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. We incubated sediment cores from four representative locations in the German Bight (permeable, semi-permeable and impermeable sediments) with labeled nitrate and ammonium to calculate benthic fluxes of nitrate and ammonium and gross rates of ammonification and nitrification. Ammonium fluxes generally suggest oxic degradation of organic matter, but elevated fluxes at one sampling site point towards the importance of bio-irrigation or short-term accumulation of organic matter. Sedimentary fluxes of dissolved inorganic nitrogen are an important source for primary producers in the water column, supporting ~7 to 59 % of the average annual primary production, depending on water depth.

We find that ammonification and oxygen penetration depth are the main drivers of sedimentary nitrification, but this nitrification is closely linked to denitrification. 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 ~68 % of the total benthic N_2 production rates, which, based solely on our data, amounts to ~1030 t N d^{-1} in the southern North Sea. Thus, we conclude that semi-permeable and permeable sediments are the main sinks of reactive N, counteracting eutrophication in the southern North Sea (German Bight).

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 possible decrease of seagrass and massive blooms of opportunistic macroalgae were attributed to eutrophication (e.g. Cadée and Hegemann, 2002). 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). Reduction of reactive nitrogen 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 only occur in sediments in the generally oxygenated North Sea. Due to its putative relevance as an ecosystem service, denitrification has been subject to many studies, but ammonification as a source of N to primary production so far received much less attention. 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 (e.g. Deek et al., 2013) showing high spatial, temporal and seasonal variability.

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 (Deek et al., 2013; Deek et al., 2011) investigated N-turnover in the Wadden Sea and in the extended Elbe estuary using core flux incubations and isotope pairing. Marchant et al. (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; Sanders et al., 2018). The isotope dilution method can be used to distinguish between net and gross rates and so help to unravel several N-processes such as ammonification and assimilation or nitrification and denitrification. ^{15}N dilution - (Koike and Hattori, 1978; Nishio et al., 2001) can be used to estimate gross N transformation rates by measuring the isotopic dilution of the substrate and product pools, respectively (e.g. Burger and Jackson, 2003). In this study, we used the isotope dilution method with labeled NH_4^+ and NO_3^- in separate sediment cores to measure gross ammonification and gross nitrification. The net rates are determined by the sediment nutrient fluxes. To measure denitrification we determined the produced N_2 independently of the labelling in the core. Sediment core incubation experiment setup can never reproduce the identical conditions related to the advective processes in permeable sediments. Nevertheless this method has advantages over just balancing sediment-water exchanges: (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,

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 denitrification at four stations across sediment types (clay/silt, fine sand, coarse sand) in the German Bight (North 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 nitrification and ammonification rates and evaluate the environmental controls underlying spatial variabilities. We further discuss 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 and sampling strategy

The study site is 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 was performed in August and September 2016 during R/V *Heincke* cruise HE-471 in the German Bight (Fig. 1).

The sampling sites are part of the NOAH (North Sea Assessment of Habitats) assessment scheme (Fig. 1). Samples were taken from 4 site (NOAH A, C, D and E) with different water depth and sediment characteristics (Table 2). The sites represent typical sediment types based on statistics of granulometric properties, organic matter content, permeability, and water depth assessed during former cruises (https://doi.org/10.1594/PANGAEA.846041). Organic matter and CN ratio data from cruises HE 383 (06/07.2012) and HE 447 (06.2015) were used.

2.2 core sampling and incubation

At each station (NOAH A, C,D and E) both water samples and sediment samples were taken. Water samples were taken with Niskin bottles attached to a CTD with additional chlorophyll and O_2 sensors. Sediment multicores equipped with acrylic tubes (PMA) with an inner diameter of 10 cm and a length of 60 cm were used. 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 (Fig. 2) in the ship's laboratory at in-situ temperature.(~19°C) directly after sampling. Cores were handled carefully to avoid disturbance that could alter benthic fluxes. Cores were incubated in the dark and the overlying site water was gently stirred with a magnetic stirrer, avoiding sediment resuspension. The overlying water column was adjusted to a height of 20 cm. Water temperature and oxygen concentration of the overlying water of sediment cores were measured continuously with optodes (PyroScience, Germany).

To measure gross ammonification, two sediment cores (Station NOAH-D 1 core only) were enriched with $^{15}NH_4^+$ (50 at-%,), the other two cores were amended with $^{15}NO_3^-$ (50 at-%) for an assessment of gross nitrification (Fig.

2). NH_4^+ and NO_3^- concentrations of the added tracer solution were adjusted to bottom water concentrations based on nutrient data of previous cruises of the same location and time (later confirmed by nutrient analyses of site water). For label addition, site water was replaced with the respective label solution. Due to the careful adjustment of concentrations, incubations were done at a tracer level, and benthic fluxes should not be altered. The label addition was calculated aiming for a maximum enrichment of 5.000 ‰ in substrates and products.

Samples were taken every 6 hours. Upon sampling, incubation water was filtered with a syringe filter (cellulose acetate, Sartorius, 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

N_2 measurements by MIMS

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) from all four cores. During the measurements, the water samples were maintained in a temperature-controlled water bath (16 °C). For calibration, we measured equilibrated water samples at four salinities, from 0 to 35 after each 10^{th} water sample. We measured the production of ^{28}N. The internal precision of the samples was <0.05 % for N_2/A_r analyses.

Oxygen penetration depth

The oxygen penetration depth in the sediment of each station was 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. The O_2 profiles were measured directly after core retrieval, i.e.within 10 – 15 minutes.

Sediment samples

The surface sediment samples (first 1 cm) of the cruises HE 383 (06/07-2012) and HE 447 (06-2015) were analyzed for total carbon and total nitrogen contents with an elemental analyzer (Carlo Erba NA 1500) 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.

Permeabilty and porosity of the sediments were conducted with sediments from the cruise He-471, the methods were described in detail elsewhere (Neumann, 2016).

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 between 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).

2.4. Rates and fluxes calculation for respiration, ammonification, nitrification and denitrification rates in core incubations

Benthic fluxes

Oxygen consumption, net ammonification, net nitrification and denitrification were calculated based on concentration changes in the sediment incubations. The respective benthic fluxes were calculated as follows:

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

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.. Positive fluxes (outflow concentrations above inflow concentrations) imply net production in the sediment.

Gross rates of ammonification and nitrification

Gross rates of ammonification and nitrification (r_{gross}) were calculated based on ^{15}N isotope dilution (Koike and Hattori, 1978; Nishio et al., 2001). For example, ammonification rates are calculated based on $^{15}NH_4^+$ additions, nitrification rates are based on $^{15}NO_3^-$ additions (Fig. 2) :

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

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 N m^{-2} d^{-1}

3 Results

Ammonification

We measured gross ammonification rates with the isotope dilution method using $^{15}NH_4^+$ as tracer, and measured net ammonium fluxes with the flux method. The highest net ammonium flux and gross ammonification rates were measured in the impermeable, organic-rich sediment at station NOAH-C (6.6 ±1.4 mmol N m^{-2} d^{-1} and 9.5 mmol N m^2 d^{-1} for net flux and gross ammonification, respectively).

The lowest net ammonium fluxes were measured in the semi-impermeable sediment at station NOAH-D (0.5 ± 0.1 mmol N m^{-2} d^{-1}). The lowest gross ammonification rate was measured at the permeable sediment station NOAH-A (2.1 ± 0.3 mmol N m^{-2} d^{-1}). The impermeable sediment station NOAH-C had the highest net ammonium fluxes (6.6 ±1.4 mmol N m^{-2} d^{-1}) and gross ammonification rates (9.5 mmol m^{-2} d^{-1}). Net and gross ammonification rates are significantly correlated (r^2=0.55; see electronical supplemental).

Nitrification

Likewise to ammonification, we measured gross nitrification rates by means of the stable isotope dilution method with $^{15}NO_3^-$ as tracer, and net nitrate fluxes employing the flux method. Net fluxes and gross nitrification rates varied significantly between stations. Net nitrate fluxes were highest at station NOAH-C and at station NOAH-E with 1.1 ± 0.5 mmol N m^{-2} d^{-1} and 1.2 ±0.5 mmol N m^{-2} d^{-1}, respectively (Fig. 3, Fig. 5). Gross nitrification rates were highest at NOAH-C (2.1 ± 0.1 mmol N m^{-2} d^{-1}). The lowest rates of net nitrate flux (0.3 ± 0.3 mmol N m^{-2} d^{-1}) and gross nitrification (1.2 ± 0.0 mmol m^{-2} d^{-1}) were observed in the permeable sediment at station NOAH-A. Net and gross nitrification rates are closely correlated (r^2=0.87; Fig. 3) with net nitrate fluxes being systematically lower than gross nitrification rates.

Denitrification

Unlike to ammonification and nitrification, we were not able to make use of the stable isotope tracers to evaluate N_2 production rates with an stable isotope technique because the requirements for the Isotope Pairing method (Rysgaard-Petersen et al., 1996) were not met. Our N_2 production estimates are thus limited to the flux method. The observed average denitrification rates ranged from 1.3 ± 1.1 mmol N m^{-2} d^{-1} to 1.9 ± 0.8 mmol N m^{-2} d^{-1} N m^{-2} d^{-1} (Fig. 5) and did not vary significantly between stations.

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) had the highest organic carbon (0.73 %) and nitrogen (0.10 %) concentrations (Tab. 2). Medium sand station (NOAH-A) had the lowest C_{org} (0.03 to 0.04 %) and total nitrogen (<0.01 to 0.01 %) concentrations. This trend does probably not apply to NOAH-E since the samples for C / N analyses were retrieved prior to the abrupt emergence of a large pockmark field at this station (Krämer et al. 2017) while the sediment cores for the incubations were retrieved after the emergence of the pockmarks. The large scale sediment resuspension event resulted in numerous newly formed depressions with increased sedimentation of organic material.

4 Discussion

4.1 Magnitude and relevance of ammonification

A principal goal of this study was to assess 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 ammonification rates is challenging, because ammonium is readily assimilated by primary producers or is rapidly nitrified, causing low ammonium concentrations and necessitating to use the isotope dilution method.

This study represents direct measured gross ammonification rates across typical sediment types of the North Sea, covering a large range from 1.9 to 9.5 mmol N m^{-2} d^{-1}: Ammonification 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 ammonium release in muddy coastal sediments (e.g. Caffrey, 1995).

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 net and gross ammonification in the sandy sediment at station NOAH-E was clearly elevated compared to the other sandy stations NOAH-A and NOAH-D. There are two possible explanations for this enhanced ammonium production: (1) enhanced supply of organic matter to the sediment surface or (2) effects bioirrigation and bioturbation.

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 C and N content is based on samples that were taken prior to the pockmark formation in 2012 and 2015 (https://doi.org/10.1594/PANGAEA.883199). The sediment samples during the cruise (He-471) in 2016 were taken from the depression inside an individual pockmark, which was about ~0.2 deeper than the surrounding sediment (Krämer et al., 2017). We assume 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, 1988).

Under completely oxic conditions, the ratio of NH_4^+ release and O_2 consumption in the entire study area should approximate Redfield ratios of about 1:8.6 (Thibodeau et al., 2010). Such ratios were observed at the semi-permeable station NOAH-D, the permeable station NOAH-A (Fig. 2), and at station NOAH-E, suggesting that in these cores most of the organic matter was degraded under oxic conditions. At station NOAH-C, however, the $N:O_2$ ratio was clearly elevated above the Redfield ratio. While this finding is based on an individual assessment, it appears plausible: 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 (e.g. Jorgensen, 1982). This is quite likely at station NOAH-C, where oxygen 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).

4.2 Ammonification coupled to denitrification by 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, suggesting that ammonium is taken up, either by assimilation or nitrification. In dark

sediments, where phototrophic organisms are light limited, we presume that nitrification is likely the more important process (Dähnke et al., 2012).

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 1.2 ± 0.0 mmol N m^{-2} d^{-1} at the sandy station NOAH-A, to 1.3 mmol N m^{-2} d^{-1} in the moderately permeable sediment at NOAH-D and to 2.1 ± 0.1 mmol N m^{-2} d^{-1} in the impermeable sediment at station NOAH-C (Fig. 3, Fig. 5). Gross nitrification at the impermeable sediment station NOAH-C accounted for around 22.2 % (±0.7 %), around 38.5 % at the semi-permeable station (NOAH-D) and around 50.6 % (±15.8 %) 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 (0.2 to 3.0 mmol m^{-2} d^{-1}; Tab. 1). Highest nitrate fluxes from the sediment and gross nitrification rates were observed at the impermeable station NOAH-C and at station NOAH-E, where pockmark structure and organic matter accumulation might have affected benthic nutrient fluxes (see section 4.1).

Lowest gross nitrification rates and nitrate fluxes are found at the permeable station NOAH-A, but apart from this, we do not see a clear correlation of nitrification and permeability in our study. Nonetheless, nitrification rates are lowest at Station NOAH-A, where oxygen penetration depth is highest, and the sediment has low organic matter content (Tab. 2). A high oxygen penetration depth can support nitrification, but it is in this case obviously substrate limited due to low organic matter content, which limits ammonification. Oxygen penetration can enhance nitrification at greater depth, but can, on the other hand, also increase diffusion limitation (Alkhatib et al., 2012). Due to this dual control of nitrification by OPD on the one hand and substrate availability on the other, the individual correlations between C_{org} or TN and nitrification are relatively weak. 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 (e.g. Sanders, 2018).

This interplay of factors is mirrored in a clear and statistically significant (a=0.05) correlation of gross nitrification and gross ammonification rates (r^2 = 0.92). Overall, the gross NO_3^- production (1.2 to 2.1 mmol m^{-2} d^{-1}) was small relative to ammonification rates (1.9 to 9.5 mmol N m^{-2} d^{-1}). We find that nitrification is governed by a complex interplay of variables such as ammonification rate, permeability, organic matter availability and oxygen penetration depth, and is likely difficult to predict based on one of these factors alone. 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). In our setting, this is reflected in a clear correlation of gross rates of ammonification and nitrification.

4.3 Denitrification

Denitrification, the reduction of NO_3^- to gaseous N_2, reduces the pool of bioavailable N, and is therefore very relevant in eutrophic coastal areas such as the southern North Sea. In our study, the measured denitrification rates ranged from 1.3 to 1.9 mmol N m^{-2} d^{-1} (Fig. 5). This estimate is on the higher end of previous measurements from sites in the German Bight (Deek et al., 2013; Marchant et al., 2016) (Tab. 1), but generally fits with previous observations. We assume that the rates in our study are elevated because sampling took place after the spring phytoplankton bloom, and not all organic matter that had been deposited at the sediment surface had been remineralized. Such a decoupling of water column production and sedimentary denitrification has been observed before in stratified water masses of the Baltic Sea (Hellemann et al., 2017). Even though our study was designed to cover diverse sediment types, and thus allow for an improved extrapolation of rates to the total German Bight area, this highlights the heterogeneity of sediments, and points out that the sampling season can have a marked effect on measured rates. Therefore, follow-up experiments should try to cover the seasonality as much as possible to improve estimates of denitrification in the German Bight area.

Important seasonal effects on denitrification can be attributed to 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 strong correlation between gross nitrification and denitrification rates ($r^2 = 0.85$).

In our study, we find that this coupled nitrification-denitrification determines the total N flux. Denitrification essentially removes, within the given uncertainties (Fig. 5) all nitrate produced by nitrification at study sites NOAH-A and NOAH-D. At stations NOAH-C and NOAH-E, where we assume a (possibly transient in case of NOAH-E) accumulation of organic matter, nitrification rates are enhanced, and a substantial amount of freshly produced nitrate is released to the water column.

In comparison to the supply of mineralized N (i.e., gross ammonification) denitrification accounts for ~20 % (1.9 mmol N m^{-2} d^{-1} / 9.5 mmol N m^{-2} d^{-1}) at the impermeable sediment station NOAH-C, ~39 % (1.3 mmol N m^{-2} d^{-1} / 3.3 mmol N m^{-2} d^{-1}) at the semi-permeable sediment station NOAH-D and ~ 62 % (1.3 mmol N m^{-2} d^{-1} / 2.1 mmol N m^{-2} d^{-1}) at permeable sediment stations (NOAH-A). As discussed above, this trend does not hold for the less representative station NOAH-E due to the transient formation of numerous pockmarks.

4.4 Significance of benthic N-recycling

Our study covers the most 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 better represents the role of nitrification, we arrive at a somewhat lower contribution of ~68 % of total denitrification occurring in moderately permeable and permeable sediments. Based solely on our data, we estimate a total nitrogen removal of ~1030 t N d^{-1} in our study area, which corresponds to an average N_2 flux of approximately 1.5 mmol N m^{-2} d^{-1}. This daily N_2 production during late summer equals the total N discharge (~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 reflect the impact of only diffusive transport and faunal activity while not accounting for advective fluxes. Based on the same data set of permeability for classification of different sediment types that Neumann et al. (2017) used, we will merge our dataset with the results of Neumann et al. (in preparation) to arrive at an improved estimate of sediment denitrification that includes benthic nitrification as a nitrate source.

In the following, we aim to put our estimates of N-transition rates into perspective by setting an upper limit of N turnover based on primary production since N cycling is linked to organic carbon availability, 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 N transition 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 in pace with N turnover. Based on Redfield stoichiometry (~12 g / mol C, ~14 g / mol N), average C fixation 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}, respectively. This sets an upper limit to the N turnover rate and compares well with the observed ammonification rate in impermeable sediment at NOAH-C (9.5 mmol NH_4^+ m^{-2} d^{-1}, Figure 5). The ammonification rates at the sandy stations are substantially lower, which certainly reflects that sandy sediments are frequently resuspended and organic particles are resuspended and degraded in the water column. For a second line of argument, we consider the annual nitrate budget of the southern North Sea (Hydes et al. 1999, van Beusekom et

al. 1999) with an annual average denitrification rate of 0.7 mmol N m^{-2} d^{-1}. This value agrees well with the average gap of 0.5 mmol N m^{-2} d^{-1} between gross nitrification and actual nitrate flux (Figure 4), which we attribute to denitrification. Both rates, the budget-based estimate and the nitrification gap are in the lower range of our measured N_2 fluxes of 0.3 to 2.9 mmol N m^{-1} d^{-1} (Tab. 1, Fig. 5). For a third line of argument, we employ the approach of Seitzinger and Giblin (1996) to link 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 2.9 mmol N m^{-2} d^{-1} are reasonable.

However, with the multitude of our approaches yielding quite a span of plausible denitrification estimates the question emerges which of the figures in the range of 0.5 to 3.3 mmol N m^{-1} d^{-1} is actually the true value for the average denitrification rate. One major reason for this level of uncertainty is the fact that the local sediment properties with regard to macrofauna composition and organic matter content varied considerably within each station, which is reflected e.g. in the variability of oxygen consumption rates (see electronic supplemental). Since we were restricted to 4 cores per station in total, and just 2 cores for labelling with $^{15}NH_4^+$ and $^{15}NO_3^-$, respectively, the inevitable spatial heterogeneity introduced a substantial degree of random error. Additionally, the preceding results we used above to evaluate our observations are certainly likewise based on imperfect data, which results in uncertainty on that side. In summary, our limited set of new observations is not sufficiently large to favor one of the preceding denitrification estimates. At least, the average of all our N_2 measurements of 1.5 ± 0.9 mmol N m^{-2} d^{-1} (N=13) falls right in the center of the interval of 0.5 to 3.3 mm and might represent our best estimate for an average denitrification rate in late summer. The remaining fraction of the initial ammonification is recycled back into the water column as DIN, which accounts for 69 ± 18 % (N=12) of the total benthic N flux (N_2 + DIN).

Since benthic N recycling substantially restocks the pelagic N inventory, we further assessed the contribution of benthic N recycling by comparing the benthic DIN (ammonium + nitrite + nitrate) fluxes with the inventory of DIN below the thermocline. Assuming steady state, we find a rapid turnover of sediment-derived DIN at NOAH-C and NOAH-E, in the range of 1-3 days (Tab. 3). This implies that even below the thermocline, DIN derived by the sediment is rapidly assimilated by phytoplankton. Previous publications showed that primary production below the thermocline contributes ~ 37 % to total primary production in the North Sea (van Leeuwen et al., 2013). Assuming Redfield stoichiometry and an average primary production of 1.05 g C m^{-2} d^{-1}, benthic DIN fluxes in our measurements can support a primary production of about 6.2 to 51.4 mmol C m^{-2} d^{-1} or 74 – 617 mg C m^{-2}

396 day^{-1}. This is within the range of previously observed and modeled primary production rates in the North Sea
397 during summer (e.g. van Leeuwen et al., 2013). We further estimate that depending on the thickness of the bottom
398 water layer below the thermocline, benthic N fluxes during the sampling time supported between 7.1 ± 2.6 % (38
399 m bottom water layer) and 58.7 ±10.6 % (10 m bottom water layer) of the annual average of primary production
400 (Tab. 3). This dependence of relative sediment contribution on water depth has been observed previously for
401 respiration processes (Heip et al., 1995). Our data also match the calculation of Blackburn and Henriksen (1983)
402 for Danish sediments, where N fluxes could support 30 to 83 % of the nitrogen requirement of the planktonic
403 primary producers (Blackburn and Henriksen, 1983).
404
405 **5 Summary and concluding remarks**
406 We evaluated a range of sedimentary nitrogen turnover pathways and found that ammonification in sediments is
407 an important N-source for primary production in the water column of the southeastern North Sea during summer.
408 Depending on water depth, 7.1 to 58.7 % of the estimated water column primary production is fueled by
409 sedimentary N release. Nitrification act as the main sinks of NH_4^+ mineralized from sedimentary organic matter.
410 Ultimately, the main factors governing nitrification are organic matter content / ammonification and oxygen
411 penetration depth in the sediment. The share of newly produced NO_3^- reduced to N_2 amounts to two thirds of NO_3^-
412 in permeable sediments, to nearly one half in moderately permeable sediment, and to one third in impermeable
413 sediments. We further showed that moderately permeable and permeable sediments account for up to ~80 % of
414 the total benthic N_2 production (~1030 t N d^{-1}) in the southern North Sea (German Bight) during the peak of benthic
415 activity in late summer. Only then, benthic N_2 production can compensate the annually averaged daily N input by
416 the main rivers (e.g. Elbe, Ems, Rhine, Weser) discharging into the southern North Sea (~1.000 t N d^{-1}). Thus
417 impermeable sediments act as an important N source for primary producers, whereas moderately permeable and
418 permeable sediments comprise a main reactive N sink counteracting eutrophication in the North Sea. Seasonal and
419 spatial variabilities, especially from nearshore to offshore, should be evaluated in future studies.
420
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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)	1233 ± 12	N.D.	N.D.	1314 ± 1087	medium sand	0.03	<0.01	08./09.2016	SIDM	this study
	1739 ± 695	N.D.	N.D.	1355 ± 876		0.04	0.01			
	1271	N.D.	N.D.	1306 ± 1042	Fine sand	0.21	0.03			
	2069 ± 63	N.D.	N.D.	1915 ± 831	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		
	1116 ±924			75 ±39*	muddy sand			03.1993		
	19.5 ±9.5			103.5 ±17.5*				04.1994		
Helgoland	1150 ±700	20 ±5	N.D.	870 ±100*	fine sand	N.D.	N.D.	05.2012	SIDM	(Marchant et al., 2016)
	210 ±50	250 ±50		2280 ±300*	medium sand					
	2980 ±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

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	Incubation time	Sediment type	C_{org}	TN	Porosity	Permeability	Temp.	Salinity	OPD
[-]	[m]	[-]	[hours]	[-]	[%]		[-]	[m²]	[°C]	[-]	[mm]
NOAH-A	31.0	1	24	medium sand	0.03 *	≤0.01*	0.37	$1.7*10^{-10}$	19.1	33.7	>15
		2	24								
		3	18								
		4	24								
NOAH-C	25.4	1	24	clay/silt	0.73	0.10	0.56	$1*10^{-15}$	19.1	32.5	3.6
		2	24								
		3	24								
NOAH-D	38.0	1	18	fine sand	0.21	0.03	0.43	$1.4*10^{-13}$	18.9	33.0	2.4
		2	24								
		3	24								
NOAH-E	28.4	1	18	medium sand	0.04	0.01	0.41	$8.8*10^{-12}$	18.7	32.4	4.2
		2	18								
		3	24								
		4	24								

* estimated

Table 3: Rates of benthic net NO_3^- and benthic net NH_4^+ fluxes per area, water depth below thermocline (average value of all sediment cores per station) 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 $NH_4^+{}_{net}$ and $NO_3^-{}_{net}$ and the effect of sedimentary N release on the reactive nitrogen available for primary production in the water column.

Station	$rNH_4^+{}_{net}$ + $rNO_3^-{}_{net}$	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	1.6 ± 0.4	29.5	0.1	< 0.1	0.6 ± 0.2	20.7	10.8 ± 0.3	14.1 ± 4.7
NOAH-C	6.6 ± 1.4	10.0	< 0.1	0.7	2.0 ± 0.2	30.0	3.4 ± 0.1	58.7 ± 10.6
NOAH-D	0.5 ± 0.1	38.0	0.1 ± 0.1	0.1	0.8 ± 0.6	26.6	28.5 ± 0.6	7.1 ± 2.6
NOAH-E	3.2 ± 0.6	10.0	< 0.1	< 0.1	0.3 ± 0.1	3.0	0.9 ± 0.1	26.5 ± 14.3

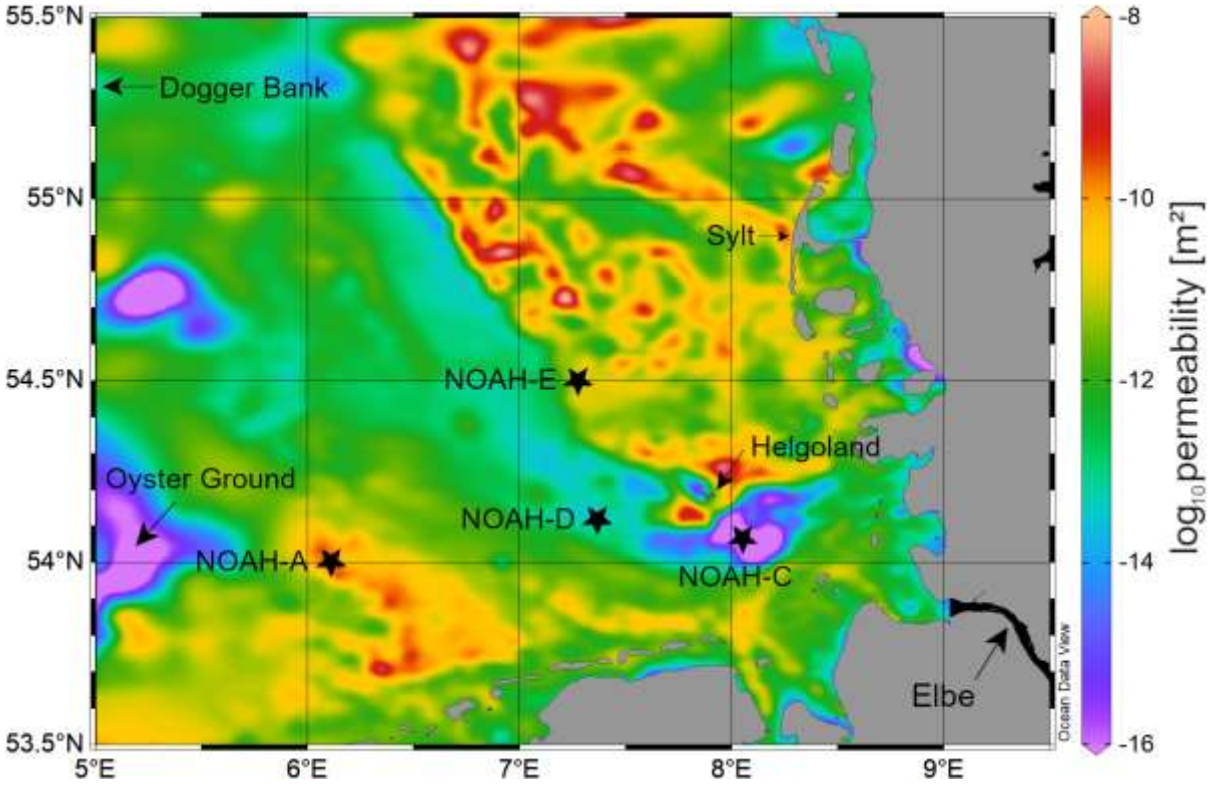

Figure 1: Map showing the sampling stations NOAH-A, NOAH-C, NOAH-D and NOAH-E in the German Bight in the North Sea. Colored areas show the spatial variability of surface sediment permeability (https://doi.org/10.1594/PANGAEA.872712).

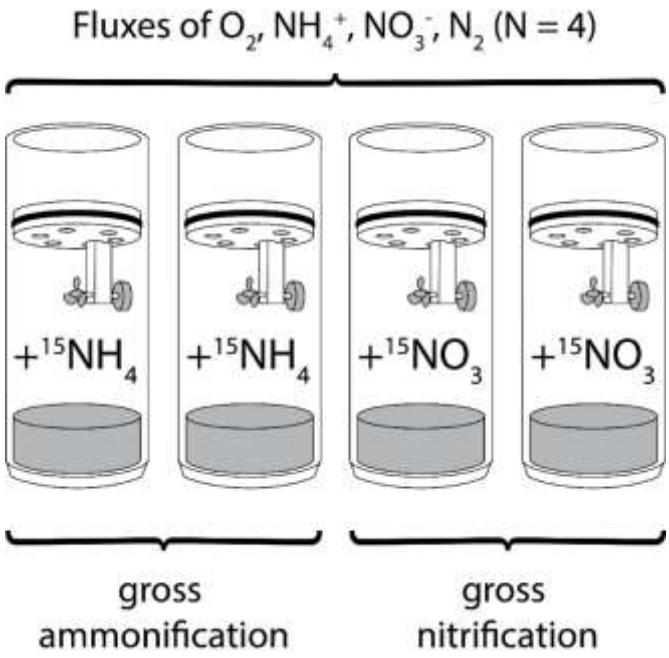

Figure 2: Schematic illustration of the experimental setup. Four sediment cores were incubated to measure benthic fluxes of oxygen, ammonium, nitrate, and N_2. Two of these flux cores were amended with either $^{15}NH_4^+$ or $^{15}NO_3^-$ for the measurement of gross rates of ammonification and nitrification, respectively.

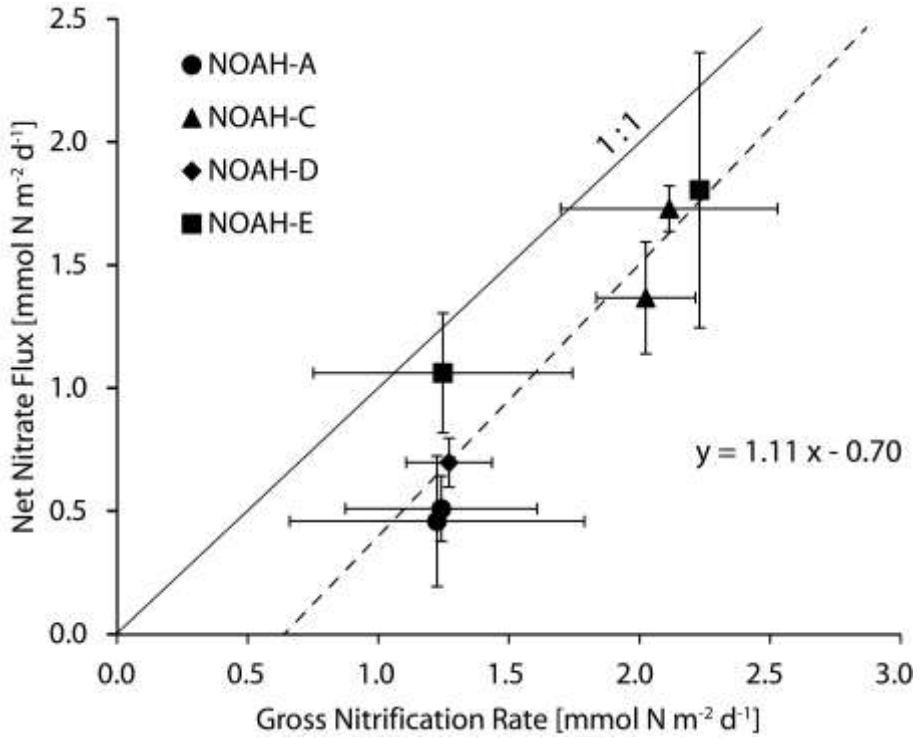

Figure 3: Correlation of gross nitrification rates and actual nitrate fluxes. The solid line indicates the 1:1 ratio, the dashed line indicates the linear regression. The error bars indicate the regression error of individual rates at the 0.95 confidence level.

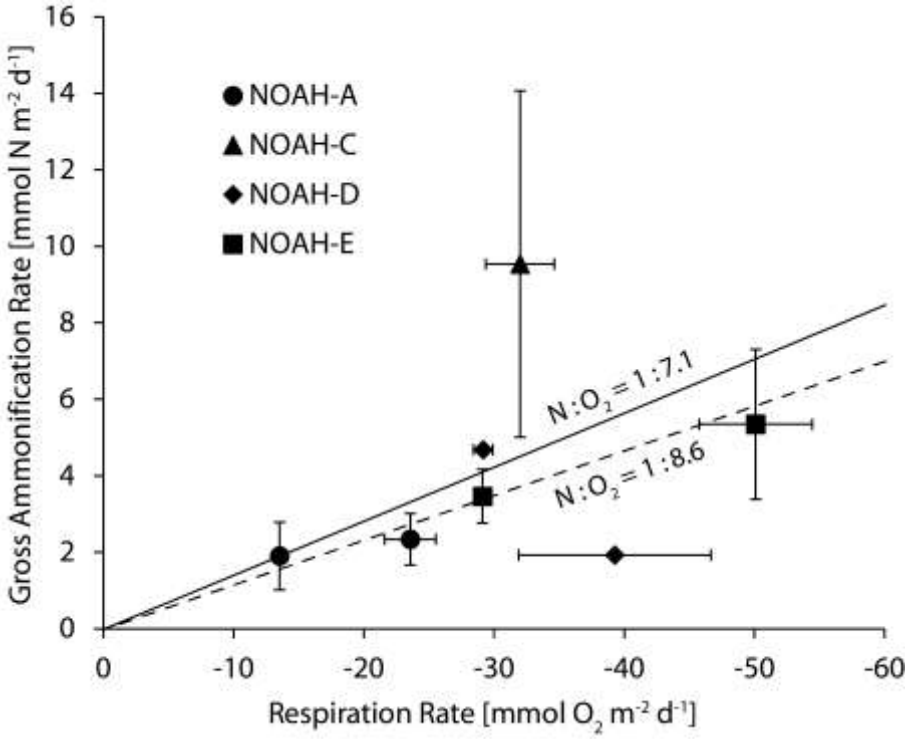

Figure 4: Benthic O_2 fluxes and gross ammonification rates of the sampled stations. The dashed line indicates the Redfield ratio of oxygen and nitrogen (N:O_2 1:8.625) (Redfield, 1958), and the solid lines indicates the ratio of oxygen and nitrogen determined by the C/N ratio in the North Sea (N:O_2 1:7.1). The error bars indicate the regression error of individual rates at the 0.95 confidence level.

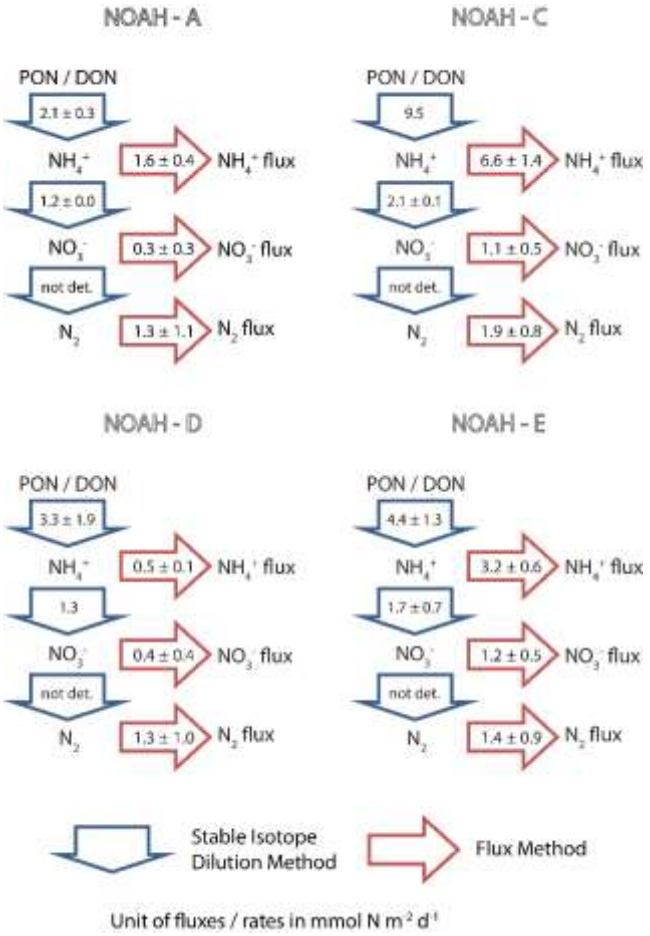

Figure 5: Benthic N-transformation rates (in mmol N m^{-2} d^{-1}) of ammonification (NH_4^+) and nitrification (NO_3^-) as measured by means of stable isotope methods (blue arrows). Simultaneously measured fluxes of ammonium (NH_4^+ flux), nitrate (NO_3^- flux), and N_2 (in mmol N m^{-2} d^{-1}) as measured by the flux method (red arrows).