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Spatial variations in sedimentary N-transformation rates in the North Sea (German Bight)

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Abstract

In this study, we investigate the role of sedimentary N cycling in the Southern North Sea. We present a budget of ammonification, nitrification and sedimentary NO_3^- consumption / denitrification in contrasting sediment types of the German Bight (Southern North Sea), including novel net ammonification rates. Dissolved inorganic nitrogen concentration (nitrate, nitrite and ammonium) in the water column showed low levels between 0.2 to 3.2 µmol L^{-1}. We incubated sediment cores with labeled nitrate and ammonium to calculate net and gross N transformation rates. The results show that impermeable sediments are the main site of ammonification (on average 10.2 ±1.2 mmol m^{-2} d^{-1}) and that they are an important source for primary producers in the water column, contributing ~17 to 61 % of reactive nitrogen in the water column. Ammonification and oxygen penetration depth are the main drivers of sedimentary nitrification. One third of freshly produced nitrate in impermeable sediment and two-thirds in permeable sediment were reduced to N_2. The semi-permeable and permeable sediments are responsible for ~80 % of the total benthic N_2 production rates (~890 t N d^{-1}) in the southern North Sea. We conclude that impermeable sediments are important sources of reactive N and that semi-permeable and permeable sediments are the main sinks of reactive N, counteracting eutrophication in the southern North Sea (German Bight).

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1 Introduction

The continental shelves and coastal margins make up for <9 % of the total area of ocean surface, but are responsible for vast majority of the biogeochemical cycling both in the water column and in the sediments (Jorgensen, 1983). For instance, 30 % of global marine primary production occurs in coastal, estuarine and shelf systems (LOICZ, 1995), and nutrient regulation in shelf sediments is a particularly valuable ecosystem service (Costanza et al., 1997).

The German Bight is part of the southern North Sea and is bordered by densely populated and industrialized countries, and receives large amounts of nutrients via river discharge (e.g., Rhine, Maas, Elbe, Weser, Ems) (Los et al., 2014). This caused clear eutrophication symptoms such as phytoplankton blooms, oxygen deficiencies and macrobenthos kills especially during the 1980s (Hickel et al., 1993; von Westernhagen et al., 1986) in the North Sea. In the adjacent Wadden Sea intense phytoplankton blooms, a decrease of seagrass and massive blooms of opportunistic macroalgae were attributed to eutrophication (Cadée and Hegemann, 2002; Dolch et al., 2013; Reise and Kohlus, 2007; Reise and Siebert, 1994). Since the mid 1980s, the nitrogen (N) loads into the German Bight have been decreasing, but the entire SE North Sea is still flagged as an eutrophication problem area (OSPAR, 2010).

Nitrogen availability increases primary production on a variety of spatial and temporal scales. At present, major nitrogen sources for the Southern North Sea are agricultural and urban waste water, and to a lesser extent, a variety of reactive N emission (e.g., nitrogen oxides from burning fossil) (Emeis et al., 2015).

Internal N cycling in sediments (e.g., assimilation, ammonification and nitrification) change the distribution and speciation of fixed N, but not the overall amount of N available for primary production (Casciotti, 2016). Removal of NO_3^- through denitrification and anammox in anoxic conditions back to unreactive N_2, however, does remove N from the biogeochemical cycle (Neumann et al., 2017).

Because these eliminating processes are confined to suboxic and anoxic conditions, they occur in sediments in the generally oxygenated North Sea. In spite of their putative relevance as an ecosystem service, very little is known about N cycling and N transformation rates in the sediment. This is in part due to the complexity created by coupled ammonification-nitrification in which different N processes, such as assimilation and denitrification, interact and affect the NH_4^+ and NO_3^- concentrations in pore waters. To our knowledge, no ammonification rates in the North Sea have been quantified, whereas nitrification rates in permeable sediments were found to be in the same order of magnitude as denitrification rates (<0.1 to ~3.0 mmol m^{-2} d^{-1}, Tab. 1) (Marchant et al., 2016). N loss in the German Bight has been studied by several authors (Deek et al., 2013; Lohse et al., 1993; Marchant et al., 2016; Neubacher et al., 2012; Neumann et al., 2017) showing high spatial, temporal and seasonal variability.

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The main N loss process in the North Sea is denitrification, whereas and anammox plays a minor role (Bale et al., 2014; Marchant et al., 2016). The main drivers of denitrification are organic matter content and permeability of the sediment (Neumann, 2012), and recent studies suggest that permeable sediments account for about 90 % of the total benthic NO_3^- consumption in the German Bight (Neumann et al., 2017).

Quantifying N dynamics based solely on changes in N concentrations provides limited insight into underlying reactions, as only net changes can be observed. Previous authors used different methods for determination of specific N rates. Lohse et al. (1993) used the acetylene block method, core flux incubations and isotope pairing in the early 1990s types to determine denitrification rates in a variety of sediment types (Tab. 1). Deek and co-authors (2013; 2011) investigated N-turnover in the Wadden Sea and in the extended Elbe estuary using core flux incubations and isotope pairing. Marchant et al. (2016) measured denitrification rates in permeable sediments obtained from slurry incubations and percolated sediment cores. More recently, Neumann et al. (2017) used pore-water NO_3^- concentration gradient profiles to determine NO_3^- consumption rates in the German Bight.

Stable isotope techniques offer several approaches to quantify N turnover processes, and ^{15}N tracer studies have been widely used to determine N transformation rates (e.g. nitrification and denitrification) (Brase et al., 2018; Deutsch et al., 2009; Henriksen and Kemp, 1988; Sanders et al., 2018; Wankel et al., 2011). In this study, we use an isotope dilution method that can unravel several N-processes like ammonification, assimilation, nitrification, denitrification, dissimilatory NO_3^- reduction to NH_4^+ (DNRA) and sedimentary NO_3^- consumption / N_2 production within sediments. ^{15}N dilution of NH_4^+ and NO_3^- (Koike and Hattori, 1978; Nishio et al., 2001b) can be used to estimate gross N transformation rates by measuring the isotopic dilution of the substrate and product pools, respectively (Burger and Jackson, 2003; Hart et al., 1994; Ward, 2008). The ^{15}N dilution method accounts for changes in both N pool size and ^{15}N enrichment during a short sampling interval. This method has four main advantages over balancing sediment-water exchanges in other studies: (1) The appearance of ^{15}N in the NH_4^+ pool during the incubation allows an estimate of ammonification rates, (2) the isotopic dilution of NO_3^- tracks nitrification rates, (3) labeling of N_2 for an estimate of N_2 production (Holtappels et al., 2011) and (4) the detection of assimilation rates.

This study is conducted within the project “North Sea Observation and Assessment of Habitats” (NOAH). One important aspect of the project is to investigate the biogeochemical status and functions of the sea floor, especially nitrogen cycling, to gauge the eutrophication mitigation potential in light of continuing high human pressures (https://www.noah-project.de).

In this paper, we investigate internal N rates of ammonification, nitrification and NO_3^- consumption / denitrification at four stations across sediment types (clay/silt, fine sand, coarse sand) in the German Bight (North

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Sea) during late summer (August/September) 2016. To assess the internal sediment N processes and the rates of reactive N release to the water column, we incubated sediment cores amended with $^{15}NH_4^+$ and $^{15}NO_3^-$. We quantify the benthic gross and net N transformation rates and evaluate the environmental controls underlying spatial variabilities. We further evaluate the role of ammonification as a source of reactive nitrogen for primary producers, of nitrification and of denitrification in the Southern North Sea.

2 Material and Methods

2.1 Study site

Sediment samples were taken in the German Bight (Southern North Sea), an area that is strongly influenced by nutrient inputs from large continental rivers. The salinity in the coastal zone of the North Sea ranges between ~30 and 35, and the average flushing time is 33 days (Lenhart and Pohlmann, 1997).

The sampling sites are part of the NOAH (North Sea Assessment of Habitats) assessment scheme (Fig. 1). The sites represent typical sediment types based on statistics of granulometric properties, organic matter content, permeability, and water depth (https://doi.org/10.1594/PANGAEA.846041).

2.2 Sampling and core incubation

The sampling was performed in August and September 2016 during R/V *Heincke* cruise HE-471 in the German Bight (Fig. 1). The water depth at the sites varied between 25.2 m (NOAH-C) to 36.0 m (NOAH-D) (Tab. 2). At each station, the water column was sampled at five depths with a rosette sampler equipped with Niskin bottles, a CTD, and chlorophyll and O_2 sensors. For the nutrient analysis, water samples were filtered thought a 25-mm diameter glass fiber filter (GF/F, Sartorius, 0.7 µm nominal pore size) and frozen immediately at -20 °C.

From each station, sediment multicores equipped with acrylic tubes (PMA) with an inner diameter of 10 cm and a length of 60 cm were recovered and four intact sediment cores from each station (exception: Station NOAH-D, only 3 cores could successfully be retrieved) were incubated in a gas tight batch-incubation setup for 24 hours. Overlying water was stirred with a magnetic stirrer coupled to an external rotating magnet. The water temperature was held constant at *in situ* conditions (~19 °C). Water temperature and oxygen concentration of the overlying water of each sediment core were measured continuously with optodes (PyroScience, Germany.

Two sediment cores (Station NOAH-D 1 core only) were enriched with $^{15}NH_4^+$ (50 at-%, manufacturer), the other two cores were amended with $^{15}NO_3^-$ (50 at-%, manufacturer). NH_4^+ and NO_3^- concentration of the added tracer solution was the same as the bottom water concentrations (Tab. 2).The label addition was calculated aiming for a maximum enrichment of 5.000 ‰ in substrates and products, because higher delta-values influence the accuracy of the mass spectrometer.

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Samples were taken every 6 hours. Upon sampling, incubation water was filtered with a syringe filter (material, manufacturer, 0.45 µm pore size) and frozen in exetainers (11.8 ml, Labco, High Wycombe, UK) at -20 °C for later analyses of nutrients and stable isotope signatures ($\delta^{15}NH_4^+$, $\delta^{15}NO_3^-$). Additional samples for the analyses of dissolved nitrogen (N_2) were taken without filtration, and were preserved in exetainers (5.9 ml, Labco, High Wycombe, UK) containing 2 % of a $ZnCl_2$ solution (1 M). Samples were stored at 4 °C under water until analysis.

2.3 Analyses

Dissolved inorganic nitrogen concentrations

NO_x, NO_2^- and NH_4^+ concentrations of the water column samples were determined in replicate with a continuous flow analyzer (AA3, Seal Analytics, Germany) according to standard colorimetric techniques (NO_x, NO_2: (Grasshoff et al., 1999), NH_4^+: (Kérouel and Aminot, 1997)). NO_3^- concentration was calculated by difference of NO_x and NO_2^-. Based on replicate analyses, measurement precision for NO_x and $NO_2^-$was better than 0.1 µmol L^{-1} and better than 0.2 µmol L^{-1} for NH_4^+.

Water samples from core incubations were analyzed in duplicate for concentration of NH_4^+, NO_2^- and NO_3^- using a multimode microplate reader Infinite F200 Pro and standard colorimetric techniques (Grasshoff et al., 1999) at the ZMT, Bremen. The standard deviations were <1 µmol L^{-1} for NO_3^-, <0.2 µmol L^{-1} for NO_2^- and <0.5 µmol L^{-1} for NH_4^+.

Nitrogen isotope analyses

The nitrogen isotope ratios of NO_3^- were determined via the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). This method is based on the mass spectrometric measurement of isotopic ratios of N_2O produced by the bacterium *Pseudomonas aureofaciens*. Briefly, 20 nmoles of sample NO_3^- were injected in a 20 ml vial containing MilliQ. Two international standards were used (IAEA-NO_3^- $\delta^{15}N$ = +4.7 ‰, USGS-34 $\delta^{15}N$ = -1.8 ‰) for a regression-based correction of isotope values. For further quality assurance, an internal standard was measured with each batch of samples. The standard deviation for $\delta^{15}N$ was better than <0.2 ‰

For ammonium isotope measurements, nitrite was removed by reduction with sulfamic acid (Granger and Sigman, 2009) before NH_4^+ was chemically oxidized to NO_2^- by hypobromite at pH ~12 and then reduced to N_2O using sodium azide (Zhang et al., 2007). 10 nmol of NH_4^+ were injected, and all samples with [NH_4^+] >1 µmol L^{-1} were analyzed. For the calibration of the ammonium isotopes, we used three international standards (IAEA-N1 $\delta^{15}N$ = +0.4 ‰, USGS 25 $\delta^{15}N$ = -30.4 ‰, USGS 26 $\delta^{15}N$ = +53.7 ‰). The standard deviations were better than 1 ‰.

N_2O produced either by the denitrifier method or the chemical conversion of ammonium was analysed with a GasBench II, coupled to an isotope ratio mass spectrometer (Delta Plus XP, Thermo Fisher Scientific).

Membrane inlet mass spectrometry

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N_2 production was measured by a membrane inlet mass spectrometer (MIMS, inProcess Instruments), which quantifies changes in dissolved N_2:Ar ratios (Kana et al., 1994). During the measurements, the water samples were maintained in a temperature-controlled water bath (16 °C). For calibration, we measured 4 salinities, from 0 to 35 after each 10^{th} water sample. We measured the production of ^{28}N, ^{29}N and ^{30}N to quantify the N_2 production. Due to the low labeling percentage, a distinction of anammox and denitrification rates was not possible. The internal precision of the samples was <0.05 % for N_2/A_r analyses.

Sediment samples

The surface sediment samples of the cruises HE 383 (06/07.2012) and HE 447 (06.2015) for NOAH-D were analyzed for total carbon and total nitrogen contents with an elemental analyzer (Carlo Erba NA 1500) via gas chromatography calibrated against acetanilide. The total organic carbon content was analyzed after removal of inorganic carbon using 1 mol L^{-1} hydrochloric acid. The standard deviation of sediment samples was better than 0.6 % for C_{org} and 0.08 % for N determination.

Respiration and transformation rates

Net process rates

The oxygen consumption, net rates of ammonification, nitrification and denitrification were calculated based on concentration changes in the sediment incubations. The respective net process rates were calculated as follows:

$$r_{net} = d(C)*V/d(t)*A \text{ [mmol } m^{-2} d^{-1}] \quad (1)$$

where d(C) is the oxygen, nutrient or the nitrogen (N_2) concentration at the start and at the end of the experiment, V is the volume of the overlying water, d(t) is the incubation time and A is the surface area of the sediment.

Gross rates of ammonification, nitrification and assimilation

Gross rates of ammonification and nitrification (r_{gross}) were calculated based on ^{15}N isotope dilution (Koike and Hattori, 1978; Nishio et al., 2001a), i.e, ammonification rates are calculated based on $^{15}NH_4^+$ additions, nitrification rates are based on $^{15}NO_3^-$ additions:

$$r_{gross} = [\ln(f^{15}N_{end}/f^{15}N_{start})]/(\ln(C_{end}/C_{start})]*(C_{start}-C_{end}/t)*(V/A*\Delta t) \quad (2)$$

where C_{start} is the initial NH_4^+ or NO_3^- concentration, C_{end} is the concentration at time t, and $f^{15}N_{start}$ and $f^{15}N_{end}$ represent ^{15}N atom% excess (Brase et al., 2018), V is the volume of the overlying water and A is the surface area of the sediment. All rates are given in mmol m^{-2} d^{-1}

Based on these calculations, we derived NH_4^+ assimilation as follows:

$$rNH_4^+{}_{ass} = rNH_4^+{}_{gross} - rNH_4^+{}_{net} - rNitr_{gross} \text{ [mmol } m_{-2} d^{-1}] \quad (3)$$

where $rNH_4^+{}_{gross}$ is the gross ammonification rate, $rNH_4^+{}_{net}$ is the net ammonification rate and $rNitr_{gross}$ represents the gross nitrification rate.

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Oxygen penetration depth

The oxygen penetration depth in the sediment of each station were measured using microoptodes (50 µm tip size; Presens, Germany). The optodes were moved vertically into the sediment with a micromanipulator (PyroScience, Germany), in steps of 100-200 µm, depending on the oxygen concentration. Three O_2 profiles were measured in one sediment core of each station.

3 Results

3.1 DIN concentrations in the water column

NO_3^- concentrations in the water column were low at all stations (0.1 µmol L^{-1} or lower, Tab. 3). NO_2^- concentrations were low at the permeable sediment stations NOAH-A, NOAH-D and NOAH-E with (≤0.1 µmol L^{-1} below the thermocline). At the impermeable sediment station (NOAH-C), NO_2^- concentration was 0.7 µmol L^{-1}. NOAH-C had also highest NH_4^+ concentrations with 2.0 ±0.2 µmol L^{-1}, whereas NH_4^+ concentrations at the permeable sediment stations were lower (0.3 to 0.8 µmol L^{-1}).

3.2 Benthic oxygen fluxes

The O_2-fluxes from the water column into the sediment (here: negative fluxes) vary between individual cores and sampling station. The lowest oxygen flux was determined at the permeable sediment station NOAH-A with -10.0 mmol m^{-2} d^{-1} (Fig. 2), the highest oxygen flux was measured at the impermeable sediment station NOAH-C with -53 mmol m^{-2} d^{-1}. The semi-permeable sediment station NOAH-D had an oxygen flux of -18.5 to -30.6 mmol m^{-2} d^{-1}.

3.3 Nitrogen transformation rates

Ammonification

The highest net and gross ammonification rates were measured in the impermeable, organic-rich sediment at station NOAH-C (6.8 ±2.3 mmol m^{-2} d^{-1} and 8.3 ±2.3 mmol m^2 d^{-1} for net and gross ammonification, respectively; Fig. 3 and Fig. 5).

The lowest ammonification rates were measured in the semi-impermeable sediment at station NOAH-D ($rNH_4^+{}_{net}$ =0.5 mmol m^{-2} d^{-1}; $rNH_4^+{}_{gross}$ = 2.3 ±0.4 mmol m^{-2} d^{-1}). The permeable sediment stations NOAH-A and NOAH-E show ammonification rates of 2.4 ±0.9 mmol m^{-2} d^{-1} and 3.6 ±1.3 mmol m^{-2} d^{-1} (net and gross, respectively). Net and gross ammonification rates are closely correlated (r^2=0.96; data not shown).

Assimilation

The NH_4^+ assimilation differed between stations, and ranged from <0.1 to 0.6 mmol m^{-2} d^{-1} (Fig. 3, Fig. 5). Rates were lowest at the impermeable sediment station NOAH-C, and highest in the moderately permeable sediment at station NOAH-D.

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Nitrification

Net and gross nitrification rates varied significantly between stations. Net nitrification was highest at station NOAH-C (impermeable sediment) and at station NOAH-D (semi-permeable sediment) with 0.9 ±0.7 and 1.0 ±0.3 mmol m^{-2} d^{-1}, respectively (Fig. 3, Fig. 5). Gross nitrification was highest at NOAH-D (1.5 ±0.2 mmol m^{-2} d^{-1}). The lowest net (0.3 ±0.2 mmol m^{-2} d^{-1}) and gross (0.7 ±0.4 mmol m^{-2} d^{-1}) rates were observed in the permeable sediment at station NOAH-A. Net and gross nitrification rates are closely correlated (r^2=0.75; Fig. 4).

Nitrate consumption

NO_3^- consumption rates did not differ significantly between the stations and ranged from <0.1 to 0.8 mmol m^{-2} d^{-1} (Fig. 3, Fig. 5).

Denitrification

The denitrification rates of ranged from 0.4 to 2.4 mmol m^{-2} d^{-1} (Fig. 3, Fig. 5).The N_2 production rates in the sediment of the stations did not vary significantly between stations. We found no indication of dissimilatory nitrogen reduction to NH_4^+ (DNRA) in the sediment.

Sedimentary organic matter descriptions

The data show a clear correlation between sediment type and organic carbon and nitrogen content. Clay and silty sediment (NOAH-C) have the highest organic carbon (0.73 %) and nitrogen (0.10 %) concentration (Tab. 2). Medium sand stations (NOAH-A and NOAH-E) show the lowest C_{org} (0.03 to 0.04 %) and total nitrogen (<0.01 to 0.01 %) concentrations.

4 Discussion

4.1 Magnitude and relevance of ammonification

A principal goal of this study was to assess for the first time the role of ammonification in the nitrogen cycle of the German Bight. Ammonification releases NH_4^+ during the decomposition of organic matter and resupplies the water-column inventory of reactive nitrogen. The quantification of gross ammonification rates is challenging, because ammonium is readily assimilated by primary producers or is rapidly nitrified, so that ammonium concentrations are often very low.

To the best of our knowledge, this study represents the first assessment of ammonification rates across typical sediment types of the North Sea, covering a large range from 2.3 to 8.3 mmol m^{-2} d^{-1}: Rates were mainly governed by sediment texture and organic matter content. The impermeable muddy sediment at station NOAH-C with high C_{org} and TN content (0.73 % and 0.10 %, respectively, Tab. 2) had highest gross and net ammonification rates. This is line with other studies showing enhanced rates in muddy coastal sediments (Caffrey, 1995; Mackin and Swider, 1989; Nichols and Thompson, 1985; Sumi and Koike, 1990).

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The sandy sediments at sites NOAH-A, NOAH-D and NOAH-E exhibited significantly lower gross ammonification rates. This reflects the lower sediment organic matter content in these sandy sediments expressed in C_{org} (0.03 – 0.04 %) and N (0.01 – <0.01 %) concentrations (Caffrey, 1995), Tab. 2).

It is striking, though, that gross ammonification in the sandy sediment at station NOAH-E was almost twice that of the other sandy stations NOAH-A and NOAH-D. There are two possible explanations for this enhanced ammonium production, either (1) effects bioirrigation and bioturbation or (2) enhanced supply of organic matter to the sediment surface. Station NOAH-E is located inside a pockmark field that had developed relatively recently, between July and November 2015 (Krämer et al., 2017). Our assessment of OC and N content is based on samples that were taken prior to the pockmark formation (Krämer et al., 2017) (https://doi.org/10.1594/PANGAEA.883199). The sediment samples were taken from the depression inside an individual pockmark, which was about ~0.2 deeper than the surrounding sediment (Krämer et al., 2017). It is possible that organic matter from the water column accumulated in these transient structures, and that the organic carbon and nitrogen content thus was elevated. A transient change in surface sediment composition, which is not captured by our compositional data, may thus have caused the enhanced ammonification rate.

An alternative explanation is an elevation of ammonium fluxes from the sediment due to sediment reworking. In the sediment incubations, we found a high benthic activity of *Spiophanes bombyx* and *Phoronis sp.*. Both benthic organisms can increase the nutrient fluxes from the sediment to the bottom water, the oxygen penetration depth, and, in turn, organic matter degradation in the oxic zone (Aller and Aller, 1998; Caffrey, 1995; Meysman et al., 2006; van Amstel et al., 2007).

Under completely oxic conditions, the ratio of NH_4^+ release and O_2 consumption should approximate Redfield ratios of about 1:8.6 (Thibodeau et al., 2010). Similar ratios were observed at the semi-permeable station NOAH-D and in 2 of 4 sediment cores of the permeable station NOAH-A (Fig. 2), suggesting that in these cores most of the organic matter was degraded under oxic conditions. At some sites (NOAH-C, NOAH-E), however, the $N:O_2$ ratio was much higher (1:7 to 1:2) than the Redfield ratio. Higher $N:O_2$ ratios may be partly related to the quality of the organic matter: (Hargrave et al., 1993) measured also higher ammonium fluxes relative to oxygen consumption in North American east coast sediments. They speculated that remineralisation of organic nitrogen is faster than that of organic carbon.

We presume that the enhanced production of ammonium relative to O_2 consumption reflects the importance of anoxic ammonium generation, i.e., during methanogenesis or sulfate reduction (Jorgensen, 1982; Jorgensen et al., 1990; Kristensen et al., 2000; Miyajima et al., 1997). This is especially evident at station NOAH-C, where oxygen

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penetration depth in the impermeable, organic-rich sediment is lowest, and where increasing NH_4^+ concentrations with depth indicate decomposition or organic matter in the absence of free oxygen (Hartmann et al., 1973).

Sedimentary ammonium production and fluxes of ammonium into the water column contribute to water column DIN concentrations. To assess the contribution of benthic ammonification to the water column N inventory, we compared gross ammonification with the inventory of DIN below the thermocline. Assuming steady state, we find a rapid turnover of sediment-derived DIN, in the order of ~<1-3 days (Tab. 3). This implies that even below the thermocline, DIN is rapidly assimilated by phytoplankton. Previous publications showed that primary production below the thermocline can amount to ~ 37 % of total primary production in the North Sea (van Leeuwen et al., 2013; Weston et al., 2005). Assuming Redfield stoichiometry, our measured benthic NH_4^+ fluxes can support a primary production of about 2.3 to 8.3 mmol m^{-2} d^{-1} or 0.2 – 0.6 g C m^{-2} day^{-1}. This is in the lower range of previously observed and modeled primary production rates in the North Sea during summer (Rick et al., 2006; van Leeuwen et al., 2013; Weston et al., 2005). In total, though, we estimate that benthic N fluxes support between 13 % (at a water depth of 38 m) and 61 % at 10 m depth (Tab. 3) of primary production. This dependence of relative sediment contribution on water depth has been observed previously for respiration processes (Heip et al., 1995). Our data also match the calculation of Blackburn and Henriksen (1983) for Danish sediments, where N fluxes could support 30-83 % of the nitrogen requirement of the planktonic primary producers (Blackburn and Henriksen, 1983).

In summary, our results show a rapid ammonification of organic matter and an intense benthic-pelagic coupling during summer in the German Bight.

4.2 Ammonia and nitrite oxidation (nitrification)

Based on the interpolation of gross rates of ammonification, it is evident that ammonification contributes significantly to nutrient regeneration in the German Bight. However, there is a clear difference between gross and net ammonification rates, and beside ammonium assimilation, nitrification is an important ammonium sink. Nitrification produces NO_3^-, which represents the largest DIN pool in the water column of the North Sea and is the substrate for denitrification, and thus the link to an ultimate removal of fixed nitrogen from the water column.

We observed gross nitrification rates at all four stations ranging from 0.7 ±0.3 mmol m^{-2} d^{-1} at the sandy station NOAH-A over 1.4 ±0.7 mmol m^{-2} d^{-1} in the impermeable sediment at station NOAH-C to 1.5 mmol m^{-2} d^{-1} in the moderately permeable sediment at NOAH-D (Fig. 3, Fig. 4). Gross nitrification at the impermeable sediment station NOAH-C accounted for around 16.2 % (±9.9 %), around 64.5 % (±9.1 %) at the semi-permeable station (NOAH-D) and around 25.6 % (±11.4 %) at the permeable sediment stations of total DIN flux to the bottom water. Overall, nitrification is in the same range as reported by Marchant et al. (2016) in sandy sediment near Helgoland

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(0.2 to 3.0 mmol m^{-2} d^{-1}; Tab. 1). We observed the highest net and gross release of NO_3^- by nitrification at the semi-permeable station NOAH-D, indicating that beside sediment texture, other processes affect the nitrification rates (Marchant, 2014).

Nitrification rates are relatively independent of permeability, in contrast to ammonification. Instead, they were negatively correlated (r^2 = 0.83) with oxygen penetration depth. The reactivity of organic matter and the bottom water oxygenation affect the OPD and the nitrate gradient across the sediment-water-interface. High organic matter reactivity will also lead to high diffusive nitrate fluxes (Alkhatib et al., 2012).

Nitrification rates are lowest at Station NOAH-A. Here, oxygen penetration depth is highest, and the sediment has low organic matter content (Tab. 2), which obviously limits nitrification rates.

While individual correlations between C_{org} or TN and nitrification are relatively weak, this indicates that organic matter turnover indirectly controls nitrification rates. Generally, organic matter deposition in the sediment supports higher ammonification rates, which in turn enhance nitrification under oxic conditions (Henriksen and Kemp, 1988; Rysgaard et al., 1996). Consequently, nitrification is affected by the NH_4^+ pool in the sediment, temperature, salinity and O_2 (Henriksen and Kemp, 1988; Vouvé et al., 2000; Wankel et al., 2011).

Given these constraints, it is surprising that gross ammonification and gross nitrification rates are not correlated (r^2 = 0.13). We suggest that this expresses a rate limitation of nitrifying bacteria. In sediments with high ammonification rates and ammonium concentrations, ammonium oxidation is the limiting step for further production of nitrate. Nitrifiers are slow-growing, with ammonium oxidation rates far below ammonification rates (Kadlec and Wallace, 2009; Myers, 1975; Vymazal, 2010; Vymazal, 2007). Marchant et al. (2016) suggest that other factors can additionally affect the rate of ammonia oxidation, such as the surface area available for microbial colonization (Belser, 1979) or oxygen availability (Henriksen et al., 1993).

Overall, the gross NO_3^- production (0.7 to 1.5 mmol m^{-2} d^{-1}) was small relative to ammonification rates (2.3 to 8.3 mmol m^{-2} d^{-1}). We find that nitrification is governed by a complex interplay of variables (ammonification rate, sediment texture, permeability, organic matter availability and O_2 concentration) determine sediment reactivity as reflected by oxygen penetration depth.

4.3 Denitrification

Denitrification, the reduction of NO_3^- to gaseous N_2, reduces the pool of bioavailable N, and is therefore of great interest in eutrophic coastal areas such as the southern North Sea. In our study, the measured denitrification rates ranged from 0.4 to 2.4 mmol N m^{-2} d^{-1} (Fig. 3). This estimate of N_2 production is in line with other data from sites in the German Bight estimated by either the isotope pairing technique or, as in our study, using isotope dilution

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(Deek et al., 2013; Marchant et al., 2016) (Tab. 1). Our study covers more diverse sediment types, and thus allows for an improved extrapolation of rates to the total German Bight area.

Variations in denitrification can be attributed to seasonal variations in oxygen supply, changing bottom water NO_3^- concentration and organic carbon content in the sediment (Deek et al., 2013). In our study, the bottom water nitrate concentration is too low (<0.5 to 4.5 µmol L^{-1}) to sustain the observed denitrification rates, and thus the major nitrate source fueling the observed denitrification must be coupled nitrification-denitrification fueled by mineralization of sedimentary organic material. This is reflected in a weak, but significant, correlation between gross nitrification and denitrification rates (r^2 = 0.35). In our study, we find that this coupled nitrification-denitrification has a strong influence on the total N flux. Denitrification accounts to 7.2 % (±1.3 %) of the total supply of mineralized N (i.e., gross ammonification) at the impermeable sediment station NOAH-C, ~29.1 % (±0.9 %) at the semi-permeable sediment station NOAH-D and ~17.1 % (±2.2 %) at permeable sediment stations (NOAH-A, NOAH-E). In permeable sediments, only a part of the freshly produced nitrate escaped to the water column, whereas a large part was denitrified again in sediments. Denitrification removed 67 % of internally produced NO_3^- in permeable sediments, ~45 % in moderately permeable sediment and ~37 % in impermeable sediment, respectively.

Our study covers diverse sediment types across the German Bight, but is based on core incubations and therefore potentially underestimates advective processes. In a recent study by Neumann et al. (2017), the authors used NO_3^- pore water profiles to calculate the NO_3^- consumption rates across a similar range of North Sea sediments. They extrapolated their nitrate consumption rates to the entire area of the German Bight based on a permeability classification of sediments. They propose that ~24 % of sediments in the southern North Sea (German Bight) are impermeable sediments (12,200 km^{-2}), ~39 % are moderately permeable sediments (19,600 km^{-2}) and ~37 % (18,800 km^{-2}) are permeable sediments. They estimated that permeable sediment were the most efficient NO_3^- sink accounting for up to 90 % of the total benthic NO_3^- consumption. In our assessment, which might better represents the role of nitrification, we arrive at a somewhat lower contribution of ~80 % of total denitrification occurring in moderately permeable and permeable sediments. Based solely on our data, we estimate a total nitrogen removal of ~894 t N d^{-1} in our study area. This daily N_2 production is close to the total N input (~1.000 t N d^{-1}) by the main rivers Maas, Rhine, North-Sea Canal, Ems, Weser and Elbe (Pätsch and Lenhart, 2004), and, as such, underscores the role of coastal sediments to counteract the eutrophication in the North Sea.

Our assessment, however, does not account for advective fluxes. Based on the same data set of permeability for classification of different sediment types that Neumann et al (2017) used, we merge our dataset with the assumptions of Neumann et al. (in preparation) to arrive at an improved estimate of sediment denitrification,

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including nitrification as a source, but also accounting for the increasing importance of advection in permeable sediments.

For impermeable sediments, advection can be neglected. The ratio of diffusive to adjective processes in moderately permeable sediments is close to 1, which suggest that, if both processes act simultaneously, our diffusion-driven estimate can be doubled. For permeable sediments, advection is far more important. Neumann et al. (2017) suggest that advective fluxes exceed diffusive fluxes by a factor of up to 250. If this holds true, the measurements by far underestimate N-cycling in permeable sediments. However, employing a factor of 250 to correct the observed denitrification rates obviously exaggerates denitrification estimates, which even exceed the simultaneously measured in-situ respiration rates of Ahmerkamp et al. (2015), indicating the limiting role of organic matter supply (see below). A further reason for this overestimation is the fact that the solute transport in our core incubations was not limited solely to molecular diffusion, but was substantially enhanced by faunal activity.

In the following, we aim to set an upper limit of denitrification based on primary production since denitrification requires organic carbon, which is ultimately provided by pelagic primary production. For the freshwater influenced regions of the German Bight, Capuzzo et al. (2018) assume a C fixation of 1.05 g C m^{-2} d^{-1}. For an estimate of the maximum denitrification rate we assume that 10 % of the fixed C is processed in the sediment (Heip et al., 1995) and that all carbon is remineralized in the sediment by denitrification. Based on the stoichiometry of denitrification (~12 g / mol C, ~14 g / mol N), this translates to [1.05 g * 10 % / 12 C * 14N =] 0.123 mg N that is removed per m^{-2} and day, or 9 mmol N m^{-2} d^{-1}. This sets an absolute upper limit to the additional denitrification that could occur in permeable sediments if all benthic C were remineralized by denitrification. Based on annual nitrate budgets, Hydes et al. (1999) and van Beusekom et al. (1999) derived average denitrification rates of 0.7 mmol N m^{-2} d^{-1}. These rates, based on annual budgets, are somewhat lower than our incubation-based summer estimates in the range of 1.1 to 1.4 mmol N m^{-1} d^{-1} (Tab. 1).

Seitzinger and Giblin (1996) linked benthic respiration and denitrification directly to the pelagic primary production. By employing their formulas and using the primary production rates by Capuzzo et al. (2018), the annual average of the sediment oxygen demand would be 14.3 mmol O_2 m^{-2} d^{-1} (1.05 g C d^{-1} m^{-2} = 87.5 mmol C d^{-1} m^{-2}), which corresponds to a benthic denitrification rate of 3.3 mmol N m^{-2} d^{-1}. Since the annual average of actually measured oxygen fluxes are close to this estimate (15.4 ± 12.9 mmol O_2 m^{-2} d^{-1}, N=175) (Neumann et al., in preparation), we are confident that our denitrification estimates of up to 1.4 mmol N m^{-2} d^{-1} are reasonable.

5 Summary and concluding remarks

We evaluated a range of sedimentary nitrogen turnover pathways and found that ammonification in sediments is an important N-source for primary production in the water column of the southeastern North Sea during summer.

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Depending on water depth, 13-61 % of the estimated water column primary production is fueled by sedimentary N release. Assimilation, and nitrification act as the main sinks of NH_4^+ mineralized from sedimentary organic matter. Ultimately, the main factors governing nitrification are organic matter content / ammonification and oxygen penetration depth in the sediment. The share of newly nitrified NO_3^- reduced to N_2 amounts to two thirds of NO_3^- in permeable sediments, to nearly one half in moderately permeable sediment, and to one third in impermeable sediments. We further showed that moderately permeable and permeable sediments account for up to ~80 % of the total benthic N_2 production (~894 t N d^{-1}) in the southern North Sea (German Bight) during summer, and neutralize nearly the total N input by main rivers (e.g. Elbe, Ems, Rhine, Weser) flowing into the southern North Sea (~1.000 t N d^{-1}). Thus impermeable sediments act as an important N source for primary producers, whereas moderately permeable and permeable sediments comprise a main reactive N sink counteracting eutrophication in the North Sea. Seasonal and spatial variabilities, especially from nearshore to offshore, should be evaluated in future studies.

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Table 1: Rates of nitrification, dissimilatory nitrogen reduction to ammonia (DNRA), anaerobic ammonia oxidation (anammox) and denitrification (DNIT) (in µmol N m^{-2} d^{-1}) in the North Sea of other published data. Abbreviation of methods: SIDM - sediment isotope dilution method; MABT - modified acetylene block technique; SSI - sediment slurry incubations, PWMI – pore-water mean fitting, IPT - isotope-pairing technique.

Location	Nitrification	DNRA	Anammox	DNIT rate / NO_3^- uptake	Sediment type	C_{org}	C:N	Sampling time	Method	Reference
	[µmol m^{-2} d^{-1}]				[-]	[% dry wt]	[atom]		[-]	
German Bight (North Sea)	728 ±444	N.D.	N.D.	1095 ±596*	medium sand	0.03	<0.01	08./09.2016	SIDM	this study
	1,090 ±312	N.D.	N.D.	1371 ±850*		0.04	0.01			
	1,493 ±211	N.D.	N.D.	1350 ±982*	Fine sand	0.21	0.03			
	1,233 ±978	N.D.	N.D.	1198 ±427*	clay/silt	0.73	0.10			
Dutch Coast	N.D.	N.D.	0.0	N.D.	fine sand	0.03	N.D.	11.2010	SSI	Bale et al., 2014
			0.2					02.2011		
			1.3					05.2011		
			0.6					08.2011		
Oyster Ground	N.D.	N.D.	0.0	N.D.	muddy sand / clay / silt	0.30	N.D.	11.2010		
			2.3					02.2011		
			10.4					05.2011		
			12.8					08.2011		
North Dogger	N.D.	N.D.	0.0	N.D.	fine sand	0.03	N.D.	11.2010		
			0.8					02.2011		
			0.0					05.2011		
			1.1					08.2011		
Elbe Estuary / coastal zones	N.D.	N.D.	N.D.	771*	coarse sand	0.6	6.0	03.2009	IPT	Deek et al., 2013
				1215*		0.1	N.D.			
				3200*		0.1				
				864*		0.6	6.0	09.2009		
				1425*		0.2	N.D.			
				47*		0.1				
				140*		0.2				
Oyster Ground	288 ±144	N.D.	N.D.	12.0*	muddy sand	0.12	6.0	08.1991	MABT	Lohse et al., 1993
	192 ±96			19.2*				02.1992		
Weiss Bank	216			21.6*		0.16	8.0	08.1991		
	120 ±120			16.8*				02.1992		
Tail End	432 ±168			2.4*	fine sand	0.16	5.3	08.1991		
	264 ±120			0*				02.1992		
Esbjiberg	408 ±216			9.6*		0.06	6.0	08.1991		
	168 ±168			91.2*				02.1992		
Helgoland	0			45.6*	silt	1.28	8.5	08.1991		
	216 ±1220			196.8*				02.1992		
Elbe Rinne	264 ±72			4.8*	muddy sand	0.46	9.2	08.1991		
	288 ±96			31.2*				02.1992		
Frisian Front	624 ±288			16.8*		0.46	9.2	08.1991		
	192 ±72			24.0*				02.1992		
Sylt	81.6 ±64.8	N.D.	N.D.	372 ±132*	coarse sand	N.D.	N.D.	06.1993	IPT, SIDM	Jensen et al., 1996
	11 ±2			44.5 ±13.5*				04.1994		
	3.8 ±1.6			17 ±4*	fine sand			04.1994		
	1,116 ±924			75 ±39*	muddy sand			03.1993		
	19.5 ±9.5			103.5 ±17.5*				04.1994		
Helgoland	1,150 ±700	20 ±5	N.D.	870 ±100*	fine sand	N.D.	N.D.	05.2012	SIDM	Marchant et al., 2016
	210 ±50	250 ±50		2,280 ±300*	medium sand					
	2,980 ±420	110 ±60		520 ±30*	coarse sand					
Sean Gras	N.D.	N.D.	24.0	48*	medium sand	0.05	8.1	04.2007	IPT	Neubacher et al., 2011
			24.0	72*		0.06	7.4	05.2007		
			0	120*		0.10	8.5	09.2007		
			48.0	144*		0.05	6.6	10.2007		
			0	24*		N.D.	N.D.	04.2008		
Oyster Ground			24	288*	muddy sand	0.28	10.2	02.2007		
			24	120*		0.22	9.0	04.2007		
			24	120*		0.20	8.4	05.2007		
			120	408*		0.22	9.2	09.2007		
			144	504*		0.23	9.4	10.2007		
			48	144*		0.27	8.7	04.2008		
North Dogger			0	24*	muddy sand	0.45	10.2	02.2007		
			0	96*		0.45	9.4	04.2007		
			24	168*		0.42	9.7	05.2007		
			48	288*		0.46	9.7	09.2007		
			48	264*		0.38	9.6	10.2007		
German Bight / Dogger Bank	N.D.	N.D.	N.D.	20.5 ±4.5**	mud	0.37 ±0.02	N.D.	05.2009	PWMF	Neumann et al., 2017
				28.5 ±23.5**		0.16 ±0.12		02.2010		
				8 ±8**	muddy sand	0.13 ±0.10		05.2009		
				12.5 ±12.5**		0.10 ±0.08		02.2010		
				59.5 ±25.5**	sand	0.16 ±0.13		05.2009		
				99 ±35.0**		0.02		02.2010		

N.D. – not determined
* Denitrification
** NO_3^- uptake

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Table 2: Characteristics of bottom water and sediment characteristics of the sampled stations in the North Sea (https://doi.org/10.1594/PANGAEA.846041). C_{org} means organic carbon content and TN means total nitrogen content of the surface sediment.

Location	Depth	Sediment core / Chamber	Method	Sediment type	C_{org}	TN	Porosity	Permeability	Temp.	Salinity	OPD	Bottom water concentration		
												NH_4^+	NO_2^-	NO_3^-
[-]	[m]	[-]			[%]		[-]	[m²]	[°C]	[PSU]	[mm]	µmol L⁻¹		
NOAH-A	31.0	1	*ex-situ*	medium sand	0.03 *	≤0.01*	0.37	$1.7*10^{-10}$	19.1	33.7	>15	0.5	0.4	0.9
		2										1.5	0.1	0.8
		3										1.8	0.0	2.4
		4										1.2	0.1	1.9
NOAH-C	25.4	1	*ex-situ*	clay/silt	0.73	0.10	0.56	$1*10^{-15}$	19.1	32.5	3.6	4.3	0.1	1.9
		2										2.3	0.1	1.4
		3										7.1	0.2	2.9
NOAH-D	38.0	1	*ex-situ*	fine sand	0.21	0.03	0.43	$1.4*10^{-13}$	18.9	33.0	2.4	2.2	0.1	1.2
		2										1.7	0.0	0.7
		3										2.5	0.1	0.6
NOAH-E	28.4	1	*ex-situ*	medium sand	0.04	0.01	0.29	$8.8*10^{-12}$	18.7	32.4	4.2	3.3	0.5	2.1
		2										9.6	0.7	1.0
		3										3.6	1.5	4.5
		4										2.9	1.2	<0.5

* estimated

Table 3: Rates of NH_4^+ assimilation, benthic net NO_3^- and benthic net NH_4^+ fluxes per area, water depth below thermocline and concentration of dissolved inorganic nitrogen (DIN) in the thermocline. Bottom water concentration of nitrate ($_cNO_3^-$), nitrite ($_cNO_2^-$) and ammonium ($_cNH_4^+$). The concentration of DIN per area was calculated by the multiplication of the water depth below the thermocline with the concentration of DIN. Turnover rates of nitrogen were calculated by the division of DIN per area with the rates of $NH_4^+{}_{net}$, $NO_3^-{}_{net}$ and $NH_4^+{}_{ass}$ and the effect of sedimentary N release on the reactive nitrogen available for primary production in the water column.

Station	$rNH_4^+{}_{net} + rNO_3^-{}_{net} + rNH_4^+{}_{ass}$	Water depth below thermocline	cNO_3^-	cNO_2^-	cNH_4^+	DIN per area	N turnover	sedimentary N support for primary production
[-]	[mmol m^{-2} d^{-1}]	[m]	[µmol L^{-1}]			[mmol m^{-2}]	[days]	[%]
NOAH-A	2.0 ±0.6	29.5	0.1	<0.1	0.6 ±0.2	20.7	0.7	17.3
NOAH-C	7.7 ±3.0	10.0	<0.1	0.7	2.0 ±0.2	30.0	3.0	61.2
NOAH-D	1.2 ±0.1	38.0	0.1 ±0.1	0.1	0.8 ±0.6	26.6	0.7	12.8
NOAH-E	4.1 ±0.9	10.0	<0.1	<0.1	0.3 ±0.1	3.0	0.7	35.2

Table 4: Sediment permeability classes with the area in the German Bight and rates of NO_3^- consumption and N_2 production in the sediment. Estimated NO_3^- consumption rates from Neumann et al. (2017).

Sediment type	Area	NO_3^- consumption	N_2 production
[-]	[km²]	[mol d^{-1}]	
Impermepable $k < 3*10^{-13}$ m²	12,200	$0.4*10^7$ ±$0.2*10^7$	$0.7*10^7$ ±$0.3*10^7$
Mod. permeable	19,600	$1.4*10^7$ ±$0.2*10^7$	$1.3*10^7$ ±$1.0*10^7$
Permeable $k > 3*10^{-12}$ m²	18,800	$0.6*10^7$ ±$0.4*10^7$	$1.1*10^7$ ±$0.6*10^7$
Weighted average total	50,600	$2.0*10^7$ ±$0.8*10^7$	$3.1*10^7$ ±$2.0*10^7$

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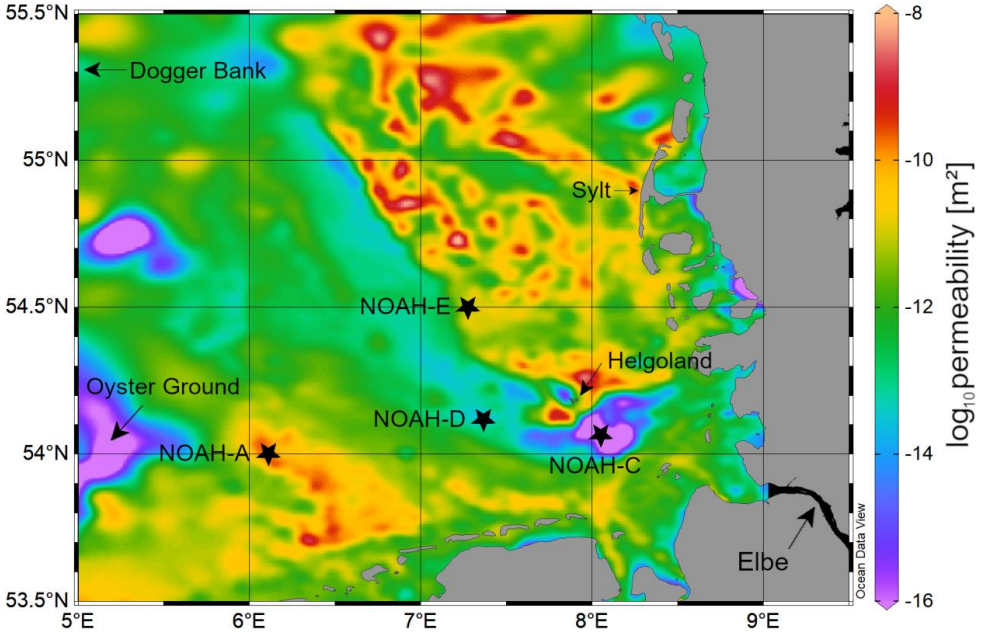

Figure 1: Map showing the sampling stations NOAH-A, NOAH-C, NOAH-D and NOAH-E in the German Bight in the North Sea. Colored areas show the spatial variability of surface sediment permeability (https://doi.org/10.1594/PANGAEA.872712).

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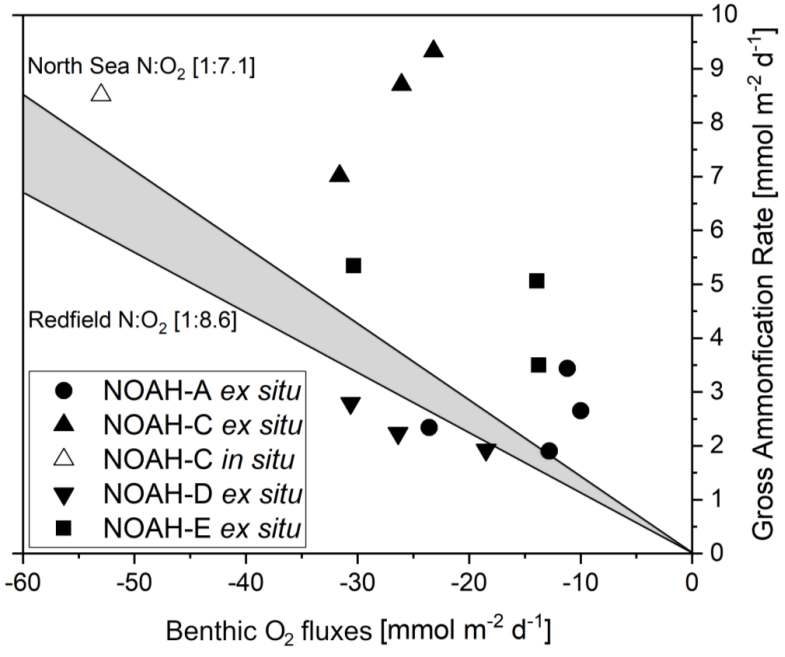

Figure 2: Benthic O_2 fluxes and gross ammonification rates of the sampled stations. The lines show the Redfield ratio of oxygen and nitrogen (N:O_2 1:8.625) (Redfield, 1958) and of the oxygen and nitrogen ratio determined by the C/N ratio in the North Sea (N:O_2 1:7.1).

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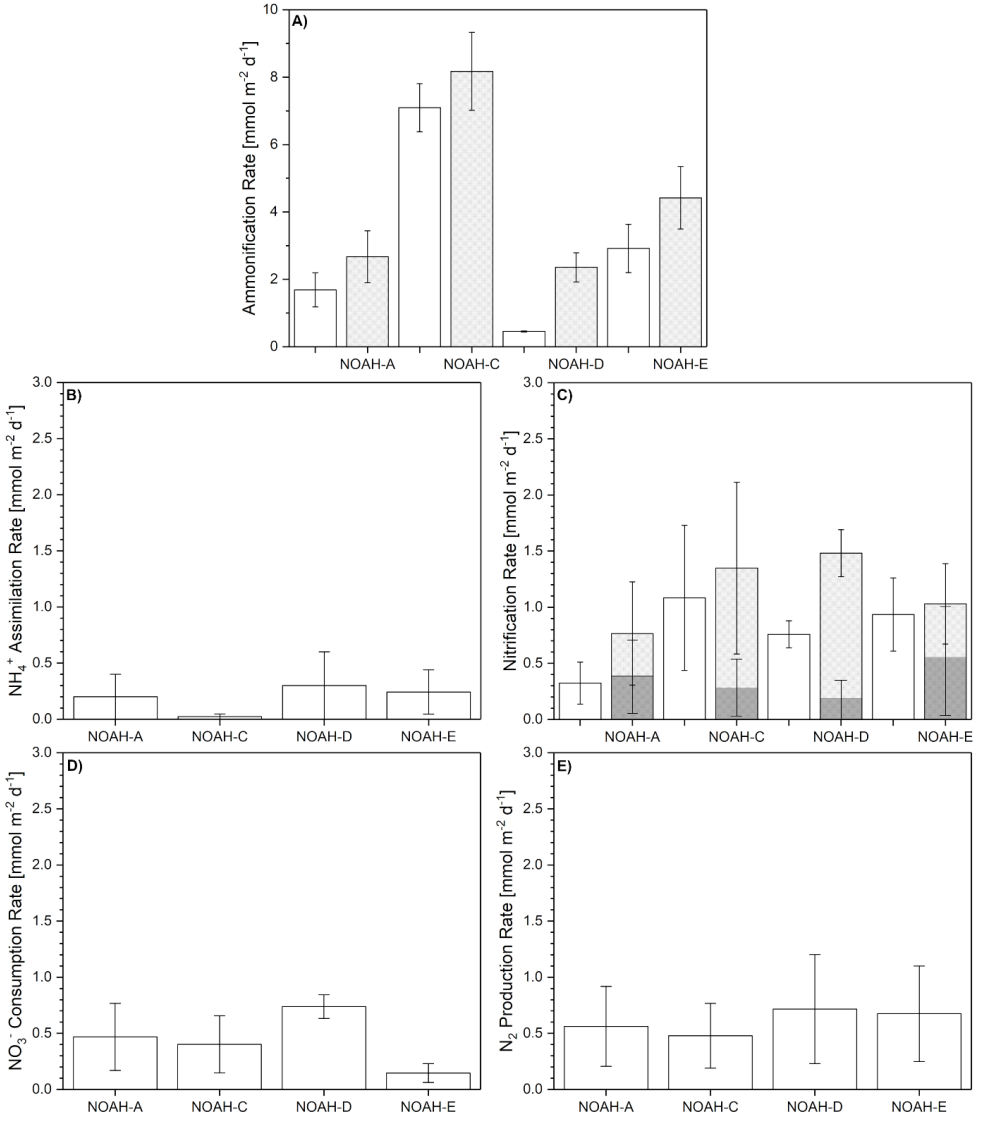

Figure 3: Benthic N-transformation rates (in mmol m^{-2} d^{-1}) of gross (grey) and net (white) ammonification (A), assimilation (B), nitrification, where white bars are net nitrification, light grey colored bars are complete gross nitrification (bottom water and sediment) and dark grey colored bars show sedimentary nitrification (C), nitrate consumption (D) and N_2 production rates (E) of the stations NOAH-A (permeable sediment), NOAH-C (impermeable sediment), NOAH-D (moderately permeable sediment) and NOAH-E (permeable sediment).

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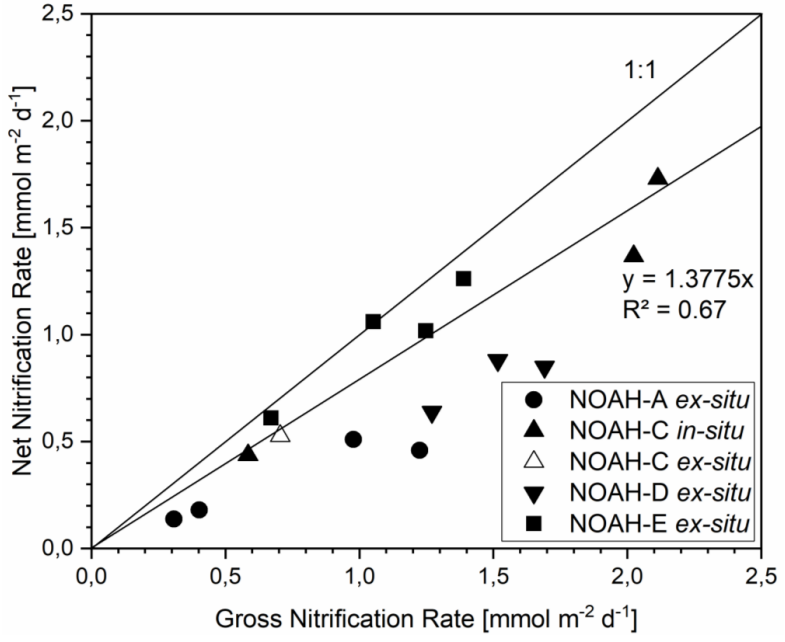

Figure 4: Correlation of gross and net nitrification rates. The lines shows the 1:1 ratio and the slope of the samples.

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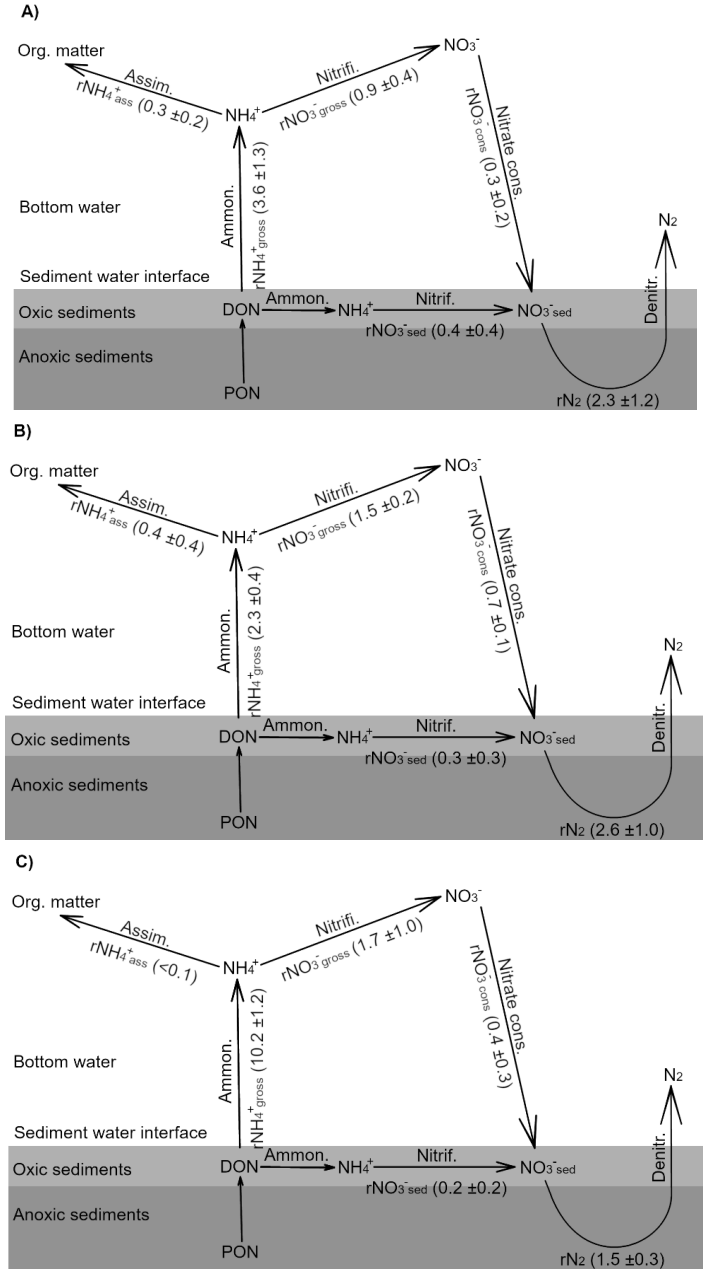

Figure 5: Benthic N-transformation rates of ammonification (ammon.), assimilation (assim.), nitrification (nitri.), nitrate consumption (nitrate cons.) and N_2 production rates (denitr.) in the southern North Sea (German Bight) in mol N d^{-1}. They values given in (A), (B) and (C) multiply with 10^7. PON means particulate organic nitrogen and DON is dissolved organic nitrogen. (A) shows the N-transformation rates in permeable sediments (k > 3*10^{-12} m^2), (B) in moderately permeable sediments (k =3*10^{-12} to 3*10^{-13} m^2) and (C) in impermeable (k < 3*10^{-13} m^2) sediments.