structures converts biogenic silicate back into its dissolved form (Demarest et al., 2009). Since highest silicate production rates at NIW coincide with highest values for O_2 consumption, TOC and phaeophytin-a at the same site (Tables 2.2 and 2.3), this suggests the presence of diatom related biomass, as a higher diatom biomass results in elevated POM and pigment concentrations and concurrently in more intense degradation and ammonification rates. Generally, the ratio at which silicate to inorganic nitrogen is released tends to be 1:1, referred to as the Redfield ratio (Turner et al., 1998). However, we find that the release of silicate is higher than the net release of inorganic nitrogen at all stations, except SAR (Table 2.3). The canonical Redfield ratio is more accurately applied to the open ocean and deviations may occur in coastal waters (Rios et al., 1998), especially when there is a high anthropogenic impact. Gross rates, however, exceed silicate release, so this discrepancy may also be a sign of immediate N uptake into heterotrophic bacteria. Furthermore, the ways in which silicate and dissolved inorganic nitrogen is released differ, because diatom frustules are more resistant to degradation, so that nitrogen can be released more rapidly. This can also affect the instantaneous Si:DIN ratio we measure in our incubations.

2.4.2. Comparison of proxies

In this section, we will now evaluate potential predictors of sedimentary remineralization, ammonium and nitrate turnover. Under oxic conditions, several parameters control remineralization processes, including salinity, temperature, organic matter and oxygen concentrations (Sanders and Laanbroek, 2018). Especially in coarse-grained permeable sediment, where advective pore water flow dominates transport processes and at high availability of oxygen, organic matter is rapidly mineralized to its inorganic components (Ahmerkamp et al., 2017; Bartl et al., 2019; De Borger et al., 2021; Marchant et al., 2018). Thus, in the sediments we investigated, the O_2 consumption rate can serve as an excellent predictor of the degradation rate (Neumann et al., 2019). In the investigated sites, we find strong correlations of net ammonium and nitrate turnover rates with O_2 consumption (Fig. 2.4). Previous authors already established correlations of benthic oxygen process rates with sediment pigments, mud content and TOC (Spieckermann et al., 2022; Neumann et al., 2019; Zhang et al., 2021). Generally, organic matter availability supports benthic remineralization processes (Bratek et al., 2020), which is reflected by a significant correlation of O_2 consumption rates with TOC (Table 2.4). Accordingly, Zhang et al. (2021) found that organic carbon content is the dominant control of oxygen fluxes across the sediment-water interface. However, although TOC may be a reasonable indicator of oxygen consumption, our result suggest that it only is an imperfect proxy for nitrification, ammonification or other sedimentary turnover processes (Table 2.4). We argue that these weaker correlations arise because much of the organic matter in the sediment is refractory or not labile, so that a similar organic matter content in two distinct sediment samples does not grant similar overall composition and sediment reactivity (Billen et al., 2015). Additionally, in our dataset, we find more robust correlations of oxygen turnover and N-process rates with mud content. This correlation is plausible, because fresh organic matter concentrations tend to correlate with the mud content: Mud content refers to small-sized particles in the clay and silt size spectrum (<63 µm). Thus, they have a large surface area to volume ratio (compared to larger particles including those present within the total TOC pool), increasing the exposure of surface area for interactions with surrounding substances. The availability of sites for microbial activity also increases with greater surface area to volume ratios (i.e. with smaller particles), promoting oxygen demand and degradation processes (De Falco et al., 2004). Therefore, we suggest that mud content overall is a more appropriate and easily measured proxy for remineralization processes and should be favored over TOC. However, it must be noted that the mud content in all our samples was below 4%. At these low levels, slight changes in mud content would also change particle surface availability and the corresponding intensity of organic matter degradation, but not substantially restrict porewater flow, possibly further strengthening correlations between mud and turnover processes within this range of mud content. With increasing levels of mud content, the sediment becomes less and less permeable, until eventually advective transport processes become irrelevant, and diffusion dominates transport processes. For more precise model predictions across a wide range of sedimentary mud contents, additional experiments should be performed to test correlations at higher mud contents. Phaeophytin-a, a degradation product of chlorophyll-a, also strongly correlates with O_2 consumption rate and N-process rates and may serve as a potential proxy of general sediment reactivity. Pigments can easily be extracted from sediment samples, making them an easily available proxy. Interestingly, there are no significant correlations of chlorophyll-a with O_2 consumption rates (Table 2.4). In the southeastern part of the North Sea, the main phytoplankton bloom occurs in April–May (De Borger et al., 2021) and the field campaign for this study took place in August–September, suggesting that there was sufficient time for chlorophyll-a degradation. Additionally, consumption by zooplankton may have fostered the chlorophyll-a degradation: Previous studies (Coelho et al., 2011; Klein and Sournia, 1987; Sathish et al., 2020) showed that zoobenthos and zooplankton break down chlorophyll-a to paeophytin-a during digestion, which leads to accumulation of phaeophytin-a in their fecal pellets. Additionally, another reason for weak correlations of chlorophyll-a with O_2 consumption rates may be that we sieved the sand prior to the incubations and subsampling of the sediment, which can cause loss of some organic matter. Indeed, comparing pigment data of sieved sediment with unsieved sediment of the same stations (different cruise), suggest that approximately 30% of the chlorophyll-a may be lost during sieving (data not shown). The mechanical forces during sieving and mixing might have damaged initially viable plankton cells, exposing the cholorophyll to degradation to phaeophytin during the incubation. Furthermore, phaeophytin-a lacks the light-sensitive magnesium ion present in chlorophyll-a, making it less prone to degradation when exposed to light. Especially, when exposed to light and oxygen, phaeophytin-a concentrations may remain more constant over time (Parusel and Grimme, 2000; Szymczak-Zyla et al., 2008). Therefore, phaeophytin-a appears to be less sensitive to sediment handling, making it a more reliable proxy. We additionally investigated carbohydrates as a possible proxy for biogeochemical turnover. In the ocean, carbohydrates are organic compounds produced during photosynthesis, and serve as an important energy source for heterotrophic organisms (Youssef et al., 2014). Carbohydrates represent a significant fraction of organic matter in the sediment, with up to 40% of fresh organic matter and up to 20% of the sediment organic matter pool being made up by carbohydrates (Burdige et al., 2000; Jensen et al., 2005; Veuger et al., 2012). Furthermore, they are directly linked to microbial activities, as carbohydrates provide a highly consumable substrate for remineralization, making them a potentially suitable proxy. However, we find only weak correlations of carbohydrates with ammonium turnover and O_2 consumption and no significant correlation with nitrate turnover (Table 2.4). One reason may be that we analyzed correlations with N based process rates, but carbohydrates do not necessarily have N incorporated within them. A large variability of the ratio of nitrogen to carbohydrates within the available substrate may thus affect possible correlations. However, the correlation of O_2 consumption and carbohydrates is also poor (Table 2.4). In this case, the ratio of refractory to labile portions in organic matter and the percentage of carbohydrates within the fresh and bulk organic matter pool may be responsible. These ratios can differ, so that we conclude that carbohydrates in sediments generally are not a good predictor for the intensity of degradation processes.

2.4.3. Nitrogen biogeochemistry in sediments

As N-processing represents an important ecosystem service in coastal systems, we specifically investigate ammonium and nitrate turnover in sediments. We find that the net rates for ammonium turnover (note that turnover here refers to ammonium consumption and production by the sediment) can be predicted using the same proxies as for O2 consumption rates, with mud content and phaeophytin-a concentrations being the best predictors, followed by TOC, carbohydrates and grain size (Table 2.4). They correlate inversely (except grain size) with net ammonium turnover rates (Fig. 2.4). This is striking, as a higher substrate availability (e.g mud, pigments, TOC) is linked to higher ammonification rates (Bratek et al., 2020; Sanders and Laanbroek, 2018), which is mirrored in increased gross turnover rates in our study. Higher substrate availability (e.g. mud, TOC and phaeophytin-a) is linked to higher O_2 consumption rates (Tables 2.2 and 2.3, Fig. 2.4), and, hence, higher gross ammonium turnover (Fig. 2.5). However, ammonium is quickly used in other processes (e.g. nitrification) rather than released to the water column. Of course, ammonium uptake in the oxic sediment reactor increases faster than ammonification. We argue that the higher substrate availability leads to an increased microbial abundance, which in turn may, albeit possibly indirectly, result in a higher rate of ammonium oxidation, which overcompensates the higher ammonification and therefore ultimately results in a reduced net NH_4^+ production. The inverse correlation of net ammonium turnover with substrate (mud, pigments, and/or TOC) availability (Fig. 2.4) shows that less NH_4^+ is made available at stations with higher substrate availability (NIW and NIE). Indeed, gross rates for ammonium and nitrate production increase with increasing substrate availability (Fig. 2.5), suggesting close coupling between ammonium and nitrate production in the presence of oxygen, and increased ammonium oxidation with increasing substrate availability. Hence, the overall sediment reactivity exerts control on the balance between ammonification and ammonium oxidation. This shows the importance of distinguishing between net and gross rates for nitrogen turnover, especially in oxic systems. Ammonium and nitrate production are closely coupled, but the quantification of NH_4^+ production is difficult due to rapid use of NH_4^+ during ammonium oxidation. This can result in an underestimation of actual (gross) rates of nitrogen turnover when only net turnover rates are considered. Similarly to oxygen consumption and ammonium turnover, nitrate release most strongly correlates with mud and phaeophytin-a as best predictor variables, but correlations are a little weaker. Nitrification is a two-step microbial process and generates less energy than heterotrophic processes that add to ammonification. Additionally, the microorganisms responsible for nitrification are more sensitive to environmental conditions (e.g. pH and temperature), which may weaken the correlations of substrate availability and nitrification, as opposed to with ammonification (Gruber, 2008). There is a discrepancy between net and gross nitrate turnover, which may be explained by aerobic denitrification. Previous authors (Gao et al., 2010; Marchant et al., 2017) indeed measured denitrification rates in permeable sediments in the presence of oxygen. Furthermore, in preliminary test experiments (HE602, data not shown), we compared oxygen consumption rates across porewater velocities within the same FTR incubation. Higher consumption rates at higher porewater velocities hint towards the presence of anoxic microniches, in which anoxic denitrification may have been carried out. In order to convert between sediment parameters and benthic reaction rates, we provide linear regression coefficients and residual standard errors to calculate uncertainties related to the conversion (Table 2.5). By utilizing sediment samples and their characteristics (such as mud and phaeophytin-a content), it becomes possible to deduce reaction rates for oxygen, ammonium, and nitrate without the need for additional measurements. Consequently, existing data on sediment characteristics can be employed to estimate these reaction rates effectively, at various depths within the sediment. This information can greatly enhance policy and decision-making processes by providing a more comprehensive understanding of the dynamics and functioning of marine ecosystems. By incorporating estimates of benthic reaction rates, policymakers gain a deeper insight into the sedimentary nutrient cycling processes and oxygen dynamics. This knowledge can inform the development and implementation of effective management strategies, conservation measures, and monitoring programs. Overall, the integration of benthic reaction rates estimation based on existing data enhances the scientific basis for marine management and monitoring. It enables a more holistic understanding of ecosystem processes, facilitates evidence-based decision-making, and promotes sustainable and effective policies for the protection and conservation of marine environments.

2.4.4. Recommendations

Based on our results, we recommend the sediment characteristics mud content and phaeophytin-a for the parameterization of benthic reaction rates of O_2 consumption, ammonium and nitrate turnover in autumn. The advantage of phaeophytin-a may be that it integrates over biological activity (via feeding mechanisms) and dredging/bioturbation, because degradation of chlorophyll-a to phaeophytin-a depends on sediment reworking (Coelho et al., 2011; Sathish et al., 2020). Mud content, on the other hand, is easily measured, less prone to seasonal variability and is a standard parameter of sediment analytics that should be widely available. Either proxy has excellent prediction capabilities, and a conversion between these is also possible. By these means, we provided linear regression coefficients for a variety of sediment parameters and reaction rates. With appropriate uncertainties, a conversion between all these parameters is possible, opening up previous observations that otherwise would be inaccessible due to missing data. If (volumetric) rates of O_2 consumption, ammonium and nitrate turnover can be provided for the entire German Bight, possible scenarios for anthropogenic pressure (e.g. trawling and dredging activities) may be computed, in order to quantify their effect on these rates. These scenarios rely on the development and improvement of ecosystem models, partly relieving the need for costly and time consuming in situ and laboratory analyses. Accurate prediction of nitrogen turnover processes and biogeochemical cycling, especially within systems that are subjected to constant anthropogenic disturbance, is crucial for the understanding and knowledge-based management of these systems. We provide a dataset that can excellently be used in model parametrization, However, our findings suggest that seasonal variation needs to be addressed, as physicochemical and biological changes within the system affect each single proxy and its respective ability to accurately predict benthic remineralization rates on a temporal scale.

Acknowledgements

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3 Benthic processes in advective sediments are insensitive to vertical substrate distribution

MINUTOLO, F., DÄHNKE, K., METZKE, M. & NEUMANN, A. Benthic processes in advective sediments are insensitive to vertical substrate distribution. *Submitted to Continental Shelf Research*

Abstract

Coastal ecosystems serve as critical interfaces between terrestrial and marine environments, playing pivotal roles in global biogeochemical cycles. Understanding the dynamics of sedimentary processes in these environments is crucial for assessing ecosystem health and informing management strategies. Our study investigates the sensitivity of benthic oxygen and nitrogen fluxes to the vertical distribution of organic matter in sandy permeable sediments. Utilizing an established pore water advection model and a parametrization framework for benthic biogeochemical processes, coupled with measured vertical profiles of sedimentary pigment and TOC concentrations, our results reveal minimal variation in fluxes in response to different vertical distributions of pigments and TOC. The intercept term in our parametrization framework, indicative of non-proxy associated baseline reactivity, emerges as a dominant factor influencing overall sediment reactivity and underscores the need for careful consideration when choosing proxies for sediment studies. Overall, this study contributes to a better understanding of the resilience of sedimentary processes in coastal ecosystems to variations in organic matter distribution, and suggests practical adjustments in sediment monitoring and management practices for enhanced efficiency and effectiveness.

3.1. Introduction

Coastal ecosystems are intricate and dynamic interfaces where terrestrial and marine influences converge, creating habitats of immense ecological importance. This interface covers only a small area of the ocean´s surface, but disproportionally contributes to marine primary production (Bratek et al., 2020, He and Silliman, 2019, Van Oostende et al., 2018, Ward et al., 2020). More than 50% of continental shelves are comprised by permeable sands, where the interaction of bedforms and the overlying currents of bottom water results in pressure-driven advective pore water flow, enhanced exchange of reactive solutes and retention of organic matter, thereby fueling microbial activity (Ahmerkamp et al., 2015, Ahmerkamp et al., 2017). The availability of organic matter in the sediment links to benthic microbial degradation (Arndt et al., 2013, Bonthond et al., 2023). Microbial degradation has a distinct depth zonation, but it is unclear whether overall process rates in permeable sediments are affected by the vertical distribution of organic matter as well. This vertical distribution of organic matter may be altered mainly through two processes. Firstly, bioturbating macrofauna reworks the sediment leading to the replacement of organic matter (OM) and changes in oxygen dynamics (Kristensen et al., 2012, Neumann et al., 2021); and secondly, by the mixing of particles through mobile bedforms (Ahmerkamp et al., 2015, Precht et al., 2004). Especially the second process is of great importance in permeable sediments in comparison to muddy, less permeable sites that have been intensely studied in the past (Huettel et al., 2014). Changes in the vertical distribution of organic matter within the sediment also control the microbial stratification due to the alteration of oxic and anoxic microenvironments (Politi et al., 2019). We thus assume that the vertical distribution of organic matter causes changes in biogeochemical reactions, ultimately affecting solute fluxes at the sediment-water interface.

The parametrization of pore water flow in permeable sediment by Elliott & Brooks (1997) has previously been used for the analysis of benthic remineralization e.g. by Ahmerkamp et al. (2017), Marchant et al. (2016) and Marchant et al. (2018). These studies, however, assume a homogeneous distribution of reaction rates within the sediment, which is not representative for real sediment profiles. The Elliott & Brooks model can explicitly calculate the pathways of pore water and solutes transported from the water column though the sediment and back into the water column. Accordingly, we use this model in combination with the benthic reactivity parametrizations of Minutolo et al. (2024) to predict oxygen and nutrient fluxes for permeable sands with variable, and presumably more realistic, distributions of organic matter across the depth profile. To do so, we introduce idealized scenarios, where the sedimentary maximum of organic matter varies with depth, so that we can assess the sensitivity of modeled fluxes and solute concentrations to the vertical organic matter distribution. We then apply the model to measured vertical profiles of sedimentary pigment and TOC concentrations, which serve as proxies for benthic sediment reactivity. In a final step, we use these results to identify the sensitivity of computed benthic fluxes to the vertical distribution of sediment organic matter. These results will help us to estimate the potential impact of sediment reworking processes such as bottom trawling and bioturbation on these benthic fluxes.

3.2. Methods

Sediment was sampled at multiple stations in the southern North Sea, a semi-enclosed area surrounded by densely populated and industrialized countries, and subject to large anthropogenic nutrient inputs from the major European rivers Elbe, Rhine, Ems and Weser. The sampling was performed between 2012 and 2022 during one R/V Alkor cruise and multiple R/V Heincke cruises (Fig. 3.1).

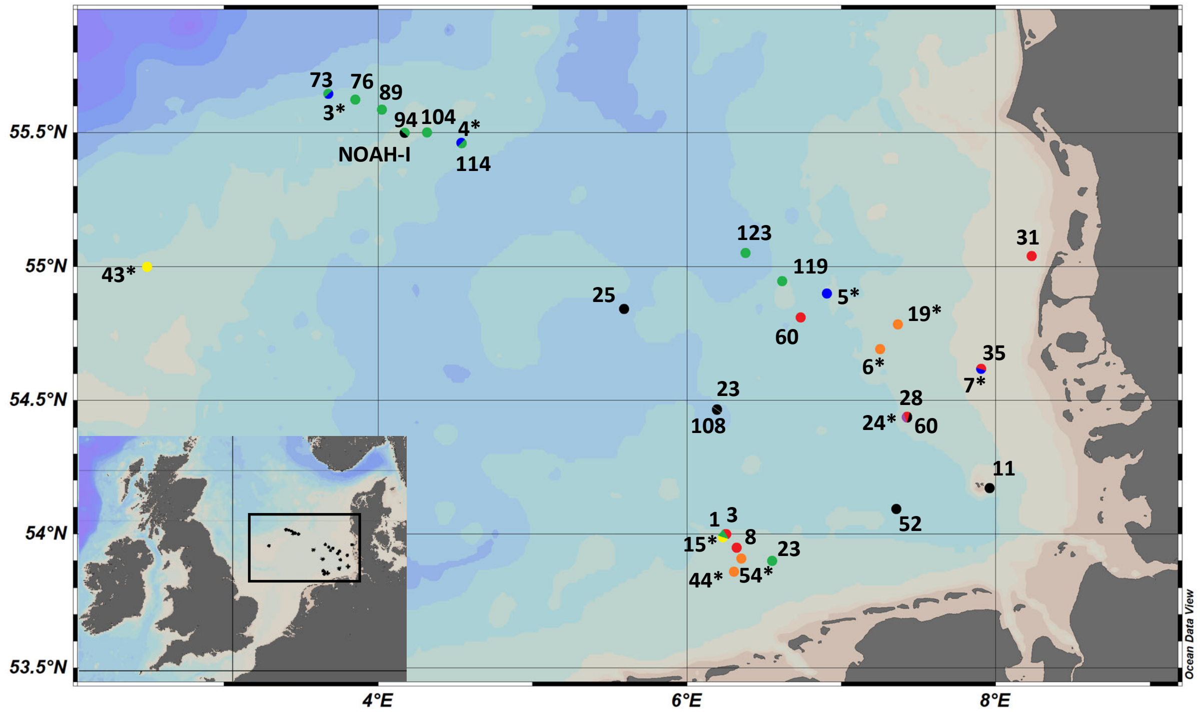


Figure 3.1: Sampled stations during the RV Alkor cruise AL557 (yellow), and the RV Heincke cruises HE581 (green), HE582 (blue), HE588 (red), HE595 (purple) and HE602 (orange). On black colored stations, TOC profiles were sampled during multiple RV Heincke cruises (HE383, HE395, HE422, HE432 and HE447). Sampling sites for FTR incubations are marked with asterisks (cruises AL557, HE582, HE595 and HE602).

3.2.1 Sediment sampling and analyses

At each station (except HE582, HE595 and HE602), one sediment core was retrieved using a multicorer equipped with acrylic tubes (PMA) of 10 cm inner diameter and 60 cm length. Supernatant was carefully removed without disturbing the sediment surface, and the sediment was sliced in 1 cm intervals to a depth of 15 cm. Samples were frozen for later analysis of pigments (AL557, HE581 and HE588) and TOC (HE383, HE395, HE422, HE432 and HE447) concentrations: frozen sediment was freeze-dried, and chlorophyll-a and phaeophytin-a were extracted with 90% acetone. Pigment concentrations were measured spectrophotometrically (DR-6000, Hach-Lange, Germany) according to Lorenzen (1967). Subsamples of the dry sediment were ground, homogenized and analyzed for their total carbon and nitrogen contents using an elemental analyzer (Euro EA, HEKAtech). To assess the total organic carbon content, inorganic carbon was first removed by treating the samples with 1 M hydrochloric acid. Subsamples of the freeze-dried sediment from flow though reactor (FTR) incubations at similar stations (AL557, HE582, HE595 and HE602, see Tab. 1) were taken for analyses of grain size distribution and amended with potassium pyrophosphate solution (7,5%) to create a slurry prior to the analysis. Samples were then measured with a laser-diffraction particle sizer (Analysette 22 NanoTec, Fritsch, Germany).

3.2.2 Water sampling and analyses

Bottom water from the sediment sampling sites was collected during AL557, HE582, HE595 and HE602 cruises. Water was sampled from ~2 m above the sea floor with 6 L Niskin bottles attached to a CTD and kept at in situ temperature. After filtration (polyethersulfone membrane, Whatman, 0.2 µm), the site water was used for FTR incubations, where oxygen concentrations were measured with flow-through optodes (PyroScience, Germany). For a detailed explanation of experiments and methods, please refer to Minutolo et al. (2024). During FTR experiments, concentrations of NH_4^+ and NO_3^- and NO2- were determined with a continuous flow analyzer (AA3, Seal Analytical, Germany) following standard colorimetric techniques (Grasshoff et al., 1999, Kerouel and Aminot, 1997).

Table 3.1: Coordinates, sampling date and water depth at the sampled stations in the southeastern North Sea.

Cruise	Station	Latitude	Longitude	Date	Depth
		(deg)			(m)
AL557	**15**	53.988935	6.230242	06.06.2021	30
AL557	**43**	54.999930	2.500715	14.06.2021	32
HE383	**60**	54.437333	7.423833	01.07.2012	25
HE395	**23**	54.466500	6.194167	12.03.2013	38
HE422	**25**	54.842222	5.592499	05.05.2014	40
HE422	**NOAH-I**	55.500000	4.169166	07.05.2014	-
HE432	**11**	54.171333	7.959667	20.09.2014	20
HE447	**52**	54.094000	7.353500	23.06.2015	32
HE447	**108**	54.466000	6.193500	30.06.2015	37
HE581	**1**	53.999690	6.249450	03.08.2021	27
HE581	**23**	53.900000	6.549260	05.08.2021	22
HE581	**73**	55.645590	3.674530	09.08.2021	37
HE581	**76**	55.624230	3.850900	09.08.2021	36
HE581	**89**	55.587050	4.023370	10.08.2021	31
HE581	**94**	55.500160	4.169670	11.08.2021	27
HE581	**104**	55.501690	4.314300	12.08.2021	29
HE581	**114**	55.461460	4.538880	13.08.2021	29
HE581	**119**	54.946370	6.615310	14.08.2021	40
HE581	**123**	55.050640	6.377840	14.08.2021	41
HE582	**3**	55.645269	3.675083	28.08.2021	36
HE582	**4**	55.462272	4.537492	30.08.2021	28
HE582	**5**	54.899801	6.906302	31.08.2021	25
HE582	**7**	54.618351	7.904198	02.09.2021	10
HE588	**3**	53.999770	6.253050	25.10.2021	28
HE588	**8**	53.949040	6.320080	26.10.2021	27
HE588	**28**	54.439030	7.424850	28.10.2021	25
HE588	**31**	55.039360	8.231010	29.10.2021	11
HE588	**35**	54.619240	7.904270	29.10.2021	11
HE588	**60**	54.810320	6.734280	02.11.2021	40
HE595	**24**	54.437832	7.421945	21.03.2022	25
HE602	**6**	54.691462	7.249521	25.06.2022	25
HE602	**19**	54.783965	7.365377	27.06.2022	22
HE602	**44**	53.860550	6.303157	03.07.2022	26
HE602	**54**	53.908608	6.351119	05.07.2022	22

3.2.3.1 2D pore water advection model

To calculate the two- dimensional flow field of a water parcel entering the sediment, we used the pore water advection model of Elliot & Brooks (1997, see Fig. 3.2 for modeled individual streamlines).

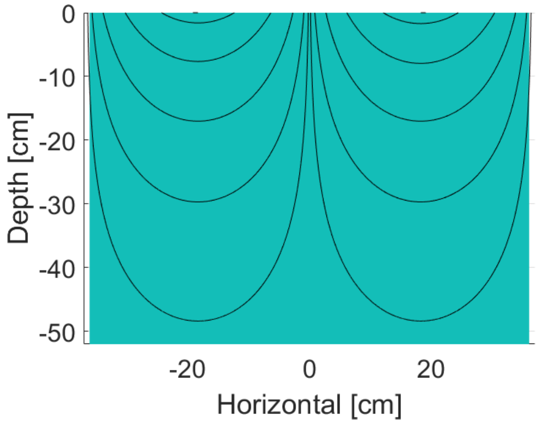


Figure 3.2: Two dimensional modelled streamlines along which water parcels travel through the sediment

The model's application to our specific sediment settings required the parameterization of the pressure field at the sediment surface, ensuring accurate representation of the internal flow dynamics. Integral to this process was the dimensional scaling of dynamic pressure head and pore water flow, for which additional sediment-specific parameters were necessary: The bedfom wavenumber was calculated based on the median grainsize according to Yalin (1985). Similarly, the bedform height was calculated likewise from the median grainsize according to Flemming (2000). The hydraulic conductivity of the sediment, a critical factor in defining water movement through the sediment matrix, was estimated from the median grain size as outlined in Neumann et al. (2017). To complement these sediment-based parameters, the characteristic bottom water velocity was estimated as the root mean square (RMS) of time series measured with an Aanderaa Z-Pulse current meter mounted to a lander during R/V Heincke cruise HE602.

Streamlines, representing the trajectories of water parcels within the sediment, are computed using a numerical approach. After setting the initial solute concentrations of O_2, NH_4^+, NO_3^- and N_2 at the sediment surface, pigment and TOC concentrations are interpolated at the calculated specific positions along these streamlines. Subsequently, the changing concentrations of the modelled solutes along the individual streamlines due to benthic biogeochemical processes, are calculated by utilizing the established parametrization framework for benthic reaction rates of Minutolo et al. (2024). The model discretizes the sediment domain and iteratively calculates the horizontal and vertical positions of streamlines (set to one hundred streamlines). After setting the initial horizontal position, new horizontal positions for a given streamline are calculated by:

$$X^* = X_0^* - \frac{t^*}{\theta} * cosX_0^* \tag{3.1}$$

Where X_0^* is the previous horizontal position and θ is the porosity of the sediment. Similarly, after setting the initial vertical position, new vertical positions are calculated by:

$$Y^* = -ln\left(\frac{cos\left(X_0^* - \frac{t^*}{\theta} * cosX_0^*\right)}{cosX_0^*}\right) \tag{3.2}$$

The normalized time step t* was set to 0.02 to balance computational efficiency while ensuring an adequate number of steps for simulating streamlines. The iterations continue until the vertical position becomes positive, indicating the streamlines exit from the sediment, providing the information for subsequent solute transport simulations. All model calculations were performed with MATLAB (R2020b Update 1 (9.9.0.1495850)).

3.2.3.2 Calculations of solute concentrations and fluxes

To calculate solute concentrations within the sediment, initial concentrations of O_2, NH_4^+, NO_3^- and N_2 were set at the sediment surface. These are based on measured bottom water solute concentrations (except N_2 which was set to 0) during the FTR incubations. The solute concentrations within the sediment were iteratively calculated along the pore water streamlines in discrete time steps (see above) as

$$C_2 = C_1 + \Delta C_{production} - \Delta C_{consumption} \tag{3.3}$$

where the amount of production and consumption was calculated with the time step and specific reaction rates. In this study, we established chlorophyll-a, phaeophytin-a and TOC as proxies for benthic reactivity and local reaction rates were calculated for each streamline position according to parametrizations by Minutolo et al. (2024). Henceforward, when referring to “proxies” we refer to organic matter in the form of sediment characteristics (phaeophytin-a, chlorophyll-a, TOC,…), if not specified otherwise. In the following, we hence use the pigment and TOC concentration as a proxy for benthic reactivity, and we interpolated rates based on these proxies and their respective vertical profile. In cases where streamlines extended to depths beyond the available proxy profile, linear extrapolation was applied to estimate proxy values. Negative values of solute concentration were taken as zero.

The resulting solute fluxes across the sediment surface were calculated as

$$J = v \times C \tag{3.4}$$

Where the pore water velocity v at the sediment surface was calculated according to Elliott & Brooks (1997) and solute concentrations C were collected from the calculated concentrations of the streamlines (see above).

3.2.3.3 Scenario calculation

We employed idealized scenarios of vertical proxy (i.e., pigment and TOC) distribution to illustrate potential effects of the vertical organic matter distribution on benthic biogeochemical processes and resulting fluxes of nutrients and oxygen. To do so, we used simplified hypothetical parametrizations adapted from Minutolo et al. (2024) in the form of y = m*x, where m is the slope of the linear regression, x is the proxy value and y is the resulting reaction rate. This approach was chosen to establish a simple link between proxy and reaction rate. We computed the depths at which 75%, 50% and 25% of the pore water volume percolate through the sediment and fitted each of those depths with a pigment maximum. This approach was based on sediment profiles from HE581 and HE588, which showed that maximum pigment concentrations could be found at depths between 0 and >10 cm (Fig. 3.3), corresponding to flow paths through the sediment. These different substrate depth maxima stem from the interplay of macrofauna (Kristensen et al., 2012, Neumann et al., 2021) and mobile bedforms (Ahmerkamp et al., 2015; Precht et al., 2004), which both can influence organic matter distributions within the sediment through burrowing related activities (i.e. bioturbation and bioirrigation) and physical redistribution/sediment sorting, respectively. In each scenario we calculated in this approach, the sum of the total proxy concentration along the vertical sediment profile remained constant.

In a next step, we moved towards an assessment of the effects of vertical proxy distribution in North Sea sediments. To assess this effect on modelled fluxes of oxygen and nitrogen (i.e. NH_4^+, NO_3^- and N_2) we implemented two scenarios with contrasting vertical distributions of pigments and TOC. In one scenario, we used the observed vertical proxy profile at the respective stations, and in a second scenario, we used the entirely homogeneous vertically averaged proxy profile. In both scenarios, the vertically integrated proxy concentration is identical, but they differ in their vertical distribution.

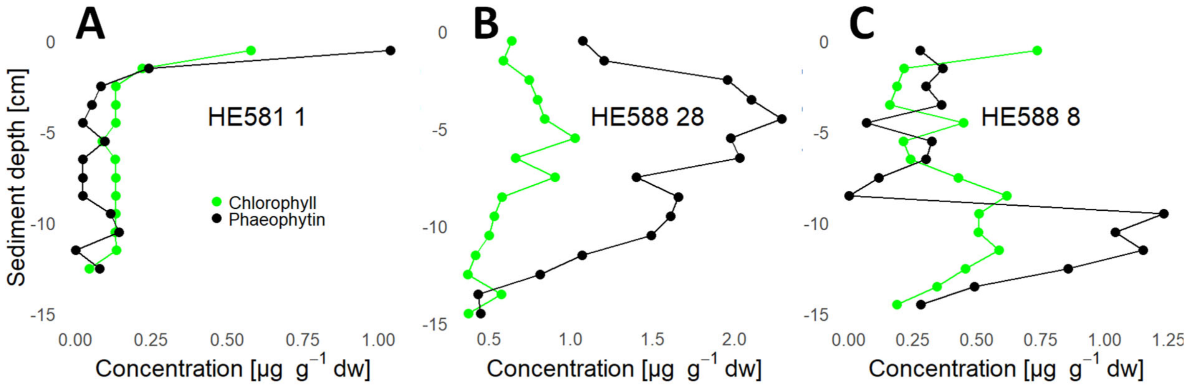


Figure 3.3: Selected vertical pigment profiles. Profiles show a maximum at the sediment surface (A) and maxima at different depths (B and C).

3.3. Results

3.3.1 Idealized scenarios

In the idealized scenarios, which are based on the Elliot & Brooks model and the parametrization by Minutolo et al. (2024), we see distinct variations in benthic turnover and in the resulting fluxes at the sediment-water interface. Generally, the zone of active turnover in the sediment deepens with depth of the substrate maximum. This applies to oxygen consumption as well as to turnover rates for other solutes in our assessment, like NH_4^+, NO_3^- and N_2. O_2 consumption decreases with deepening of the substrate maximum from 10.62 mmol m^{-2} d^{-1} for the 75% scenario to 5.25 mmol m^{-2} d^{-1} for the 25% scenario. The NO_3^- flux accordingly increases from 0.10 in the 75% scenario to 0.20 mmol m^{-2} d^{-1} for the 25% scenario. In contrast, benthic fluxes of NH_4^+ remain relatively constant across scenarios. Total N_2 fluxes are small, and across scenarios, sediments are a net N_2 source (-0.03 mmol m^{-2} d^{-1} in the 75% scenario) that intensifies to -0.09 mmol m^{-2} d^{-1} for the 25% scenario. The deepening of the substrate maximum is also reflected in the corresponding deepening of reaction zones for the different solutes in our assessment (Fig. 3.4). Overall, we see that fluxes in the idealized scenarios strongly depend on the assigned substrate depth.

Table 3.2: Model output for benthic fluxes of O_2, NH_4^+, NO_3^- and N_2 in three idealized scenarios. Units: mmol m^{-2} d^{-1}. Negative fluxes denote fluxes out of the sediment.

Scenario	**O_2**	**NO_3^-**	**NH_4^+**	**N_2**
75%	10.62	0.10	-0.32	-0.03
50%	9.31	0.14	-0.32	-0.05
25%	5.25	0.20	-0.30	-0.09

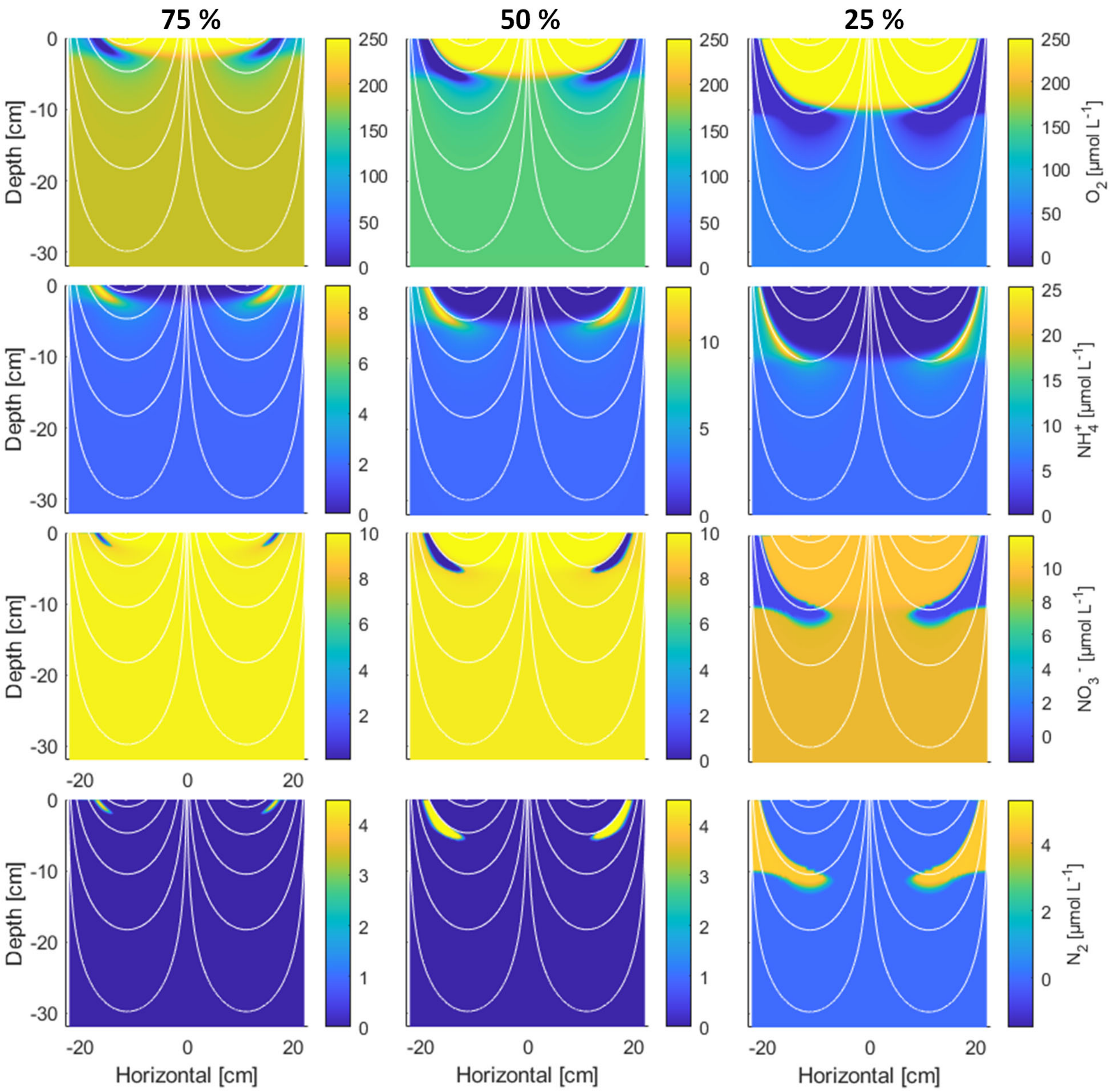


Figure 3.4: Distribution of concentrations of O_2, NH_4^+, NO_3^- and N_2 within the sediment for the three idealized scenarios 75% (top), 50% (middle) and 25% (bottom). Reaction zones for different solutes and their deepening (from the 75% to the 25% scenario) can be identified.

3.3.2 Modelling benthic fluxes in natural sandy sediments

The idealized scenarios helped us to establish a link between pigment and TOC concentration used as a proxy, and sedimentary turnover rates of O_2 and N-bearing compounds. Moving forward towards sedimentary N and O_2 fluxes from the sampling stations, we used measured vertical profiles of phaeophytin-a, chlorophyll-a and TOC as proxies to calculate O_2, NH_4^+, NO_3^- and N_2 fluxes for the respective sampling stations. Using the real profiles of phaeophytin-a and chlorophyll-a in the parametrization, fluxes (O_2, NH_4^+, NO_3^- and N_2) at stations in the southern North Sea range from 0.75 - 40.63, -2.26 – 0.19, -3.38 – 0.05, -0.33 - -0.01 and 0.74 – 49.95, -0.56 - -0.01, -8.04 – 0.01, -0.71 - -0.04 mmol m^{-2} d^{-1}, respectively (Fig. 3.5). Using real TOC profiles the same fluxes range from 0.88 – 72.37, -5.23 - -0.78, -7.95 – 0.05 and -2.07 - -0.08 mmol m^{-2} d^{-1}.

To evaluate the effect of the vertical substrate distribution, we set up an additional model calculation using homogeneous substrate distribution. Across all sampled stations, the fluxes of O_2, NH_4^+, NO_3^- and N_2 were similar to those that were computed based on the measured substrate distribution (Fig. 3.5). Values for the same fluxes using the averaged profile of phaeophytin-a and chlorophyll-a range from 0.74 - 45.49, -2.29 – 0.18, -3.11 – 0.06, -0.38 - -0.02 and 0.74 – 51.62, -0.59 - -0.04, -7.81 – 0.01, -0.76 - -0.06 mmol m^{-2} d^{-1}, respectively. Using averaged TOC profiles the same fluxes range from 0.88 – 41.99, -5.19 - -1.69, -4.52 – 0.06 and -1.23 - -0.08 mmol m^{-2} d^{-1}. The percentage difference between modelled fluxes using different vertical substrate distribution (measured and averaged) therefore is small as well (Tab. 3.3). Seemingly larger differences of -58.78 ± 221.62 and 53.42 ± 178.35 %, for NO_3^- (proxy: phaeophytin-a) and NH_4^+ (proxy: chlorophyll-a) fluxes, respectively, are due to extreme outliers.

Overall, we find that the model fluxes contradict the results based on the idealized scenarios. The inclusion of the full parametrization of proxy reactivity, including the offset calculated by Minutolo et al. (2024) for the respective proxy, blurs the dependence of fluxes on substrate distribution and suggests that sediment fluxes of O_2, NH_4^+, NO_3^- and N_2 are relatively independent of the location of the substrate maximum within the sediment.

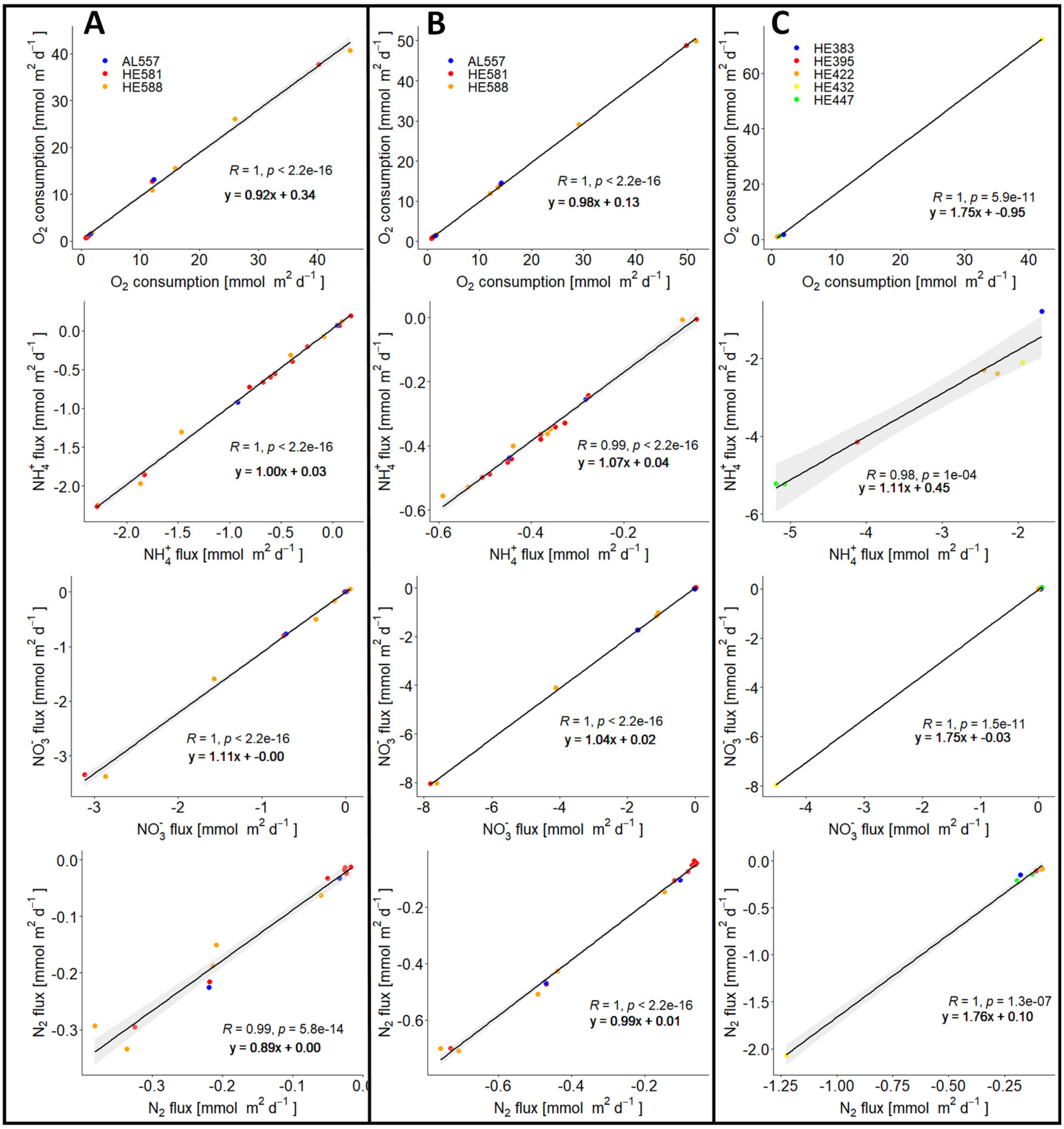


Figure 3.5: Model output for fluxes of O_2, NH_4^+, NO_3^- and N_2 based on the observed (y-axis) vs. the averaged proxy profile (x-axis). A: phaeophytin-a as proxy. B: chlorophyll-a as proxy. C: TOC as proxy.

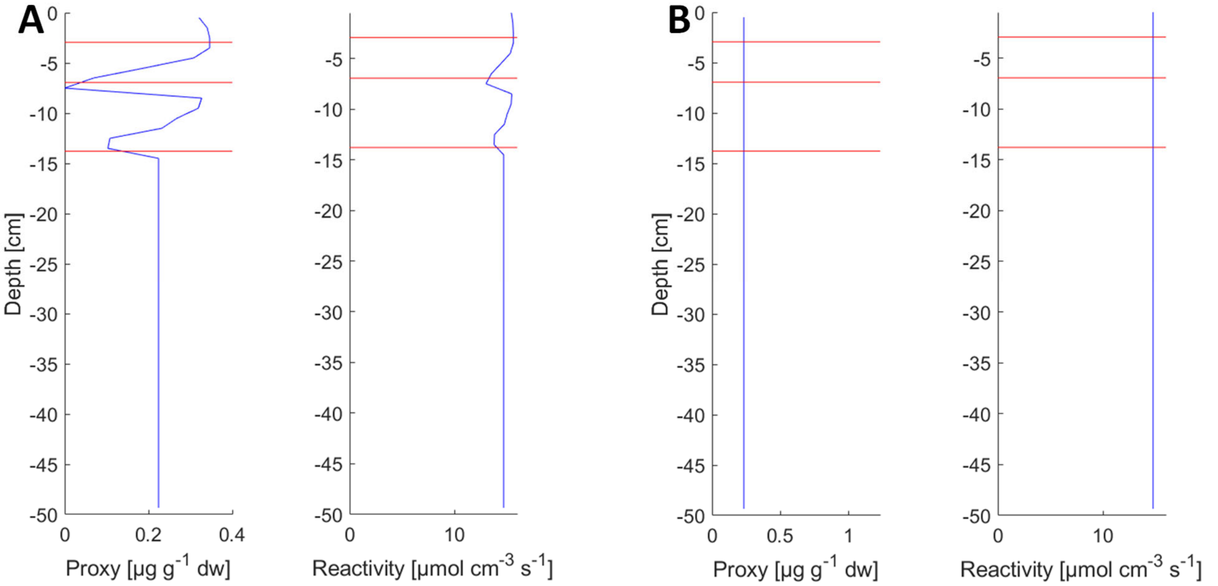


Figure 3.6: Observed (a) and averaged (b) vertical proxy (here phaeophytin-a) profiles and the resulting reactivity (here benthic reaction rate of oxygen) for station HE588-35.

Table 3.3: Mean differences ± standard deviations in modelled solute (O_2, NH_4^+, NO_3^- and N_2) fluxes between using observed and averaged pigment profiles. Note: positive/negative values indicate an increase/decrease in fluxes in calculations based on averaged values vs. observed profiles.

	Mean difference [%]
Proxy: Phaeophytin-a	
O_2	0.56 ± 5.13
NO_3^-	-58.78 ± 221.62
NH_4^+	1.66 ± 15.39
N_2	33.53 ± 57.61
Proxy: Chlorophyll-a	
O_2	-0.09 ± 1.41
NO_3^-	-4.97 ± 3.47
NH_4^+	53.42 ± 178.35
N_2	13.63 ± 22.09

3.4. Discussion

3.4.1 Fluxes in idealized scenarios decrease with substrate depth

Our initial expectations were shaped by the model outcome of the three idealized scenarios, where the substrate maximum aligns with the 75 %, 50 % and 25 % scenario of the pore water percolation depth, meaning that 75 %, 50 %, and 25 % of the pore water volume percolates up to these depths. The rationale behind the placement of substrate maxima at varying depths is rooted in the interplay of macrofauna activity and the influence of mobile bedforms. These factors affect the vertical distribution of substrates within the sediment. Macrofauna, through their burrowing activities such as bioturbation, redistribute organic matter and sediment particles deeper into the sediment (Kristensen et al., 2012; Meysman et al., 2006; Neumann et al., 2021). Concurrently, the presence of mobile bedforms (e.g. ripples and dunes), driven by currents and wave action, further modifies the spatial distribution of substrates by redistributing sediments across the sediment surface (Ahmerkamp et al., 2015, Precht et al., 2004, Huettel et al., 2014). Consequently, the combined effects of macrofaunal activity and mobile bedforms create distinct patterns of substrate distribution, resulting in substrate maxima at varying depths within the sediment (Fig. 3.3).

Clear variations in modelled fluxes of O_2, NO_3^- and N_2 in the idealized scenarios (Tab. 2) suggest that the vertical distribution of substrate does affect biogeochemical processes within the sediment and the resulting fluxes (Fig. 3.4, Tab. 3.2). O_2 fluxes decrease two-fold from the 75% to the 25% scenario (Tab. 3.2): With increasing depth in the sediment, less oxygen is available for aerobic remineralization, resulting in reduced O_2 fluxes, as most of the oxygen entering the sediment at the surface never reaches the substrate buried in the 25 % scenario. Concurrently, NO_3^- fluxes increase two fold and N_2 fluxes out of the sediment increase three fold. This is plausible and aligns well with the distribution of solute concentrations within the sediment (Fig. 3.4). In the 75 % scenario, the substrate maximum lies relatively close to the sediment surface and thus much of the oxygen entering the sediment is respired during organic matter degradation. Less oxygen reaches the substrate maximum for the 50 % and 25 % scenario as the maximum is buried deeper within the sediment, therefore less oxygen is respired, ultimately resulting in reduced oxygen fluxes. During respiration of organic matter, NH_4^+ is produced and accumulates in anoxic sediment horizons. Simultaneously, NO_3^- concentrations are reduced substantially at the depth of the substrate peak, because intense respiration quickly generates anoxic conditions where nitrate is respired to N_2. Concurrently, theses reaction zones deepen from the 75 % to the 25 % scenario and nitrate and N2 fluxes increase, due to enhanced denitrification. In sediments with organic matter at depth, the depletion of oxygen can create an aerobic-anaerobic transition zone, with high microbial abundances, making it a hotspot for biogeochemical processes (Wu et al., 2021). Here, nitrate produced by nitrification can be immediately used for denitrification.

3.4.2 Modelling benthic fluxes under natural conditions

In addition to the calculation of idealized scenarios, we performed a more advanced model calculation that took the entire parametrization by Minutolo et al. (2024) into account. In contrast to the distinct variations of benthic flux rates in the idealized scenarios, this approach yielded somewhat surprising results. Contrasting the anticipated changes in benthic fluxes with vertical substrate distribution scenarios in the idealized settings (Tab. 2), the model simulations for the sampled stations showed only minimal variation in fluxes based on the observed measured proxy profile in relation to the averaged vertical proxy profile (Fig. 3.5).

This difference arises, mathematically speaking, when the calculated offset in sediment reactivity (cf. Minutolo et al., 2024) is integrated into the calculation. In this previous study, we provided the parametrization in the form of linear regression equations, with the general regression formula $y = m*x + b$. This intercept “b” gains in importance as absolute numbers for the respective proxy represented by x, e.g., pigment or TOC concentration, become smaller. Figure 3.6 illustrates the consequences of this effect: With small proxy values, even with large relative variations in the observed proxy profile (Fig. 3.6 A), the reactivity shows minimal variation across the sediment depth. The vertically averaged proxy profile and the calculated resulting reactivity across sediment depth (Fig. 3.6 B) shows nearly the same outcome. We find no changes in reactivity and it is this lack of change in reactivity between using the measured and averaged proxy profile that leads to the similarity of computed benthic fluxes.

This indeed is due to the relatively large intercept term in the regression equations (Minutolo et al., 2024), that dominates the model output at the range of proxy concentrations in our dataset. We interpret this offset as a baseline reactivity in the sediment and in the following refer to it as non-proxy associated activity. This baseline reactivity reflects the inherent reactivity of the sediment and is crucial in understanding microbial activity and the general explanatory power of approaches based on proxies for sediment reactivity. Independent of one particular proxy, sediment microbes utilize diverse organic compounds, such as proteins and carbohydrates, for decomposition (Zinke et al., 2019).

The choice of a specific proxy thus plays a pivotal role, as any proxy can only capture a fragment of overall microbial activity in sediments. Chlorophyll-a, and its degradation product, phaeophytin-a, are commonly used as proxies for recent primary production and hence as indicators of potentially labile organic matter in marine sediments, which can enhance microbial activity and biogeochemical transformations. Their concentrations in sediment are linked to oxygen consumption and other remineralization processes (Minutolo et al., 2024; Lessin et al., 2018). TOC measures the total amount of carbon found in organic compounds within sediments. It is widely used to assess the overall quantity of organic matter available for microbial degradation and its presence generally supports benthic remineralization processes (Bratek et al., 2024).

In the case of our study, one might argue that proxies with a smaller non-proxy associated baseline reactivity may be more suitable. Any proxy for reactivity that shows a smaller intercept, i.e., smaller-non-proxy associated baseline reactivity, should thus capture a larger portion of the microbial metabolic diversity adding to overall sediment reactivity. In consequence, the calculated reactivity values should align more closely with the actual organic matter utilized by microbes in sediment decomposition processes. A closer inspection of sediment data collected during FTR incubations on different cruises (AL557, HE582, HE595 and HE602) reveals that the relative contribution of the intercept to total sediment reactivity (note that sediment reactivity here again refers to reaction rates of oxygen) is 85 ± 14 % and 62 ± 18 % for chlorophyll-a and phaeophytin-a, respectively (data not shown). Pigments thus represent valuable predictors of sediment reactivity and benthic fluxes, but nonetheless do not encompass the entire reactivity within the sediment. A potential candidate with a larger predictive capability and a lower non-proxy associated baseline reactivity may be either TOC or carbohydrates, which have a substantially lower intercept contribution of 22 ± 8 % and 26 ± 8 %. This suggests that TOC and carbohydrates may be more suitable as proxies for sediment reactivity, since they align more closely with the actual organic matter metabolized by microbes. Despite the previous findings in our earlier paper (Minutolo et al., 2024), where carbohydrates were observed to be a less favorable proxy for sediment reactivity, our findings here suggest reconsidering carbohydrates as a suitable proxy. While Minutolo et al. (2024) did observe weaker correlations of sediment reactivity with carbohydrates (compared to e.g. phaeophytin-a), the observed trend was the same and correlations still existed. However, differences in their microbial lability and thus in their contribution to overall sediment reactivity may have previously shadowed the potential of carbohydrates as a suitable proxy. It's possible that the specific types of carbohydrates present in the sediment samples of our previous study were less reactive, leading to a lower observed correlation. Therefore, carbohydrates may be able to play a more significant role than previously understood in predicting sediment reactivity and benthic fluxes. The main purpose of any proxy, though, is to use it in areas that were not captured in respective sampling campaigns. For maximum predictive power, a useful proxy should thus be easily obtained and widely available. We therefore recommend sedimentary TOC as a proxy to assess sediment oxygen consumption and overall reactivity, as it is a frequently measured parameter and is available with high spatial resolution in North Sea sediments.

In permeable sediments where advection-driven processes dominate, the influence of the vertical distribution of organic matter on biogeochemical processes is markedly different compared to diffusion-dominated, less permeable sediments (Huettel et al., 1996; Huettel et al., 2014; Boudreau and Jørgensen, 2001). The key distinction lies in the dynamic transport mechanisms inherent in these sediments. Advective transport, facilitated by the high permeability and porewater flow, continuously redistributes organic matter throughout the sediment matrix (Ahmerkamp et al., 2015; Precht et al., 2004). This constant movement leads to a more uniform distribution of these elements, effectively diluting the localized effects that distinct layers of organic matter would otherwise have on microbial activity and biogeochemical cycling. As a result, the precise vertical positioning of organic matter becomes less critical in controlling biogeochemical processes in these environments. The water flow in permeable sediments not only disperses organic matter but also enhances the exchange of solutes (e.g. oxygen and nutrients) between the sediment and overlying water column, further minimizing the impact of organic matter stratification (Ahmerkamp et al., 2015, 2020). This contrasts with less permeable sediments, where the absence of significant advective flows leads to a more pronounced effect of organic matter distribution on biogeochemical activities, as diffusion is the primary, and often limited, transport mechanism. In such settings, the location and concentration of organic matter strongly dictate the rates and patterns of oxygen consumption and nutrient cycling, leading to more localized and stratified biogeochemical processes (Glud 2008; Huettel et al., 1998).

3.4.3 Conclusion

We examined the sensitivity of modelled benthic fluxes to the vertical distribution of organic matter, and got conflicting results. The observed lack of differences in model output when employing either the observed or the averaged vertical proxy profiles carries important implications for sediment management and monitoring strategies. If the model consistently yields comparable results regardless of the vertical distribution of proxies, it suggests that the intricacies of substrate variations may not exert a substantial influence on the predicted biogeochemical processes in permeable sands with low concentrations of organic matter. Consequently, from a practical standpoint, this finding implies that sediment sampling procedures could be optimized. Instead of sampling multiple depths within the sediment column, the homogenization of sediment prior to subsampling may be considered. By homogenizing the sediment, extracting a single sample may provide representative insights into the overall biogeochemical dynamics, potentially streamlining monitoring efforts. Considering the limitations of pigment proxies in capturing sediment reactivity, we propose alternative proxies such as total organic carbon (TOC), which exhibit lower intercept contributions and thus may offer more accurate representations of microbial activity. The widespread availability of TOC data further strengthens the case for its suitability as a proxy in sediment studies, offering valuable insights into organic matter dynamics and microbial processes. This shift in sampling strategy could offer cost and time efficiencies while still capturing the essential features of sedimentary processes, contributing to more practical and resource-efficient sediment management practices.

Acknowledgements

We want to acknowledge the great support by the captains and crews of R/V Alkor and R/V Heincke. We also gratefully acknowledge Leon Schmidt from the Helmholtz-Zentrum Hereon for analyses of nutrients.

4 Application of a benthic model for the implementation of management scenarios

NEUMANN, A., MINUTOLO, F. & DÄHNKE, K. Application of a benthic model for the implementation of management scenarios. *In preparation for publication*

Abstract

The Coastal North Sea is an area exposed to diverse and in parts counteracting pressures from multiple anthropogenic uses. Following EU legislation, Marine Protected Areas (MPAs) have been assigned in the North Sea to alleviate pressure from e.g., bottom trawling fisheries. We apply a benthic model and use available climatological and sediment data to evaluate the effects of this management measure on bentho-pelagic fluxes. Our results suggest that changes in fluxes in the marine protected areas are diminutive, and that strongest effects of this measure are to be expected in the near-coast regions and parts of the Paleo-Elbe Valley. Nonetheless, the scenarios suggest that even in these regions, changes would be so small that they may be disguised by natural seasonal or spatial variability.

We propose that an accurate model assessment of flux changes demands inclusion of fauna properties, and of changes in TOC accumulation and grain size changes that are supported by changes in the benthic faunal community. To support management and to accurately predict the effects of individual management decisions, a more integrative view on sedimentary properties and recognition of the key role of fauna is urgently needed.

4.1 Introduction

Coastal marine waters such as the shallow German Bight are not only habitats for diverse ecosystems but also subject to various anthropogenic activities, which comprise e.g. fishing (Bruns et al., 2020), sand extraction (Mielck et al., 2021), shipping (Seyler et al., 2017), construction of offshore installations (Brandt et al., 2018; Galparsoro et al., 2022; Teschke et al., 2023), but also recreation and nature conservation efforts. Some of these activities are mutual exclusive at a given site (e.g. construction and sand removal) while others might benefit from synergistic effects like wind turbine farms and nature conservation (De Borger et al., 2021; Watson et al., 2024). Moreover, natural processes and anthropogenic activities are linked by complex interactions, and not all of these interactions are obvious. From a management perspective the guiding question is: Which is the best use for a particular habitat type to balance the contrasting interests?

An emerging tool for the analysis and management of complex systems are models, which enable to implement scenarios and provide insight in the consequences of planned management measures (Pillai et al., 2022; Schneider et al., 2023; Skákala et al., 2023; Zhihan et al., 2023). The models that are currently developed become increasingly complex, and recently, for these complex models the term ‘digital twin’ was coined to emphasise their claimed capabilities.

Here we demonstrate the application of a benthic model for the implementation of scenarios to study the effects on benthic processes after the exclusion of mobile ground-touching fisheries. In a recent study, Zhang et al. (2024, in review) used modelling and estimated the effects of bottom trawling on the sediment TOC content. This relationship can be used to calculate changes in TOC content in relation to bottom trawling intensity. Our model integrates the pore water flow parametrization by Elliott and Brooks (1997), which calculates the transport of solutes through the sediment influenced by bedform structures, with the benthic reactivity parametrization provided by Minutolo et al. (2024). The combination enabled us to predict benthic oxygen and nutrient fluxes (chapter 2), capturing the dynamic interactions between sediment structure and biochemical processes. By applying this integrated model to the German Bight, we extrapolate our findings to larger spatial scales.

The scope of this study is to combine available data on sediment characteristics with new parametrizations of reaction rates into a simple sediment model to estimate benthic fluxes and their change in a hypothetical scenario of complete exclusion of bottom trawling. It aims to test the ensemble in a real application, assess its performance, and to identify conditions where it fails. We then draw conclusions from the failures to adjust the next development steps towards a reliable and capable sediment model that can be employed for model-based decision making.

4.2 Methods

4.2.1 Model description

The porewater flow through the sediment was modelled by employing the parameterizations provided by Elliott & Brooks (1997). Similarly to Minutolo et al. (submitted / chapter 3), the model resolves 100 individual streamlines along which the succession of 1) oxygen consumption with nitrification, and 2) denitrification with ammonium accumulation was modelled. Unlike to Minutolo et al. (submitted / chapter 3), we here did not resolve explicitly all time steps along the porewater flow paths. Instead, we calculated the times along each streamline where 1) oxygen is depleted, 2) nitrate is depleted, and 3) the porewater reemerges from the sediment as there 1) oxygen consumption and nitrification cease, 2) denitrification and ammonium accumulation ceases, and 3) the streamline ends. Additional metabolic pathways such as sulphate reduction or carbonate reduction have not been implemented in this model.

The time t at which the oxygen and nitrate were depleted along each streamline were calculated using the initial concentrations in the bottom water (C_{oxy}, C_{nit}) and reaction rates (R) according to the parametrizations of Minutolo et al. (2024)

$$t = \frac{C}{R} = \frac{t*}{k^2\ K\ h_m} \tag{4.1}$$

We further assume that all reactions are sufficiently described as first-order kinetic, where the reaction rate is independent from the substrate concentration. Accordingly, we calculated the consumption of dissolved substrate (oxygen, nitrate, ammonium) and production of metabolites (ammonium, nitrate, dinitrogen) at the 3 times for each streamline, and tracked the concentrations of oxygen, ammonium, nitrate, dinitrogen. The resulting fluxes of these solutes we then calculated by horizontally averaging the particular fluxes of all individual streamlines, which were calculated from the vertical porewater velocity (v) and the initial and final solute concentrations (C_{in}, C_{out}) (equation 4.2):

$$J = v\ (C_{in} - C_{out}) \tag{4.2}$$

The combined porewater advection and biogeochemistry model described above was applied to each grid cell of the modelled sector of the south- eastern North Sea. The spatial model grid consisted of rectangles with the dimensions of 3.3 km by 3.3 km. The temporal resolution is 1 month, and fluxes of 12 successive months were averaged for annual averages.

The dimensions of bedforms (wave length, amplitude) were derived from the median grain size according to parameterizations from Flemming (1988), and Yalin (1985).

4.2.2 Data sources

The model implementation used data from several sources to provide the necessary input data. The median grainsize (D_{50}) and the mud content were derived from Bockelmann et al. (2018). Bottom water concentrations of oxygen and nitrate, water temperature, and current velocity were derived from North Sea Biogeochemical Climatology (NSBC), a data compilation from Hinrichs et al. (2021). Data of the fishing intensity expressed as Swept Area Ratio (SAR) was provided by OSPAR. The latest available data set is from 2017. All datasets were mapped to the model grid by spline interpolation.

4.2.3 No-trawling scenario description

The observations on sediment mud content reflect the impact of the current fishing effort. The hypothetical effect of a total exclusion of bottom- trawling on the sediment mud content was estimated using the relation of fishing intensity and organic carbon to mud ratio of Zhang et al. (2023, submitted). We derived an equation to directly estimate the TOC content for the no fishing scenario ($TOC_{notrawl}$) based on the current Swept Area Ratio (SAR) and the current TOC to mud content ratio. Since we assume that the mud content of the sediment is not significantly affected, the equation can be simplified (equation 4.3):

$$TOC_{notrawl} = \frac{TOC_{current}}{-0.037\, SAR + 1} \tag{4.3}$$

The remaining environmental parameters (oxygen, nutrient concentrations, temperature, current velocity) were kept identical.

4.3 Results

4.3.1 Boundary conditions

The relevant boundary conditions that were used to calculate the reference data and scenario results are presented in the following. The fishing pressure in the German EEZ (Fig. 4.1, black polygon) expressed as annual Swept Area ratio (SAR) was in the range of 0 to 4, and the fishing pressure was at the low end of that range in the working areas (Fig. 4.1, white polygons).

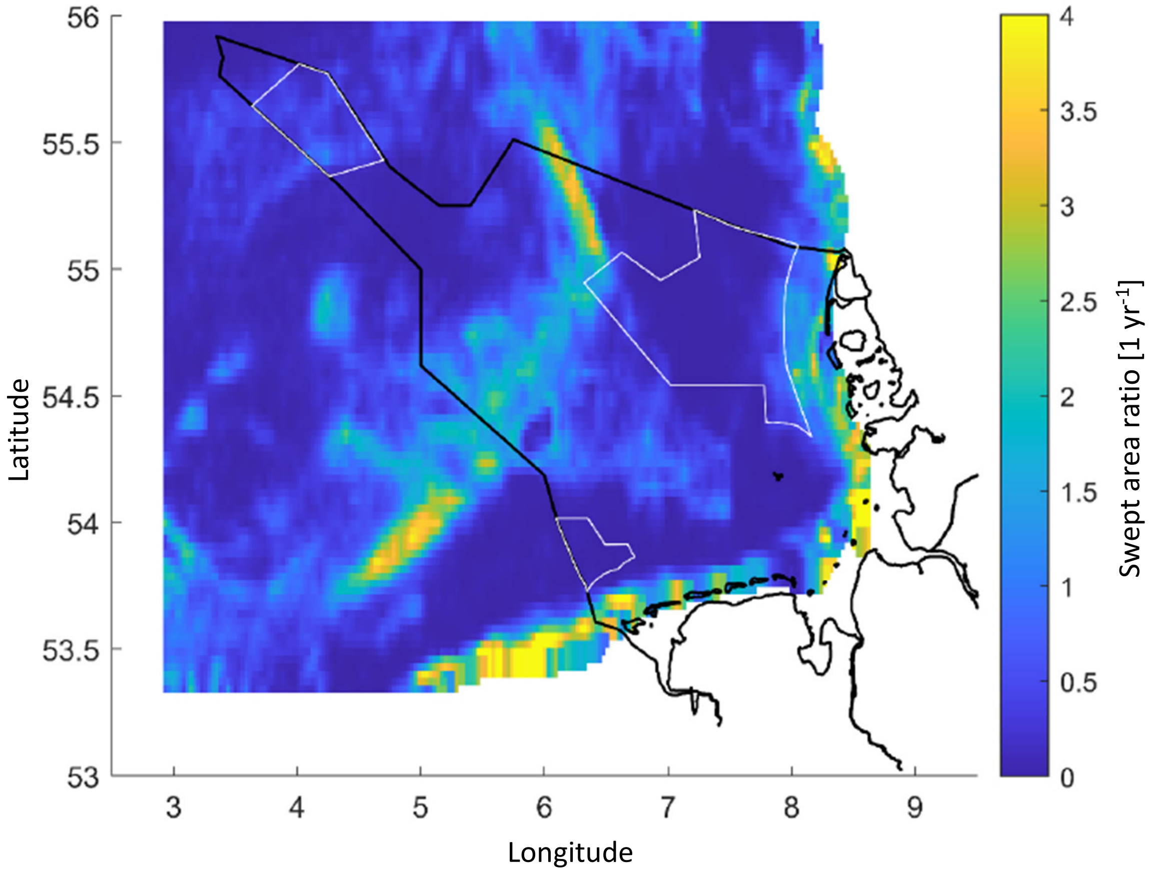


Figure 4.1: Map of fishing pressure in German Bight expressed as Swept Area Ratio (SAR). Higher values indicate higher frequency of bottom trawling. Black polygon indicates outline of German EEZ, white polygons indicate outlines of German marine protected areas. Data: OSPAR 2017

For the German Bight, there is an excellent data coverage with regards to several sediment characteristics. The current distribution of total organic carbon (TOC) values in the surface sediment are mapped in Figure 4.2. This present day status represents the reference for our scenario calculations. In the German EEZ, values exceed 1 % dry mass in the depot center Helgoland Mud Area at approx. 54° N 8° E (Fig. 4.2, yellow). The TOC content in the German EEZ was generally lower at approximately 0.3 % dry mass, and was particularly low in the three working areas (Fig. 4.2, blue). The scenario values of sediment TOC were calculated according to equation 4.3 on the basis of reference TOC and fishing pressure, and are mapped in Figure 4.3. In the no fishing scenario, the TOC content is increased by up to 15 % along the coast and in parts of the Paleo-Elbe Valley (Fig. 4.3, yellow), whereas the TOC content in the three working areas was increased by 0 – 5 % only (Fig. 4.3, blue).

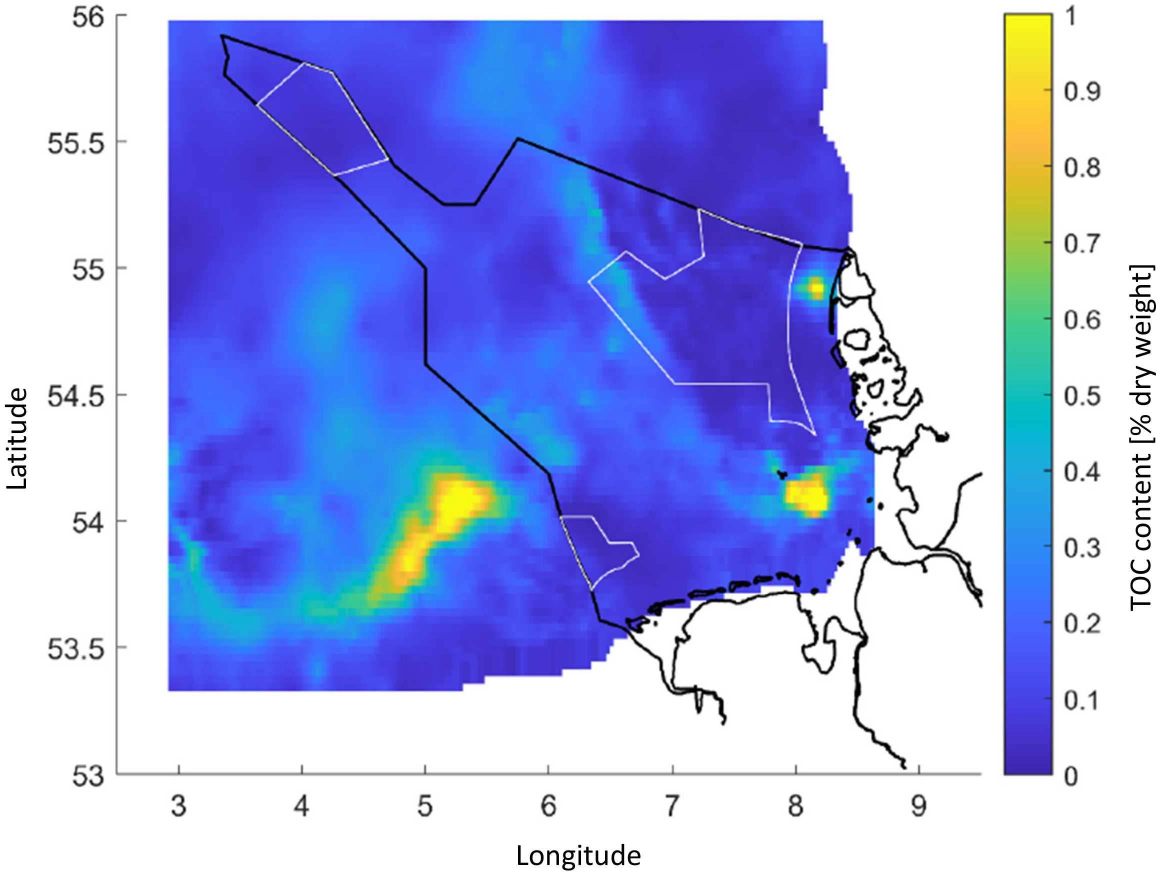


Figure 4.2: Map of reference TOC content in the surface sediment in the German Bight.

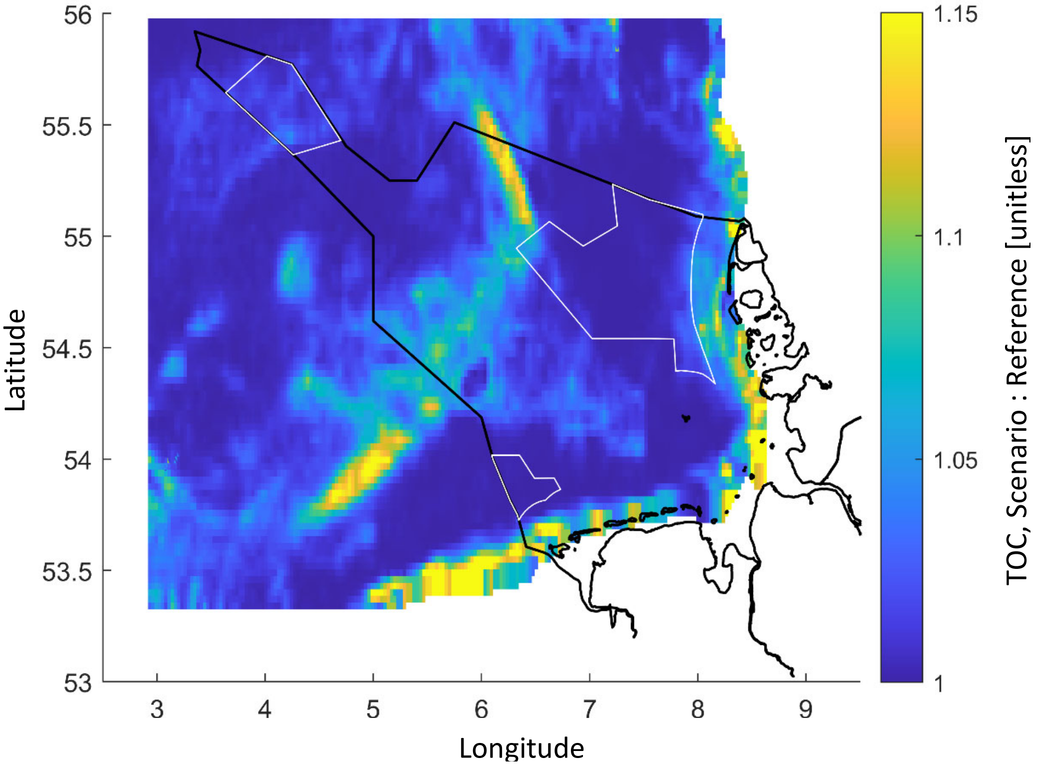


Figure 4.3: Map of hypothetical TOC content in the surface sediment according to the no fishing scenario. The hypothetical TOC content is mapped as ratio of scenario TOC to reference. TOC values representing changes of up to 15% in the near coast area (see text, section 4.4.1 for details). Values above 1 indicate that the TOC content is increased in the no fishing scenario relative to the reference TOC value.

The sediment permeability is mapped in Figure 4.4 and is indicative of the sediment type. Permeable sands in which pore water advection is dominant over molecular diffusion are indicated by permeability values above 10^{-12} m^2 (Fig. 4.4, yellow). The investigated nature protection areas are characterized by high permeability and advective pore water fluxes.

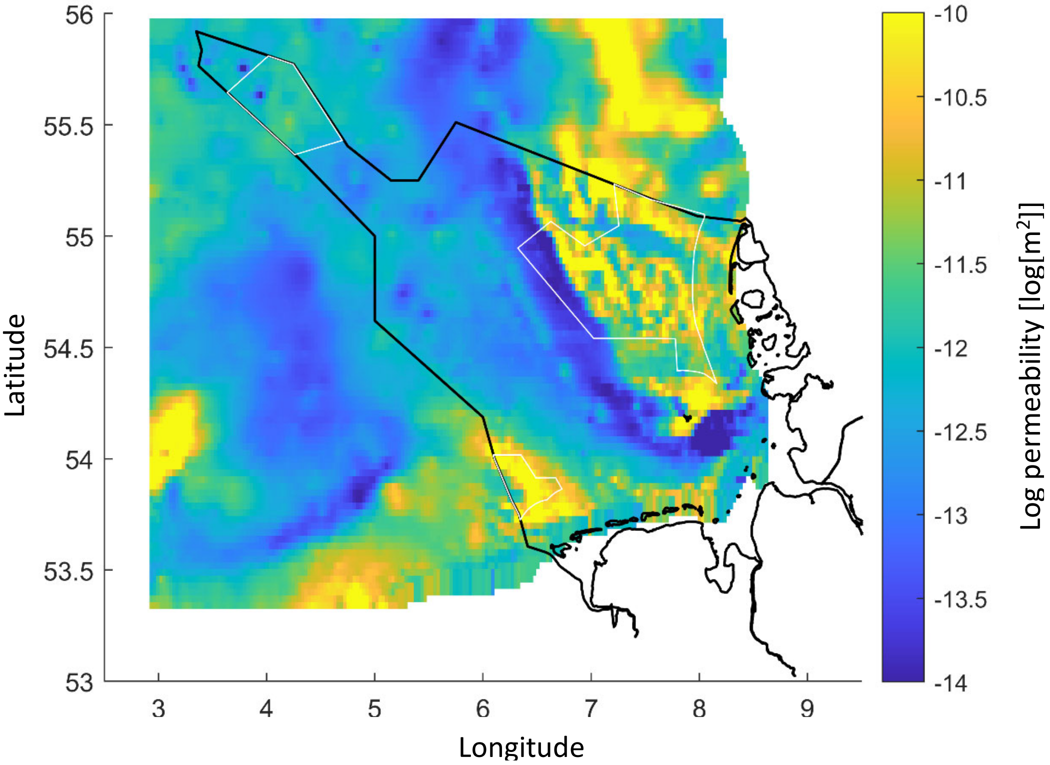
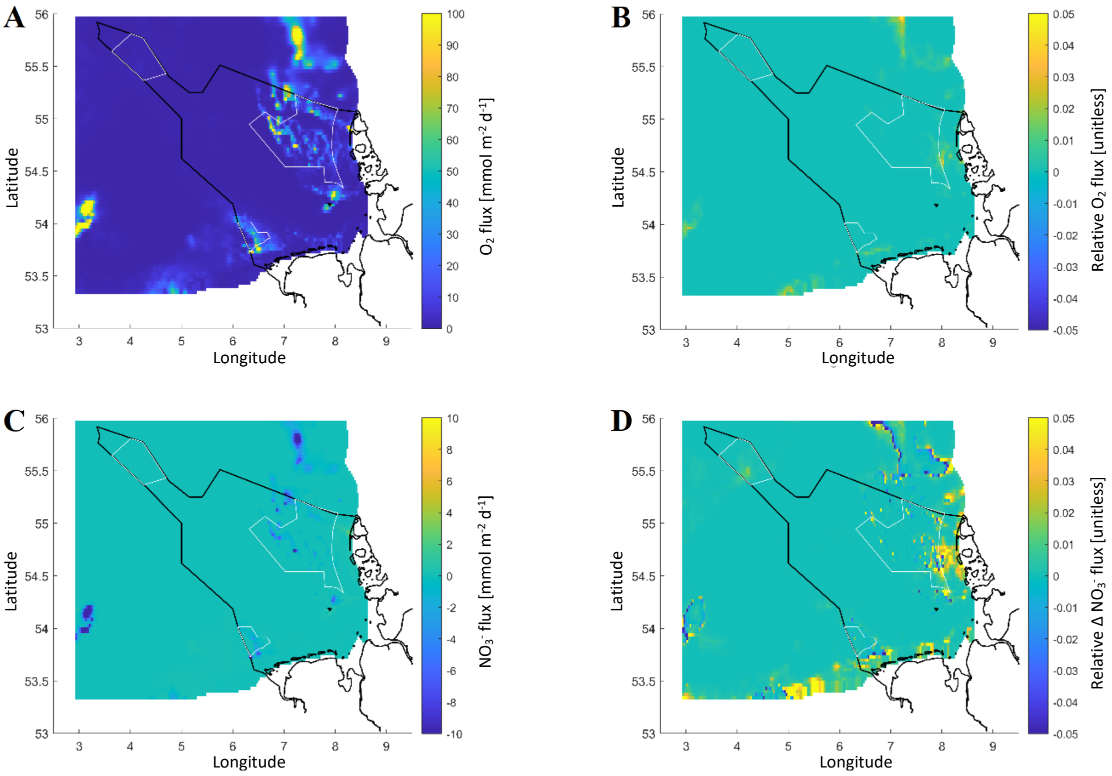


Figure 4.4: Map of sediment permeability in the German Bight. Values above -12 (green – yellow hue) indicate permeable sediment, values below -12 (bluish hue) indicate impermeable sediment. Note the inverse correlation with sediment TOC content, Figure 4.3 above.

4.3.2 Comparison of reference and scenario values of benthic fluxes

Benthic fluxes were modelled based on available data on sediment parameters (TOC, grain size, Bockelmann et al. 2018), and on bottom water concentrations of oxygen, nutrients, temperature (NSBC). These fluxes are based on present-day conditions and thus constitute the reference data. German Bight sediments are minor sinks of oxygen (<10 mmol m^{-2} d^{-1}) for most of the German Bight area, with higher oxygen consumption in the coastal MPAs and in the Heligoland mud area. These regions also exhibit measurable nitrate fluxes into the sediment, while nitrate fluxes are small and directed out of the sediment for the rest of the German Bight. Similarly, the regions in the Paleo- Elbe Valley and the coastal region are sources of ammonium and N2, whereas these fluxes are much smaller in the (advectively controlled) rest of the German Bight sediments. The results are mapped in Figure 4.5 A, C, E, G as annual averages.

Based on the scenario of no bottom trawling, the sediment TOC content changed in the calculated scenario (see previous section), and the benthic fluxes were recalculated based on the modified TOC content, while keeping all other boundary conditions unchanged. The change in the fluxes is presented in Figure 4.5 as difference between scenario data (exclusion of fisheries) to reference (present day) data, normalized by the reference data (Fig. 4.5, B, D, F, H). Overall, this analysis suggests relatively minor changes in sedimentary fluxes, with most prominent changes in the near coast area and especially for ammonium fluxes, in further offshore regions with high TOC content (Fig. 4.5 F). For a closer evaluation of our three working areas Figure 4.6 (presented as bar plots) suggests that, equivalent to minor changes in TOC, fluxes in these regions change only very little due to the exclusion of bottom trawling. The calculated relative differences were in the range of 0.01 – 0.02 % in oxygen fluxes (Fig. 4.6, A), 0.07 – 0.2 % in nitrate fluxes (Fig. 4.6, B), -0.2 – 1.6 % in ammonium fluxes (Fig. 4.6, C), and 0.05 – 0.2 % in N_2 (Fig. 4.6, D).



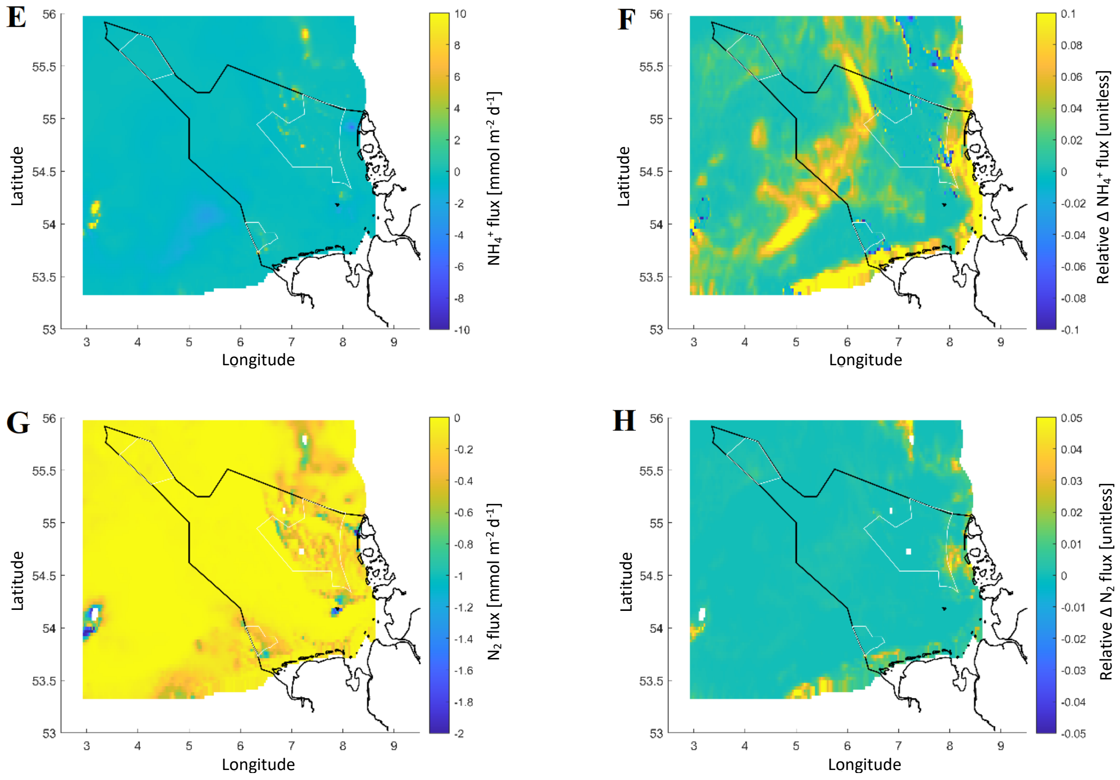


Figure 4.5: Benthic fluxes of reference model (left) and relative changes in benthic fluxes assuming a scenario with no bottom trawling (right). Positive fluxes are directed into the sediment, negative fluxes are directed into the water column. Black polygon indicates German EEZ, white polygons indicate MPAs.

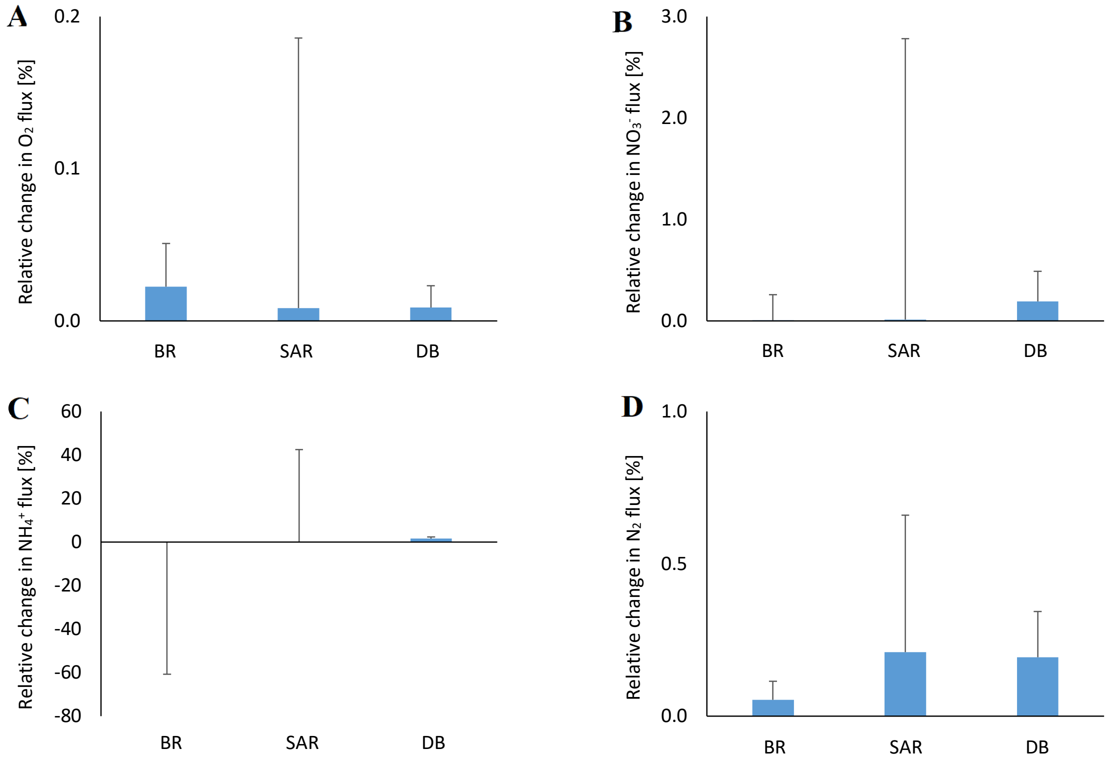


Figure 4.6: Averages of cell-wise calculated relative changes in annual fluxes of oxygen (A), nitrate (B), ammonium (C), and N_2 (D) in the three MPAs ‘Borkum Riffgrund’ (BR), ‘Sylt Außenriff’ (SAR), and ‘Dogger Bank’ (DB). Error bars indicate one standard deviation.

4.4 Discussion

4.4.1 A glimpse on the magnitude of effects

We have used a simple sediment percolation model to implement a scenario to estimate the hypothetical effect of the total exclusion of bottom trawling on the intensity of bentho - pelagic exchange of oxygen and nitrogen. In the proposed scenario, we used the current sediment TOC content as the reference and modified the TOC content according to the model calculations by Zhang et al. (2023, submitted). The scenario assumes that sediment reworking by bottom trawling removes TOC from the sediment, which is driven by a combination of resuspension and increased remineralisation due to increased exposure to oxygen (Zhang et al., 2023, submitted). Consequently, the estimated TOC values in the no fishing scenario generally exceed the reference values of the current status with bottom trawling, which indicates that undisturbed sediment is likely accumulating more TOC than disturbed sediment. However, the estimated TOC gain in the scenario scales with the initial TOC content and the current fishing pressure (Fig. 4.1-4.3). As it is, both parameters are low within the assigned German MPAs in the North Sea (Fig. 4.1 & 4.2), and thus, the resulting TOC gain after exclusion of bottom trawling is low and does not exceed 5 % (Fig. 4.3 delta TOC). For comparison, the hypothetical TOC gain is up to 15 % in the northern Paleo-Elbe Valley, where the initial TOC content and the current fishing pressure are both much higher than in the MPAs.

The benthic fluxes of oxygen, nitrate, ammonium, and N_2 we calculated with this simple and untuned model (Fig. 4.5 A, C, E, G) are plausible by comparision with measured fluxes in permeable sediment where pore water advection is dominant (Ahmerkamp et al., 2017; Marchant et al., 2016). Previous investigations (Neumann et al., 2021) suggested that these calculated fluxes are significantly underestimated in sediment with low permeability where faunal transport (bioirrigation, bioturbation) and molecular diffusion control the bentho- pelagic exchange. This should, however, not be the case at our study sites. The sediment in the MPAs is dominated by permeable sand (Fig. 4.4, permeability), so we are confident that our model is applicable for this study that focusses on the MPAs. Nevertheless, we point out that the model has severe limitations in diffusively controlled sediments.

The model output shows that in the no fishing scenario results, the sediment gains TOC, which then increases the volumetric consumption rate (Minutolo et al., 2024). However, this increased reaction rate does not result in linearly increased oxygen fluxes because the majority of pore water streamlines already become eventually anoxic in the sediments of the reference scenario. The flow rate and the bottom water oxygen concentration are unchanged in the scenario data, so that the resulting fluxes are already limited by the transport of oxygen into the sediment. Hence, whether pore water streamlines become anoxic at a somewhat shallower depth in the sediment has only a very limited effect on the resulting oxygen fluxes (Fig. 4.5 B delta oxygen, Fig 4.6 A oxygen bar plot).

Evaluating the patterns of modelled nitrate, ammonium, and N_2 fluxes is more complex because the combined effect of the intertwined processes ammonification, nitrification, denitrification are not only governed by the overall reactivity of the sediment (controlled by the TOC content) but also by the availability of ammonium and nitrate from the bottom water. Permeable sands appear as sources of nitrate and sinks of ammonium whereas these fluxes are reciprocal in impermeable sediment, and fluxes are often almost an order of magnitude higher than in permeable sediments (Fig. 4.5 C, E fluxes). For this reason, the role of bentho-pelagic nitrogen fluxes in permeable sediments has long been overlooked, and only recently, more studies addressed these processes in permeable sediments (e.g. Ahmerkamp et al., 2015, 2017, 2020; Marchant et al., 2016, 2018). However, the TOC gain in the scenario results in an increase of nitrate and N_2 fluxes of less than 1 % (Fig. 4.6 B, D bar plots). An interesting exception are the ammonium fluxes in Borkum Riffgrund and Sylt Außenriff, where the area-wide average is similarly low, but where the significantly higher standard deviation indicates that some parts of these working areas have much higher ammonium fluxes (Fig. 4.6 C bar plot). In both areas, individual cells have a very high permeability and consequently very high initial ammonium fluxes, which is not the case in the MPA in the Dogger Bank area (Fig. 4.5 E, flux map). Our interpretation is that individual and potentially erroneous median grain size data was used for the grainsize map from Bockelmann et al. (2018). In these areas, local reef structures can occur, with a substantial content of pebbles and rocks, which may result in much higher median grain sizes that are not necessarily representative for the hydraulic characteristics of the sand matrix at these sites. This indicates that the otherwise commonly employed median grain size might be inappropriate for the prediction of the permeability when the grain size distribution is significantly multimodal. Additionally, the biased median grain size at these reef sediment sites with high content of large grain sizes is substantially beyond the analysed grain sizes used in Neumann et al. (2017a) to derive the grain size to permeability model used here. The implausibly high permeability of individual model cells results in also implausibly high estimated fluxes, which should thus be regarded as potentially overestimated. However, these model cells in question represent only a small fraction of the overall model output data. These overall data are conclusive and do not exhibit unusual standard deviations, so we are confident that the overall trend is appropriate and that the predicted fluxes and magnitudes of the effect of fisheries exclusion are valid.

In summary, our model implementation predicts relatively low changes in the sediment TOC content in the no-fishing scenario, which consequently results in likewise small changes to benthic fluxes of oxygen and nitrogen. More importantly, the magnitude of modelled changes in benthic fluxes after the planned exclusion of bottom trawling in the MPAs is also small by comparison with the typical within station scatter of measured fluxes (20 – 100 %, depending on parameter) or typical seasonal variations as reported by Neumann et al. (2021). This implies that it might become challenging to detect the effect to bottom trawling exclusion on benthic fluxes in the presence of substantially higher levels of spatial and seasonal variability based on bentho-pelagic oxygen and nitrogen fluxes.

4.4.2 Constrains and limitations

The model used here implements exclusively fluxes resulting from pore water advection evoked by flow over a rippled bed, while completely ignoring benthic fluxes due to molecular diffusion and biotransport by macrofauna. However, previous studies have highlighted that fauna-driven exchange contributes significantly to the overall bentho- pelagic coupling, especially in less permeable sediment (Neumann et al., 2021). The recovery of the benthic macrofauna after the exclusion of bottom trawling is a major anticipated effect, which makes it plausible to assume that the recovery of the benthic community may further increase the contribution of fauna-driven fluxes to the overall bentho- pelagic exchange. If that decreases shear stress, current velocity and tidal sediment reworking, this may in turn increase the sedimentary TOC load due to finer grain sizes accumulating. This can, in turn, increase sedimentary oxygen and nitrogen fluxes beyond the scale we anticipate based on this simple model.

Our model implementation further ignores the effect of increased TOC accumulation in the sediment on the sediment permeability. Hedtkamp (2005) has demonstrated that the accumulation of particulate organic matter in the sediment similarly to the accumulation anticipated after the exclusion of bottom trawling does significantly reduce the permeability. This may be especially true if a benthic community at these sites is established that reduces physical stress and allows for accumulation of finer particles at these sites. Given that the fluxes in the no- fishing scenario are typically increased only by less than 1 %, there is a substantial probability that the reduction in permeability reduces or even inverts the effects on nitrogen biogeochemistry, so that sediments would for example act as sources of ammonia and substantial sinks for nitrate.

In summary, the simple model implementation used for this study allows us to address the effect of the exclusion of bottom trawling in an initial approximation. Nonetheless, sediment interactions are complex, with strong feedbacks between sediment geochemistry and biology, to name but one example. Hence, this simple model does not enable us to reliably estimate the full effect of bottom trawling exclusion on benthic fluxes. The results of this study should thus be considered exclusively as a method demonstration and must not be used as a basis for policy decisions. We anticipate that changes in the real lifeworld may exceed the anticipated flux changes considerably.

4.4.3 Conclusion

We combined available data on sediment characteristics, established parametrization of pore water flow and novel parametrizations of sediment reaction rates to implement a simple model that we then used to estimate the effects of bottom trawling exclusion on benthic fluxes. The model output suggests that in the chosen MPAs, changes in benthic fluxes will be near insignificant. We propose, however, that this may be in parts due to the simplicity of the model itself, and identified a number of issues that need to addressed in a reliable model that is capable to predict effects of planned interventions such as exclusion of bottom trawling: First, the model must include faunal transport modes because these can alter benthic fluxes significantly. In a second step, the model must include the effect of particle accumulation on permeability, because feedback mechanisms between changing benthic communities and permeability must be reproduced in the model for a reliable assessment. Last, we note that in the present model, the underlying parametrizations to calculate permeability and reaction rates do not yet frame all parameter values that occur in the German Bight, which limits the predictive power of the model.

Despite these shortcomings of the model we used for this study, our results allow us to draw some relevant conclusions for the implementation of a monitoring program that aims to evaluate the effects of an actual bottom trawling exclusion on biogeochemical processes in the sediment: The change in TOC content of the sediment of the MPA is small where the bottom trawling exclusion is currently planned. The modelled TOC gain is several times larger in other parts of the German EEZ, e.g. along the submerged Paleo-Elbe Valley. This suggests that effects of management measures may be larger in these regions of the German Bight. Moreover, a change in TOC content does not linearly translate into a change in fluxes, which let´s the change in fluxes appear less favourable with respect to management measures than it appears based on volumetric rates. Lastly, we find that the modelled changes in benthic fluxes are especially low by comparison with the variability in measured fluxes that is due to spatial heterogeneity, seasonal changes, and inter annual variability. Therefore, it may be very difficult to detect first order effects of fishing exclusion on benthic fluxes, even in detailed before/after studies in the field. Notwithstanding the model limitations outlined above, our results suggest that an exclusion of bottom trawling in the prospective MPAs may not be sufficient to significantly improve sedimentary ecosystem services to move towards a sustainable use of the coastal ocean.

5 Conclusions and outlook

5.1 Conclusions

In this thesis, benthic oxygen and nutrient dynamics have been examined, with focus on the implementation of a model that predicts benthic fluxes of O_2, NH_4^+, NO_3^- and N_2 under the current ecosystem state and hypothetical "what-if" scenarios.

The comprehensive analysis of sediment dynamics in the German Bight highlights the critical influence of sediment characteristics, such as mud content and phaeophytin-a, on benthic reaction rates within the German Bight. Our findings underscore the predictive strength of these parameters in determining O_2 consumption and NH_4^+ and NO_3^- turnover. By establishing correlations between these sediment characteristics and key biogeochemical processes, this study provides an empirical basis for future research. Linear regression coefficients for the examined sediment parameters and reaction rates are given, facilitating the conversion between all parameters.

This parametrization in conjugation with an already established pore water advection model allowed for the implementation of a benthic model that predicts benthic fluxes of O_2, NH_4^+, NO_3^- and N_2. Reworking of the sediment through macrofauna or mobile bedforms alters the vertical distribution of organic matter within the sediment. Benthic fluxes showed only minimal variations when comparing fluxes calculated from measured vertical proxy profiles against those from averaged profiles. This lack of significant variation is attributed to the large intercept term in the regression model, suggesting that inherent baseline reactivity within the sediment plays a dominant role over the measured proxies when their concentrations are close to the lower threshold. These findings suggest that traditional proxies (e.g. pigments) might not fully capture the complexity of microbial activity and sediment reactivity. This is particularly relevant in permeable sediments, where advective processes minimize the impact of the vertical stratification of organic matter on biogeochemical cycling. This thesis highlights that TOC, despite previously being considered less suitable, might be a more accurate proxy for sediment reactivity due to its lower non-proxy associated baseline reactivity. These insights have practical implications for sediment management and monitoring strategies, proposing that sediment sampling could be simplified by homogenizing the sediment before subsampling. This method could still provide comprehensive insights into biogeochemical dynamics, streamlining efforts and potentially reducing costs. The recommendation to use TOC as a proxy is further supported by its widespread availability.

These findings are extrapolated and the model is applied to larger spatial scales, using available data on sedimentary TOC concentrations and bottom trawling fishing intensity, to evaluate the impact of bottom trawling exclusion on benthic fluxes within the MPAs of the southern North Sea. The model results suggest that the exclusion of bottom trawling results in only minimal changes in the sedimentary TOC content and consequently only in slight alterations in benthic fluxes of oxygen and nitrogen. This limited response is attributed to the low initial TOC content and fishing pressure in these MPAs, coupled with the model's focus on areas dominated by permeable sand, which inherently supports advective processes over diffusive ones. Even with increased TOC concentrations, the response in benthic fluxes remains subdued due to the rapid onset of anoxia in pore water streamlines, maintaining fluxes at levels comparable to current conditions. Notably, while ammonium fluxes exhibited some variability, especially in areas like Borkum Riffgrund and Sylter Außenriff, this may be attributed to local variations in sediment grain rather than a direct effect of trawling activity. The magnitude of modelled changes in benthic fluxes after the planned exclusion of mobile ground touching fisheries in the MPAs is so small, that it might become challenging to distinguish direct effects of fisheries exclusion from seasonal, as well as inter annual variability and the prevalent spatial heterogeneity in the southern North Sea. Therefore, to move towards a more sustainable use of the southern North Sea, it might not be sufficient to only exclude bottom trawling fisheries from the MPAs.

5.2 Outlook

The analysis presented in this thesis reveals several ways for advancing our understanding of benthic processes in the southern North Sea. One critical aspect for future research is the incorporation of additional transport mechanisms into our benthic flux models. Specifically, the influence of molecular diffusion and biotransport by macrofauna has not been adequately represented. These processes are integral to the overall bentho-pelagic exchange and could significantly alter the outcomes of our models.

Incorporating a broader range of parameter values, particularly by including the full variability of proxy concentrations observed in the German Bight would further enhance the predictive power of our current model. Moreover, by expanding the parametrizations to include a wider range of sediment characteristics and reaction rates, the models accuracy and its applicability would be enhanced, allowing for more robust predictions across the varied environments of the German Bight.

Additionally, the incorporation of seasonal and temporal variability into our models is essential. The current study's focus on relatively stable proxy concentrations limits its applicability across different seasonal cycles and annual variations, which are prominent in marine environments like the southern North Sea. By integrating these variations, future models could offer more nuanced predictions and better understand how biogeochemical fluxes respond to natural and anthropogenic changes over time. This enhanced understanding is crucial when evaluating the impacts of management strategies, such as the exclusion of bottom trawling fisheries and their effectiveness over various temporal scales.

In conclusion, while this dissertation has laid a foundational understanding of sediment reactivity and benthic fluxes under current management scenarios, there is a significant scope for refining the models discussed. Intriguingly, the findings reveal that the vertical distribution of substrates has minimal influence on benthic fluxes, suggesting a potentially high level of dynamism within the tide-influenced sediment of the southern North Sea, a factor that may have been previously underestimated. This raises important questions about the effectiveness of current management measures. If benthic biogeochemical processes within the MPAs remain largely unchanged with the exclusion of mobile ground touching fisheries, it must be evaluated whether current management strategies are adequate or capable of achieving the intended good environmental status as defined in the OSPAR´s Quality Status Report 2023. Future studies should aim to develop more comprehensive models that account for the complex interactions of physical, chemical, and biological processes in marine sediments. By addressing these gaps and considering the dynamic nature of these environments, it is possible to inform management strategies and conservation efforts more appropriately, ultimately leading to more sustainable usage of marine resources in the southern North Sea.

Abbreviations

CO_2	Carbon dioxide
DIN	Dissolved inorganic nitrogen
DNRA	Dissimilatory nitrate reduction to ammonium
FTR	Flow through reactor
HCl	Hydrochloric acid
i.e.	id est
IAEA	International Atomic Energy Agency
N_2	Dinitrogen
N_2O	Nitrous oxide
NH_4^+	Ammonium
NO_x	Sum of nitrite and nitrate
NO_2^-	Nitrite
NO_3^-	Nitrate
O_2	Oxygen
OPSAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
p	Level of significance
R	Pearson correlation coefficient
R/V	Research vessel
res	reservoir
ss	steady state
T	Temperature
USGS	United States Geological Survey
δ	Isotope ratio relative to standard isotope ratio

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ZHIHAN, LV., HAIBIN, LV. & FRIDENFALK, M. 2023. Digital Twins in the Marine Industry. *Electronics,* 12.

List of publications

This thesis is composed of three individual scientific publications, which are either published (chapter 2), submitted (chapter 3) or in preparation for submission (chapter 4) in a peer review journal. The following publications arose as part of this thesis and the author contributions are specified.

***Minutolo, F.**, Dähnke, K., Metzke, M., Holtappels, M. and Neumann, A.: Sedimentary mud and phaeophytin-a are reliable predictors of oxygen consumption and nitrogen turnover in the southern North Sea. Continental Shelf Research, 272, 105161, https://doi.org/10.1016/j.csr.2023.105161, 2024*

AN designed the research. FM and MH carried out the field work. FM performed sediment incubations and isotope analyses. CN measurements were performed by MM. FM, AN, MH and KD interpreted the data. All authors contributed to the paper, led by FM, with major contributions from AN. All authors approved the final submission.

***Minutolo, F.**, Dähnke, K., Metzke, M. and Neumann, A.: Benthic processes in advective sediments are insensitive to vertical substrate distribution. [Submitted to Continental Shelf Research]*

AN designed the research and implemented the model. AN and FM carried out the field work. FM performed FTR sediment incubations. CN measurements were performed by MM. FM, AN and KD interpreted the data. All authors contributed to the paper, led by FM, with major contributions from AN. All authors approved the final submission.

*Neumann, A., **Minutolo, F.** and Dähnke, K.: Application of a benthic model for the implementation of management scenarios. [In preparation]*

AN designed the research and implemented the model. AN prepared the manuscript with contributions by FM and KD.

Furthermore, the following papers were published independently of my doctoral thesis:

Bach, L. T., Paul, A. J., Boxhammer, T., Von der Esch, E., Graco, M., Schulz, K. G., Achterberg, E., Aguayo, P., Arístegui, J., Ayón, P., *Baños, I., Bernales, A., Boegeholz, A. S., Chavez, F., Chavez, G., Chen, S.-M., Doering, K., Filella, A., Fischer, M., Grasse, P., Haunost, M., Hennke, J., Hernández-Hernández, N., Hopwood, M., Igarza, M., Kalter, V., Kittu, L., Kohnert, P., Ledesma, J., Lieberum, C., Lischka, S., Löscher, C., Ludwig, A., Mendoza, U., Meyer, J., Meyer, J.,* **Minutolo, F.**, *Cortes, J. O., Piiparinen, J., Sforna, C., Spilling, K., Sanchez, S., Spisla, C., Sswat, M., Moreira, M. Z. and Riebesell, U. Factors controlling plankton community production, export flux, and particulate matter stoichiometry in the coastal upwelling system off Peru. Biogeosciences, 17, 4831-4852, https://doi.org/10.5194/bg-17-4831-2020, 2020*

Spisla, C., Taucher, J., Bach, L. T., Haunost, M., Boxhammer, T., King, A. L., Jenkins, B. D., Wallace, J. R., Ludwig, A., Meyer, J., Stange, P., **Minutolo, F.**, *Lohbeck, K. T., Nauendorf, A., Kalter, V., Lischka, S., Sswat, M., Dörner, I., Ismar-Rebitz, S. M. H., Aberle, N., Yong, J. C., Bouquet, J. M., Lechtenbörger, A. K., Kohnert, P., Krudewig, M. and Riebesell, U. Extreme Levels of Ocean Acidification Restructure the Plankton Community and Biogeochemistry of a Temperate Coastal Ecosystem: A Mesocosm Study. Frontiers in Marine Science, 7, 611157, https://doi.org/10.3389/fmars.2020.611157 , 2021*

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Taucher, J., Lechtenbörger, A. K., Bouquet, J.-M., Spisla, C., Boxhammer, T., ***Minutolo, F.****, Bach, L. T., Lohbeck, K. T., Sswat, M., Dörner, I., Ismar-Rebitz, S. M. H., Thompson, E. M. and Riebesell, U.: The appendicularian Oikopleura dioica can enhance carbon export in a high* CO_2 *ocean. Global Change Biology, 30, https://doi.org/10.1111/gcb.17020, 2023*

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