



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

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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.

1. Introduction

Coastal systems cover only a small area of the ocean's surface, but disproportionately 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; Heintz 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

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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. Methods

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. 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, NOAA-I West (NIW), NOAA-I East (NIE), Sylter Außenriff (SAR) and Amrum Bank (AB).

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 grain sizes, where diffusion dominates transport processes. Therefore, the manipulation through sieving likely had minimal impacts on intrinsic sediment properties. Furthermore, this ensures a homogeneous sediment distribution in the flow-through-reactors (FTRs). Fig. 1.2 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).

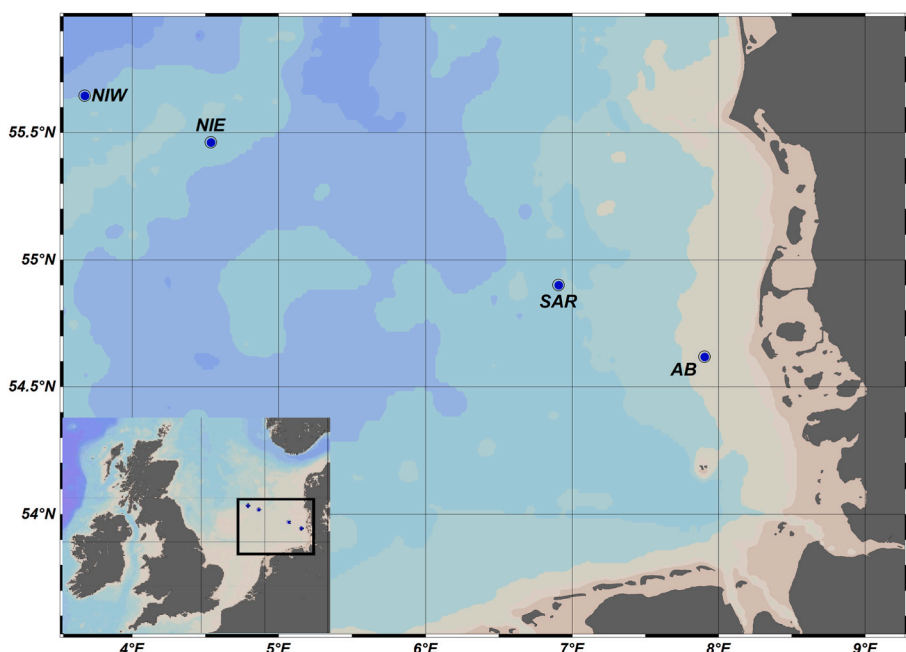


Fig. 1. Sampling stations in the southern North Sea during the HE582 cruise.

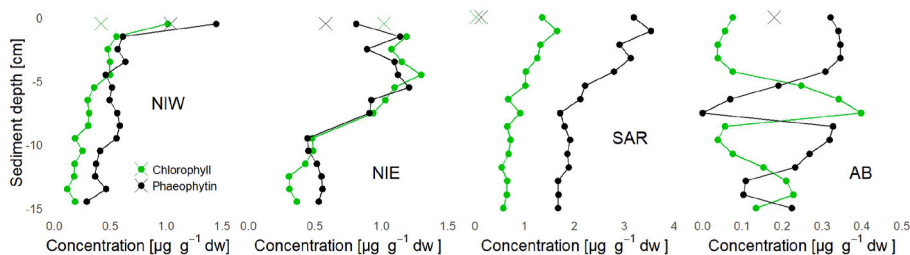


Fig. 1.2. Sediment depth profiles of pigment data from other cruises (HE581 for NIW, NIE and SAR, and HE588 for AB) at the same stations. Crosses represent pigment values of the FTR sediment from this study. Note: No FTR chlorophyll-a value for station AB.

2.3. 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 ($\sim 15^\circ\text{C}$). 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 $^{15}\text{NH}_4$ and $^{15}\text{NO}_3$ (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). 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 $\text{mM}^{15}\text{NO}_3$ solution to the 10 L water reservoir raised the nitrate concentration from initial 7.00 $\mu\text{mol L}^{-1}$ NO_3^- to a final NO_3^- concentration of 7.13 $\mu\text{mol L}^{-1}$ and yet resulted in the desired isotope enrichment. When ammonium or nitrate concentrations were low ($<10 \mu\text{mol L}^{-1} \text{h}^{-1}$), 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.

2.4. Analyses

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 $\mu\text{mol L}^{-1}$ and better than 0.05 $\mu\text{mol L}^{-1}$ for NO_2^- and NH_4^+ .

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.

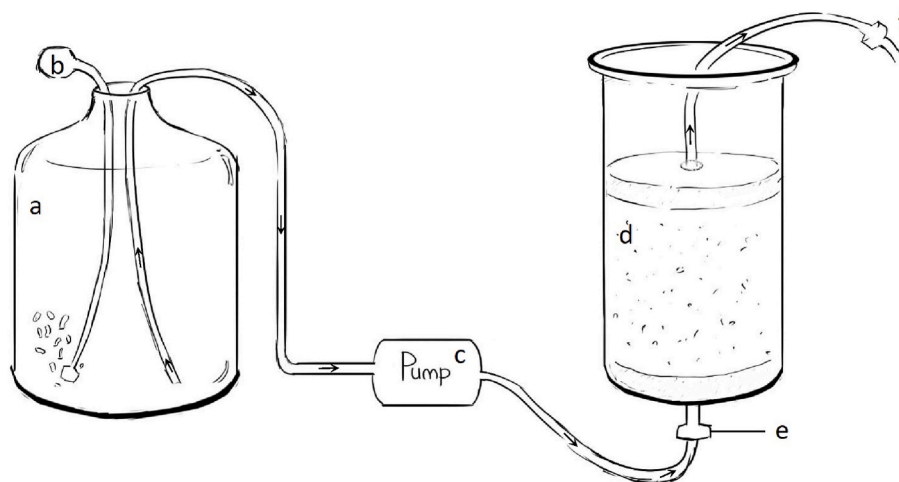


Fig. 2. FTR incubation setup. a: water reservoir. b: aquarium pump aerating the FTR water reservoir. c: peristaltic pump, pumping water from the reservoir through the FTRs. d: FTR containing homogenized sand. e: inlet sampling and flow through optode, measuring oxygen concentrations. f: outlet sampling and flow through optode, measuring oxygen concentrations. Pump direction: \rightarrow

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, 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.

2.4.3. 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 N₂O produced by the bacterium *Pseudomonas aureofaciens*. Two international standards (IAEA NO₃⁻ δ¹⁵N = +4.7‰, USGS34 δ¹⁵N = -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 N₂O using sodium azide (Zhang et al., 2007). For calibration purposes we used three international standards (IAEA N1 δ¹⁵N = +0.4‰, USGS25 δ¹⁵N = -30.4‰ and USGS26 δ¹⁵N = +53.7‰).

N₂O produced by either method was analyzed with a Gas-Bench II, coupled to an isotope ratio mass spectrophotometer (Delta Plus XP, Thermo Fisher Scientific).

2.5. Benthic volumetric rates

Volumetric rates of oxygen consumption, net dissolved inorganic nitrogen (DIN = NO₃⁻ + NO₂⁻ + NH₄⁺) and silicate (SiO₄⁴⁻) 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/O₂ 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 r_t = L_c/u with u as the bulk porewater velocity/flowrate and L_c as the length of the FTR (Ahmerkamp et al., 2020):

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

2.6. Gross rates of ammonium and nitrate production

Gross rates of ammonium and nitrate turnover were calculated according to the ¹⁵N dilution method (Norton and Stark, 2011), based on ¹⁵NH₄⁺ and ¹⁵NO₃⁻ additions, respectively:

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

Where C is the nutrient concentration, r_t is the retention time and I is the ¹⁵N 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 Q₁₀ coefficient, relating biological processes to temperature dependence (Mundim et al., 2020):

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

Where k₂ is the measured rate at the measured temperature (T₂) during the incubation and k₁ is the calculated rate at the desired temperature of 10 °C (T₁). The value for Q₁₀ was always set to 2, which is representative for biological reactions (Aisami et al., 2017).

3. Results

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).

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 NH₄⁺ 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 NH₄⁺ at station SAR FTR 3 and 4), concentrations were set to zero. Specific O₂ consumption rates (Table 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).

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

Table 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 | August 28, 2021 | 36.0 |
| NIE | 55.462272 | 4.537492 | August 30, 2021 | 28.2 |
| SAR | 54.899801 | 6.906302 | August 31, 2021 | 24.7 |
| AB | 54.618351 | 7.904198 | September 02, 2021 | 10.1 |

Table 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 |
|---------|-------------------------|-------------|-------------|-------------|-------------|-------------|
| | $\mu\text{g g dw}^{-1}$ | | | (%) | | |
| 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 |

Table 3

Volumetric rates for O₂ consumption, net and gross dissolved inorganic nutrient turnover rates at the sampled stations in the southeastern North Sea. Note: Net turnover includes negative NH₄⁺ rates. Values represent the average per station.

| Station | O ₂ consumption | NH ₄ ⁺ turnover | | NO ₃ ⁻ turnover | | SiO ₄ ⁻ turnover |
|---------|----------------------------|---------------------------------------|-------------|---------------------------------------|-------------|--|
| | | Net | Gross | Net | Gross | |
| | | $\mu\text{mol L}^{-1} \text{h}^{-1}$ | | | | |
| 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 |

one of the four values for ammonium turnover, respectively, were left out because NH₄⁺ concentrations at the FTR outlets were below the detection limit. Across all four sampling stations, a correlation analysis (Table 4) reveals that net ammonium turnover significantly correlates ($p < 0.001$) with mud content ($R = -0.96$), phaeophytin-a ($R = -0.95$) and specific O₂ consumption rate ($R = -0.94$). We also find that net NO₃⁻ turnover significantly ($p < 0.001$) correlates with the same parameters (mud content, $R = 0.85$, phaeophytin-a, $R = 0.81$, and specific O₂ consumption rate, $R = 0.93$). Both process rates also scale with and significantly ($p < 0.001$) correlate with sedimentary silicate release (Table 4). Similarly to net rates, gross rates (Fig. 4) 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 5).

4. Discussion

4.1. Processes in the sediment

Overall, volumetric O₂ consumption rates (up to 25.6 $\mu\text{mol L}^{-1} \text{h}^{-1}$) 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 O₂ 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 O₂ consumption rates. Furthermore, they did not exclude macrofauna, which may have further increased oxygen consumption. Our net rates for nitrogen turnover (Table 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. 4) 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 NH₄⁺ turnover sometimes are poor predictors of overall NH₄⁺ turnover. This variability of the intensity of NH₄⁺ 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 O₂ consumption is highest at the highest water depth (Tables 1 and 3). This is surprising, because in shallow coastal areas, large fractions of particulate material from e.g.

Table 4

Pearson correlation coefficients of rates of O₂ consumption, net dissolved inorganic nutrient turnover (NH₄⁺, NO₃⁻ and SiO₄⁻) 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: O₂ con. = O₂ consumption. For net NH₄⁺ 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 ⁻ | 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 | | | |

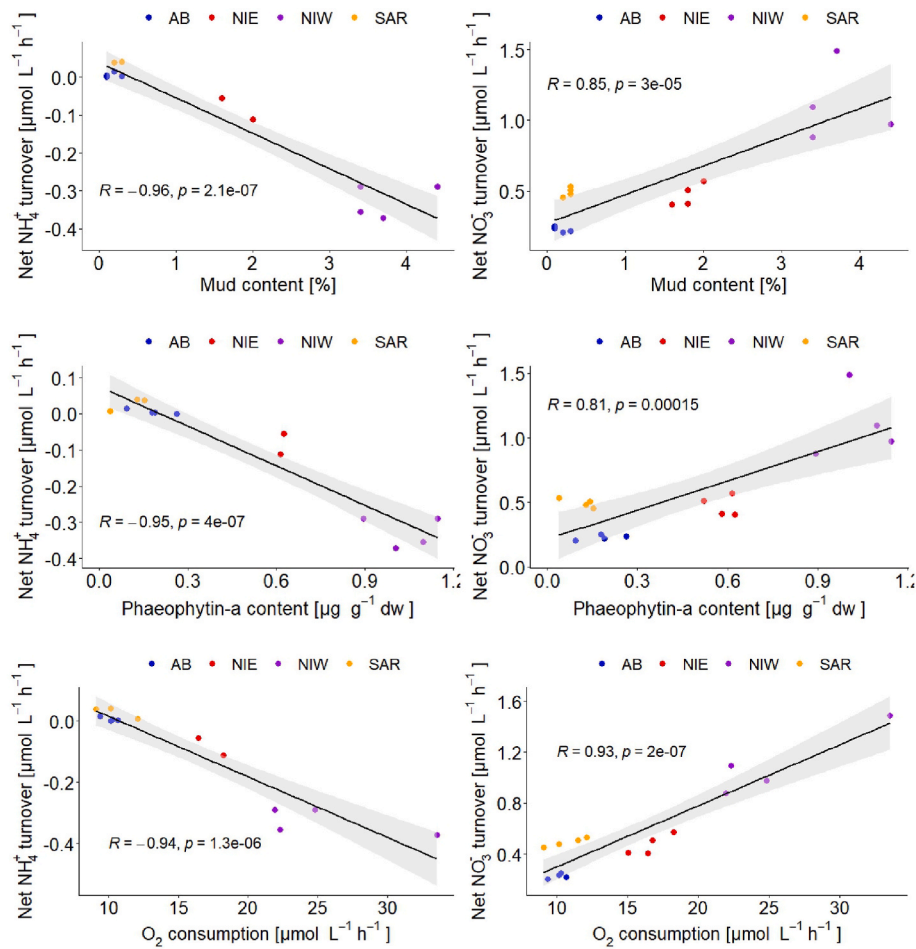


Fig. 3. Pearson correlation of net NH_4^+ (left) and NO_3^- (right) turnover rates with mud (top), phaeophytin-a content (middle) and O_2 consumption (bottom). Note: Net turnover includes negative NH_4^+ turnover rates. The solid lines indicate the linear regression. Grey bands indicate confidence intervals. 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.

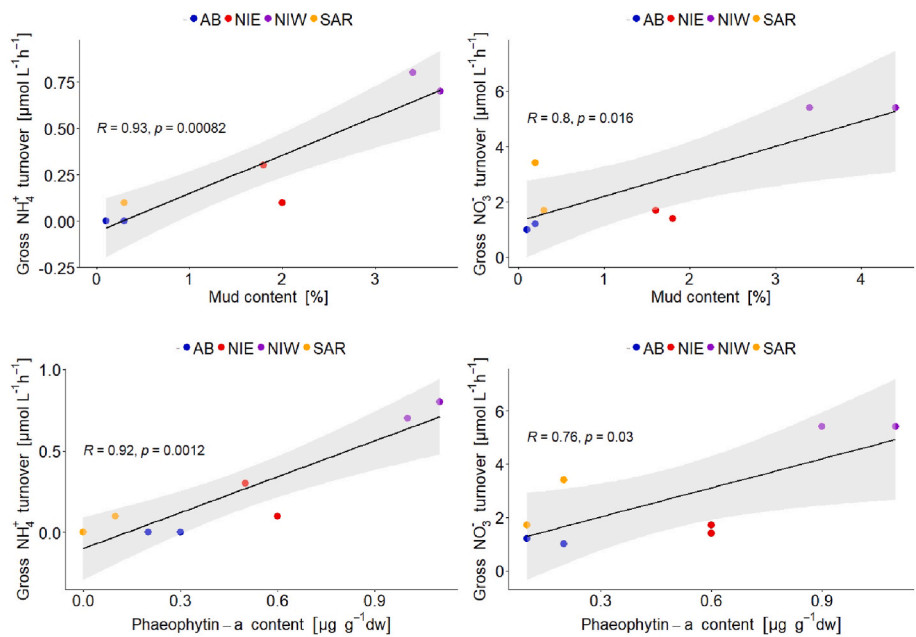


Fig. 4. Pearson correlations of gross NH_4^+ (left) and NO_3^- (right) turnover rates with mud (top) and phaeophytin-a (bottom) content. Note: The solid lines indicate the linear regression. Grey bands indicate confidence intervals. Duplicate measurements per station.

Table 5
Conversion table with values for the intercept (b0), slope (b1) and residual standard errors (e) of linear regression line to calculate benthic O₂ consumption, net and gross benthic reaction rates of dissolved inorganic nutrient turnover from sediment parameters, using the linear regression formula $y = b0 + b1 * x + e$.

| | O ₂ consumption | | | Net turnover | | | 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 | 0.22 | 0.43 | -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 | 2.37 | 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 |

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 O₂ consumption coincides with smallest grain sizes. Our interpretation is, that fine organic and mineral particles as the main constituents of mud and 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 O₂ consumption (Ahmerkamp et al., 2020).

All process rates clearly scale with silicate release (Tables 3 and 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 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 O₂ consumption, TOC and phaeophytin-a at the same site (Tables 2 and 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 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.

4.2. Comparison of proxies

In this section, we will now evaluate potential predictors of sedimentary remineralization, ammonium and nitrate turnover. Underoxic 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 Berger et al., 2021; Marchant et al., 2018). Thus, in the sediments we investigated, the O₂ 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 O₂ consumption (Fig. 3). 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 O₂ consumption rates with TOC (Table 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 4). We argue that these weaker correlations arises 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 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 chlorophyll 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 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 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.

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 O_2 consumption rates, with mud content and phaeophytin-a concentrations being the best predictors, followed by TOC, carbohydrates and grain size (Table 4). They correlate inversely (except grain size) with net ammonium turnover rates (Fig. 3). 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 and 3, Fig. 3), and, hence, higher gross ammonium turnover (Fig. 4). 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. 3) 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. 4), 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 micro-niches, 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 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.

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 O₂ 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 O₂ 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 parameterization. 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.

Authors' contribution

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.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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