

Seasonal variations of Benthic Carbon and Nutrient fluxes in the southern North Sea

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Abstract

In shallow water regions, such as the coastal areas of the North Sea, nutrient and carbon cycles are driven by a close coupling of benthic-pelagic processes. Due to shallow water depths, a substantial amount of organic matter which is produced via primary production in surface waters is transferred to the seafloor. Most of the organic matter is degraded within surface sediments and nutrients such as NH_4 or PO_4 are transported back into the water column, whereas a small amount of organic carbon is buried within the sediment. Consequently, benthic carbon and nutrient fluxes have a direct impact on biological and geological processes such as the availability of nutrients in the water column, nutrient budgets or the storage of carbon within marine sediments. Even though coastal carbon and nutrient cycles are intensively investigated, their seasonal and diurnal variability is poorly understood. The aim of this study was to quantify benthic carbon and nutrient fluxes in the southern North Sea during different seasons. The results are used for carbon and nutrient mass budgets. Furthermore processes which affect carbon and nutrient fluxes over seasonal and diurnal scales were identified.

Chapter 2 and 3 present a seasonal study on benthic carbon and nutrient fluxes in the southern North Sea. During five cruises on *RV Heincke*, carried out in June 2012, August 2012, March 2013, November 2013 and March 2014, carbon and nutrient cycles were studied with the benthic lander NuSObs (Nutrient and Suspension Observatory) and shipboard sampling techniques. Chapter 4 presents laboratory experiments in which the diurnal variability of benthic carbon and nitrate fluxes were studied in light:dark cycles.

The first manuscript (chapter 2) presents benthic oxygen and nitrogen fluxes derived from *in situ* incubations and pore water data. Both oxygen and nitrogen fluxes followed the seasonal cycle with highest fluxes in summer and autumn and lowest fluxes in winter. Detailed investigations of the benthic macrofauna and tracer flux studies showed the importance of faunal induced transport of solutes along the sediment water interface for the benthic oxygen consumption in summer and autumn. Over spatial scales the suspension feeder *Ensis directus* had a considerable impact on benthic oxygen consumption. Estimated recycling efficiencies of organic bound carbon revealed that most of the carbon (76-93 %) and nitrogen (87-97 %) reaching the seafloor is remineralized within surface sediments.

The second manuscript (chapter 3) discusses benthic silicic acid (Si(OH)_4) fluxes which were determined with different sampling techniques including *in situ* incubations with the benthic lander NuSObs, *ex situ* incubations and calculated fluxes based on pore water profiles. A comparison of the different sampling techniques shows that in shallow water coastal areas *in situ* techniques are

required for a precise quantification of benthic fluxes. Strong seasonal variations in silicic acid effluxes were measured by *in situ* and *ex situ* incubations with highest fluxes in summer and autumn and lowest fluxes in winter. Estimated annual rain rates of biogenic silica (bSi) reaching the seafloor of the southern North Sea are within a range of 1.7 to 2.2 $\text{mol bSi m}^{-2} \text{a}^{-1}$.

The third manuscript considers the results of laboratory experiments on diurnal cycling of oxygen and nitrate in a coastal sediment. An oxygen optode (PyroscienceTM) and an optical nitrate sensor (SatlanticTM) were applied to closed microcosm experiments in order to monitor oxygen and nitrate continuously in incubation experiments. A diatom dominated sediment was incubated over 12 hour light:dark shifts. During daylight oxygen was most likely produced by benthic primary producers and during night time consumed by heterotrophs and the oxidation of reduced solutes. The consumption of oxygen was regulated by the presence or absence of benthic macrofauna. Monitoring nitrate continuously with the nitrate sensor revealed that at the onset of light, while sediments and bottom waters were anoxic, a nitrate reducing or assimilating process takes place within surface sediments.

Kurzfassung

In Flachwassergebieten, sowie dem Küstenbereich der Nordsee, sind benthische und pelagische Prozesse stark miteinander gekoppelt. Durch Primärproduktion erzeugter organischer Kohlenstoff sinkt auf den Meeresboden und wird dort von Mikroorganismen und benthischer Makrofauna zersetzt. Die freigesetzten Nährstoffe (NH_4 , PO_4) werden zu großen Teilen zurück in die Wassersäule transportiert, während ein kleiner Teil des organischen Kohlenstoffs in marinen Sedimenten vergraben wird. Benthische Kohlenstoff- und Nährstoffflüsse haben somit einen direkten Einfluss auf die Verfügbarkeit von Nährstoffen in der Wassersäule und die langfristige Speicherung von Kohlenstoff in marinen Sedimenten. Obwohl Kohlenstoff- und Nährstoffkreisläufe intensiv untersucht werden, ist verhältnismäßig wenig über ihre saisonale Variabilität in benthischen Küstenbereichen bekannt. Ziel dieser Untersuchung war es, benthische Kohlenstoff- und Nährstoffkreisläufe in der südlichen Nordsee zu unterschiedlichen Jahreszeiten zu quantifizieren. Diese Ergebnisse sind für Kohlenstoff- und Nährstoffbudgets von essentieller Bedeutung.

Kapitel 2 und 3 der vorliegenden Arbeit befassen sich mit der saisonalen Variabilität benthischer Stoffkreisläufe in der südlichen Nordsee. Kohlenstoff- und Nährstoffkreisläufe wurden während fünf Expeditionen auf dem Forschungsschiff *RV Heincke* mit dem benthischen Lander NuSObs („Nutrient and Suspension Observatory“), sowie mit konventionellen Beprobungstechniken untersucht. Im dritten Manuskript wurde die zeitliche Variabilität benthischer Kohlenstoff- und Nitratflüsse in Laborexperimenten über zwölfstündige Licht:Dunkel Zyklen untersucht.

Im zweiten Kapitel werden benthische Sauerstoff- und Stickstoffflüsse, welche mittels *in situ* Inkubationen gemessen wurden, beschrieben. Die Sauerstoff- und Stickstoffflüsse zeigten eine hohe saisonale Variabilität mit hohen Flussraten im Sommer und Herbst und niedrigen Flussraten im Winter. In diesem Zusammenhang hatte die benthische Makrofauna im Sommer und Herbst einen wichtigen Einfluss auf die benthische Sauerstoffzehrung. Über räumliche Skalen hatte der Suspensionsfresser *Ensis directus* einen großen Einfluss auf den benthischen Sauerstofffluss. Massenbudgets zeigen an, dass 76 bis 93 % des organischen Kohlenstoffs und 87 bis 97 % des organischen Stickstoffs, welche den Meeresboden der südlichen Nordsee erreichen in den oberen Sedimentschichten remineralisiert werden.

Das dritte Kapitel behandelt benthische Kieselsäureflüsse, welche mit unterschiedlichen Methoden (*in situ* Inkubationen, *ex situ* Inkubationen, Berechnungen von Porenwasserprofilen) untersucht wurden. Ein Vergleich der unterschiedlichen Methoden zeigte an wie essentiell *in situ* Messungen sind, um benthische Stoffflüsse zu quantifizieren. Die benthischen $\text{Si}(\text{OH})_4$ Flussraten folgten dem saisonalem Zyklus mit höchsten Flussraten im Sommer und Herbst und niedrigsten

Flussraten im Winter. Massenbudgets zeigen an, dass die Menge an biogenem Silikat, welches pro Jahr den Meeresboden der südlichen Nordsee erreicht, im Bereich von 1.7 bis 2.2 $mol\ bSi\ m^{-2}$ liegt.

Im vierten Kapitel werden Laborexperimente diskutiert, die den Einfluss von Tag:Nacht Zyklen auf benthische Sauerstoff- und Nitratflüsse untersuchen. Sauerstoff und Nitrat wurden kontinuierlich in geschlossenen Inkubationsversuchen mit einer Sauerstoffoptode (Pyroscience™) und einem optischen Nitratsensor (Satlantic™) gemessen. Sedimentkerne, welche mit benthischen Diatomeen besiedelt waren, wurden über zwölf stündige Licht:Dunkel Zyklen inkubiert. Sauerstoff wurde am Tag durch benthische Algen produziert und in der Nacht durch heterotrophe Atmung und durch die Oxidation von reduzierten Komponenten aufgebraucht. Der O_2 Verbrauch wurde durch benthische Makrofauna reguliert. Durch das kontinuierliche Messen von Nitrat wurde erstmals ein Mechanismus entdeckt, bei dem Nitrat bei Tagesanfang (Licht) reduziert oder assimiliert wurde.

Preface

This introduction provides an overview on carbon and nutrient (silicic acid, nitrogen) cycles in surface sediments of temperate coastal regions such as the North Sea. In particular, seasonal variations in benthic carbon and nutrient fluxes, and the impact of transport processes (e.g. bioirrigation) on benthic fluxes are highlighted. Furthermore, *in situ* measuring techniques for the quantification of benthic carbon and nutrient fluxes are introduced.

Primary production and benthic oxygen uptake

During the last decades the global carbon cycle was extensively investigated since it was recognized that the greenhouse gas CO₂ plays a crucial role in controlling the earth's climate and might be responsible for the increase in the average temperature of the Earth's surface since the mid-20th century. It is now understood that the present-day coastal ocean is a net sink of atmospheric CO₂, a burial site for organic and inorganic carbon and an important zone for carbon transformation and sequestration (Bauer et al. 2013).

In coastal areas, the carbon cycle is crucially dependent on the net primary production in the water column. Primary production is essentially controlled by the availability of light and nutrients in the water column (Wollast 1998). In coastal areas high nutrient input (e.g. continental runoff, benthic remineralisation), fuel the production of phytoplankton and produce large amounts of organic carbon (~230 g C m⁻² a⁻¹ on a global average) (Nixon and Oviatt 1986; Gattuso et al. 1998). Silicic acid and nitrogen are often limiting nutrients for primary production in the water column and are thereby strongly intertwined into the carbon cycle (Gruber 2004; Tréguer and De La Rocha 2013). For example, diatoms are one of the dominant primary producers in coastal areas and assimilate nutrients and carbon in specific ratios (e.g. C:N:P:Si = 106:16:1:22 (Stefánsson and Richards 1963)).

In shallow waters (<200 m) approximately 15 to 50 % of the organic matter which is produced during primary production in the water column settles at the seafloor (e.g. Canfield et al., 1993; Wollast, 1998). Most of the organic matter is degraded within surface sediments and mineralization products (e.g. nutrients) are transported back into the water column. A smaller part of the organic carbon reaching the seafloor is buried and stored in the sediment. On a global estimate, about 75 g C m⁻² a⁻¹ may deposit at the seafloor, of which about 10 % may be buried and stored within the sediment (Wollast 1998). This balance between organic carbon burial and benthic mineralisation within surface sediments has a profound impact on the biosphere and over geological time scales on

the climatic conditions on earth (Berner 1980; Berner and Canfield 1989; Archer and Maier-Reimer 1994).

In surface sediments oxygen is consumed directly or indirectly during the degradation of organic material. The total oxygen uptake (TOU) can thus be used as a proxy for benthic carbon mineralization of marine sediments (Canfield et al. 1993). Together with carbon accumulation rates in sediments, the amount of organic carbon reaching the seafloor and its burial efficiency within surface sediments can be estimated from mass budget calculations. Furthermore, the ratio between diffusive oxygen uptake (DOU) and the total oxygen uptake (TOU) indicates the importance of benthic fauna on benthic mineralisation rates. A global compilation of DOU and TOU measurements shows that the relative importance

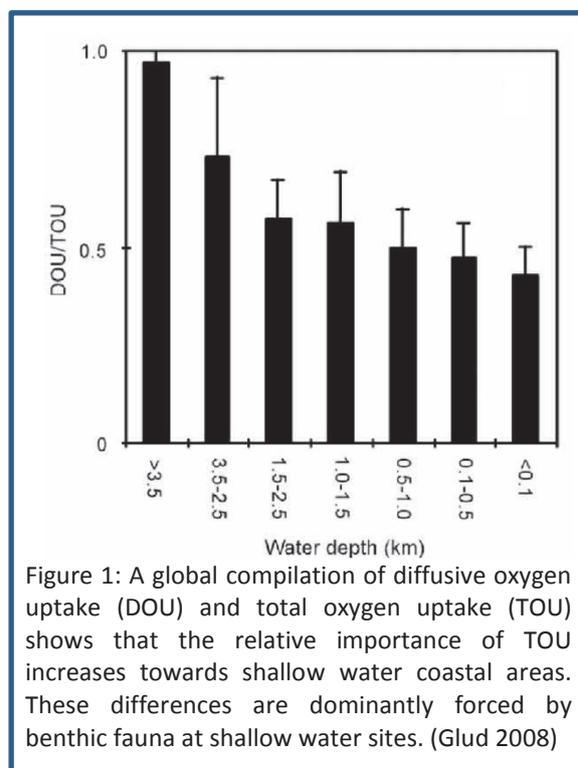


Figure 1: A global compilation of diffusive oxygen uptake (DOU) and total oxygen uptake (TOU) shows that the relative importance of TOU increases towards shallow water coastal areas. These differences are dominantly forced by benthic fauna at shallow water sites. (Glud 2008)

of TOU increases towards shallow water coastal areas (fig. 1), which is dominantly forced by benthic macrofauna (Glud 2008).

Studies on the total oxygen uptake rates are rather limited as shown by Seiter et al. (2005) (fig. 2). In particular, little is known about the seasonal dynamics of temperate coastal areas, even though these areas are important sites for carbon production by phytoplankton in the water column (Wollast 1998; Laruelle et al. 2013). In the southern German Bight (southern North Sea) *in situ* measurement of TOU were only determined by Forster et al. (1999) and Janssen et al. (2005) (fig. 2 B).

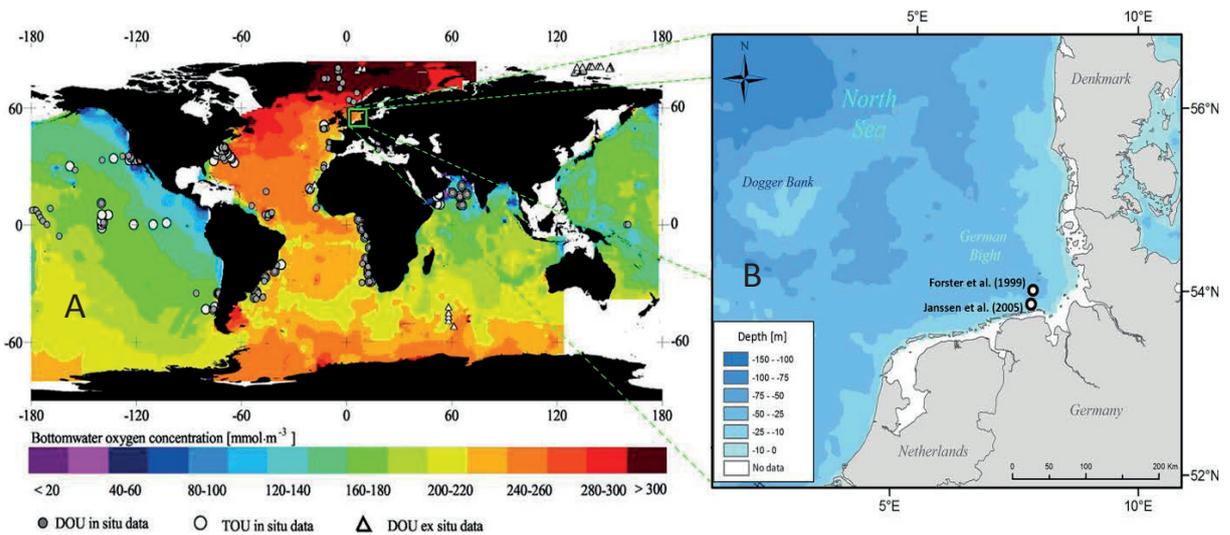


Figure 2: A global compilation of measurements of sediment oxygen uptake rates and distribution of bottom water oxygen (A). Total oxygen uptake (TOU, measured by *in situ* sediment incubation) and diffusive oxygen uptake (DOU, measured *in situ* and *ex situ* from O_2 pore water profiles) are used as a proxy for the benthic mineralization of organic carbon. Modified from Seiter et al. (2005). In the southern North Sea (B) data about *in situ* determined TOU is available from Janssen et al. (2005) and Forster et al. (1999).

The role of benthic macrofauna for the benthic mineralisation of organic matter

The importance of benthic macrofauna on the benthic mineralization of organic matter and exchange of solutes along the sediment water transition zone was shown in numerous studies (e.g. Kristensen 1988; Aller 1998, 2001). Benthic fauna can incorporate organic carbon from the water column into the benthic food chain and digests organic matter making it more accessible for microbial turnover (Wollast 1998; Glud 2008; Kristensen et al. 2012). Within the sediment, particle mixers can transport labile organic material and metal oxides downwards and reduced metal sulphur complexes upwards, homogenizing the upper sediment layer over the long run (Aller 1990; Thamdrup and Canfield 2000). Faunal induced ventilation of burrows (bioirrigation) transports solutes along the sediment water continuum. Thereby, oxygen enriched bottom waters are transported along burrows into the sediment, stimulating the mineralisation of organic matter (fig. 3). Conversely, nutrients (e.g. NH_4 , $\text{Si}(\text{OH})_4$) are transported out of the sediment (Aller 1982; Marinelli 1992). The relative importance for fauna-

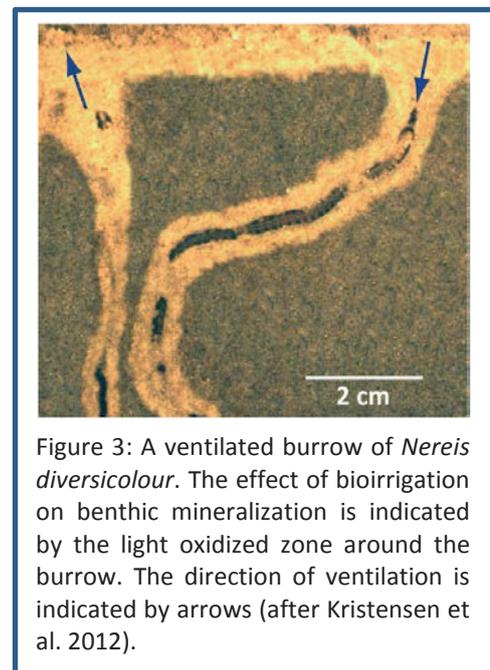


Figure 3: A ventilated burrow of *Nereis diversicolour*. The effect of bioirrigation on benthic mineralization is indicated by the light oxidized zone around the burrow. The direction of ventilation is indicated by arrows (after Kristensen et al. 2012).

induced irrigation on the exchange of solutes depends on sediment chemistry and species involved (Glud 2008). For example, suspension feeders can extensively stimulate organic matter mineralisation in impermeable organic rich sediments by transporting oxygen rich water into otherwise anoxic sediments. The relative importance of benthic macrofauna on benthic mineralization rates tends to increase from open waters to the coast (fig. 1) and is dominantly forced by an enhanced input of organic matter from the water column to the sediment in shallow coastal areas (Glud 2008). In cohesive sediments of shallow coastal waters (<100 meters), macrofauna induced oxygen uptake rates can account for 57 % of the total oxygen uptake rate of a sediment body (Glud 2008).

Sources and sinks of nitrogen in coastal environments

Coastal waters are affected by large inputs of dissolved inorganic nitrogen (e.g. NH_4 , NO_3), dominantly due to river run-off and benthic recycling of nitrogen (Herbert 1999). In many coastal waters large inputs of nitrogen from anthropogenic sources cause eutrophication. For example, large amounts of nitrate are transported by the rivers Elbe and Weser into the coastal waters of the German Bight (southern North Sea) (Keppner et al. 2012). The evaluation of the ecological state of the North Sea according to the “Water Frame Work Directive” of the European Union (Europäische Union 2000), revealed that most coastal waters are in a “dissatisfactory” state due to the large riverine input of nutrients (Voß et al. 2010) (fig. 4). In this context biogeochemical processes such as denitrification and anaerobic oxidation of ammonium (anammox) provide an important mechanism to remove excess nitrogen and reduce the amount of eutrophication (Seitzinger 1988; Herbert 1999; Thamdrup and Dalsgaard 2002). In rivers and coastal areas denitrification possibly reduces the supply of fixed nitrogen from continents by 40 % (Seitzinger 1988).

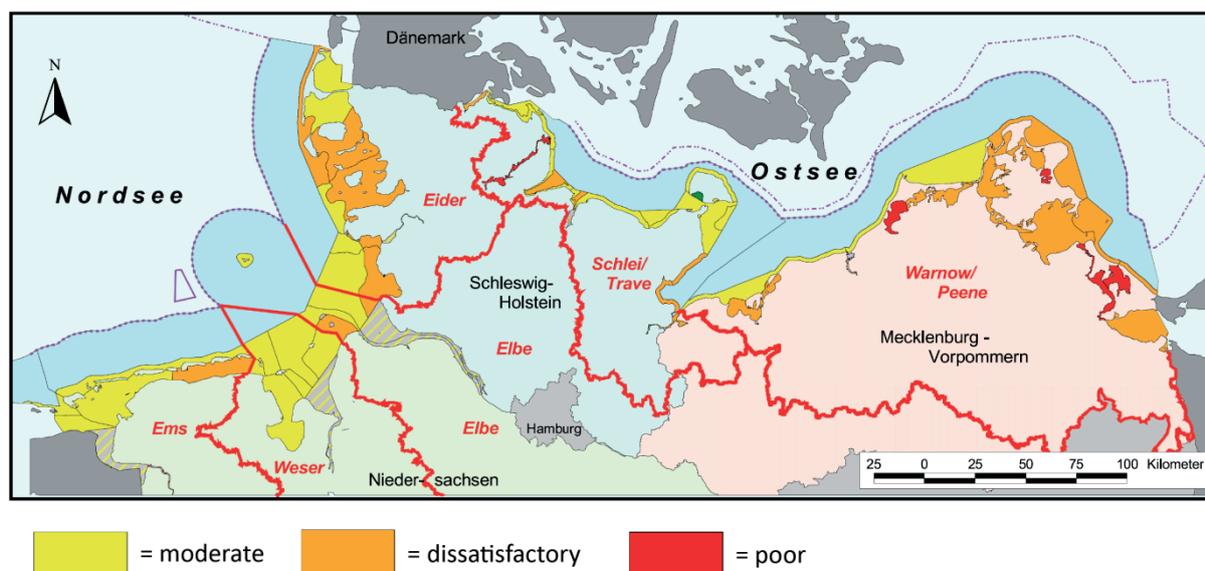


Figure 4: A map showing the evaluation of the ecological status of the coastal waters of Germany (Voß et al. 2010). Ecological problems arise mostly due to the high input of nutrients into the coastal regions. The evaluation is based on the „Water Frame Work Directive” (Europäische Union 2000).

Prokaryotes and eukaryotes require fixed nitrogen (also called reactive nitrogen or combined nitrogen) in form of nitrate, ammonium or organic bound nitrogen for assimilation. Furthermore, prokaryotes and eukaryotes utilize nitrogen for dissimilatory energy gaining processes, in which nitrogen compounds may act as an oxidant or reductant (Thamdrup 2012). Dissimilatory nitrogen transformations either transform fixed nitrogen from one redox-state into another redox-state (nitrification, dissimilatory nitrate reduction to ammonium), or remove fixed nitrogen from the ecosystem via denitrification or the anaerobic oxidation of ammonium (anammox) (Herbert 1999; Thamdrup and Dalsgaard 2002).

Nitrate transformations are affected by various environmental factors (e.g. temperature, substrate) and can therefore vary over seasonal and diurnal scales. For example, seasonal variations in denitrification rates are in general regulated by the availability of carbon and nitrate which is supplied by diffusion from the overlying bottom water or by nitrification within the sediment (Canfield et al. 2005). In temperate coastal sediments, denitrification rates in general reach an annual maximum in spring, due to a combination of increasing temperatures, an enhanced nitrate supply from the overlying water column, higher nitrification rates and supply of labile organic matter from phytoplankton spring blooms. In summer lower denitrification rates are mostly due to a lower availability of nitrate and oxygen. During autumn a small maxima in coupled nitrification-denitrification develops due to a combination of higher oxygen and nitrogen availability. On the

contrary, low denitrification rates in winter are probably a direct temperature effect since oxygen and nitrate concentrations are usually present in sufficient amounts (Canfield et al. 2005).

Seasonal variations of the carbon and nutrient cycle in the southern North Sea

The coastal area of the southern North Sea extends along the coast-lines of the Netherlands, Belgium, Germany and Denmark (fig. 2, B). Its shallow water column is in general mixed throughout the year by wind and tides (Beusekom and Diel-Christiansen 2009). Due to its proximity to the coast it is strongly affected by the input of nutrient rich continental freshwater (Beusekom and Diel-Christiansen 2009). Consequently, relatively large amounts of organic matter are annually produced by primary producers ($\sim 200 \text{ g C m}^{-2} \text{ a}^{-1}$) (Reid et al. 1990). For the North Sea Thomas et al. (2005) estimated that the annual primary production is about three orders of magnitude larger than the terrestrial (riverine) input of organic matter.

The seasonal and temporal variability of phytoplankton blooms is forced by the availability of light and nutrients in the water column (Radach et al. 1990; Reid et al. 1990; Wollast 1998). Within the North Sea the photosynthetically active radiation, which is available for phytoplankton growth, accounts for approximately 48.3 Wm^{-2} (Reid et al. 1987), whereas clouds reduce light availability by a factor of five between overcast and clear condition (Reid et al. 1990). Furthermore, light penetration into the water column is dependent on sediment turbidity and phytoplankton biomass and can range between 3 and 12 m (Reid 1990).

In winter, the water column of the North Sea is enriched in nutrients and the growth of phytoplankton is limited by the availability of light. In spring phytoplankton blooms start to grow exponentially, as soon as the light availability reaches a critical level (Sverdrup 1953; Gieskes and Kraay 1977). The timing of spring phytoplankton blooms can vary over spatial scales. In low turbid waters like off the Dutch west coast they can occur as early as January-February, whereas in turbid coastal waters such as in the German Bight they occur mostly within the second half of April (Radach et al. 1990; Joint and Pomroy 1993). Spring blooms occur in two different phases. The first bloom is dominated by diatoms and limited by the availability of silicic acid in the water column. The second bloom is dominated by flagellates and is limited by the amount of nitrogen and phosphate which is left in water column after the first bloom (Gieskes and van Bennekom 1973). In summer nutrient concentrations in the North Sea are in general very low (Brockmann et al. 1990) and primary production is possibly nitrogen limited (Woodward and Owens 1990; Riegman et al. 1990). The coastal zone is affected by a continuous input of nutrients due to continental freshwater discharge and the mineralisation of organic matter (Beusekom and Diel-Christiansen 2009). In general, one or

two diatom blooms may occur which are mostly followed by flagellate blooms during summer (Radach et al. 1990; Beusekom and Diel-Christiansen 2009). In the German Bight phytoplankton production reaches another maximum in August, followed by a decrease down to lowest winter production in October-November (Radach et al. 1990; Beusekom and Diel-Christiansen 1994).

Benthic mineralization of organic matter is closely coupled to primary production in the water column, due to the flux of particulate organic matter from the water column to the seafloor (Soetaert et al. 2000; Lancelot et al. 2005). The amount and the relative importance of benthic nutrient fluxes in respect to processes in the water column can vary over spatial and temporal scales (Wollast 1998; Herbert 1999). Within the Belgian part of the southern North Sea the benthic mineralisation of organic matter is to a dominant part forced by the availability of organic matter and the bottom water temperature (Provoost et al. 2013). The mineralization of spring bloom organic matter is delayed until summer when temperatures are highest. Consequently the sediment acts as a buffer for water column nutrients during spring, slowly releasing them again during summer.

At the Dutch coast of the North Sea, Rutgers van der Loeff et al. (1980) studied the relative importance of benthic silica fluxes in respect to nutrient budgets in the water column over seasonal scales. The authors estimated that benthic silica fluxes can contribute 30 to 50 % of the total silica input into the area under study in summer, when the river water is depleted in Si(OH)_4 . Within the German Bight benthic mineralisation rates of organic matter and nutrient fluxes are affected by a marked seasonality and belong to the highest measured flux rates of the North Sea. Due to the high mineralisation rates, oxygen is consumed within the upper millimetres of the sediment and large amounts of nutrients accumulate within the sediment (Lohse et al. 1995). Within a sediment depth of approximately 10 cm, extraordinarily high concentrations of ammonium ($\sim 2500 \mu\text{mol l}^{-1}$) and silicic acid ($750 \mu\text{mol l}^{-1}$) pore water concentrations were observed by Gehlen et al. (1995) and Lohse et al. (1995), leading to high nutrient effluxes of $13.7 \text{ mmol Si(OH)}_4 \text{ m}^{-2} \text{ d}^{-1}$ and $11.5 \text{ mmol NH}_4 \text{ m}^{-2} \text{ d}^{-1}$ in summer. In summer an extremely fast turnover time of ± 9 days of pelagic Si(OH)_4 with respect to benthic regeneration was estimated by Gehlen et al. (1995) for the German Bight. Furthermore, the benthic ammonium efflux could contribute up to 75 % of the nitrogen requirements for primary production in the water column (Lohse et al. 1995).

Measuring benthic oxygen uptake and effluxes of solutes

The mineralisation of organic matter and the transport of solutes across the sediment water interface can be studied by a wide variety of different approaches (Zabel 2000). Vertical concentration gradients of solutes within the sediment can be studied with microsensors (Jørgensen and Revsbech 1985), optodes (Wenzhöfer et al. 2001) and pore water analysis (Schulz and Zabel 2006). The diffusive exchange of solutes along the sediment water interface can be calculated from concentration gradients along the sediment water



Figure 5: *In situ* measurement of the diffusive oxygen uptake (DOU) of a marine sediment with microelectrodes (Glud 2008)

boundary by applying Fick's first law of diffusion (Boudreau 1997). For example, the diffusive oxygen uptake (DOU) of impermeable sediments can be measured with Clark type O_2 microelectrodes (fig. 5). Measurements are preferentially carried out *in situ*, because *ex situ* measurements often lead to an overestimation of DOU, caused by sediment disturbance during core recovery and an improper establishment of *in situ* conditions in the lab (Glud 2008). In the deep sea, the DOU gives reliable estimates of the total amount of oxygen which is taken up by marine sediments whereas in shallow coastal waters advective fluxes caused by burrowing fauna within the sediment (e.g. bioirrigation) can considerably exceed diffusive fluxes (Wenzhöfer and Glud 2004) (fig. 1).

An approach that considers both diffusive and faunal induced advective transport processes are enclosed chamber systems which incubate sediment samples and the overlying bottom water in a closed system (Glud 2008). The flux of respective solutes can be calculated from the change of the concentration of solutes in the overlying water over time. Incubations are preferentially carried out under *in situ* conditions, at which sampling artefacts, such as decompression, temperature variations or stress of the benthic macrofauna, can be neglected (Glud 2008). In this context the benthic lander NuSObs (Nutrient and Suspension Observatory) was developed and for the first time applied in this study (fig. 6).

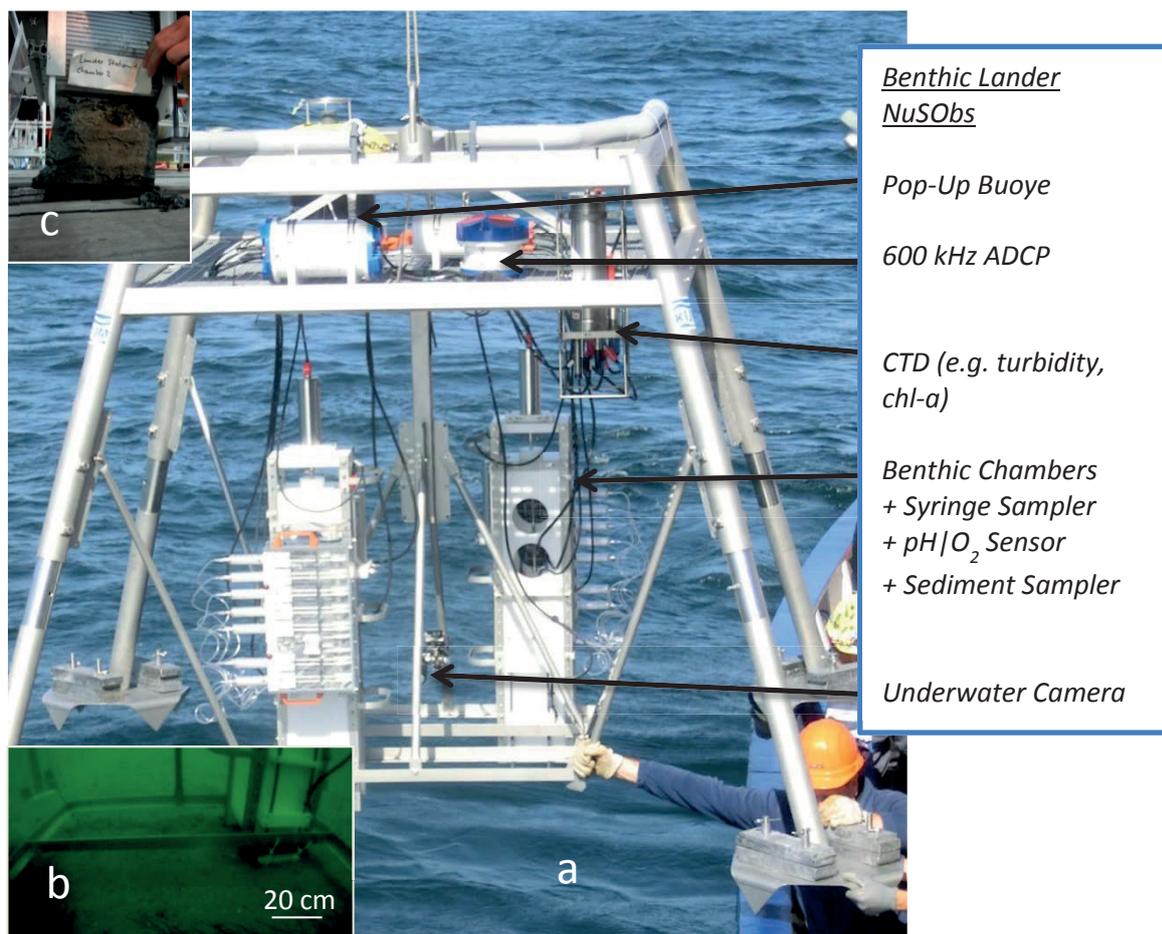


Figure 6: The benthic lander NuSObs including lander frame, benthic chambers, sensors and cameras (a). *In situ* incubations are carried out with benthic chambers at the seafloor (b). After recovery the incubated sediment can be sampled from the chambers (c).

The lander frame was designed for harsh environments (e.g. strong tidal currents), because other lander systems had stability problems within the area under study (e.g. Forster et al. 1999). After positioning, the lander stayed for about 12 to 24 hours at the seafloor. Two “Mississippi” type chambers (Witte and Pfannkuche 2000) are driven slowly into the sediment without disturbing the sediment surface. Each chamber is equipped with an oxygen optode (AanderaTM/4330), a pH sensor (AMT/OEMTM) and a syringe sampler. Each syringe sampler consisted of seven sampling ports and one injection port. The injection of chemical tracers allows the detection of faunal induced transport processes. After the incubation, a lid is driven underneath the chambers by a motor. This allows sampling the incubated sediment and macrofauna from the chambers after the recovery of the lander (fig. 6, c). Accordingly, fauna respiration and the functional type of benthic fauna can be estimated.

Currents and waves in the overlying water column were monitored with a 600 kHz ADCP (Teledyne RD InstrumentsTM/Workhorse). A multiparameter CTD (Sun&SeaTM/CTD115M) was

mounted approximately one meter above the seafloor and parameters such as temperature, pressure, salinity, oxygen, turbidity and chlorophyll-a were monitored in the bottom water. Furthermore an underwater camera was monitoring the seafloor (fig. 6, b).

Aim and outline of the thesis

In the previous sections seasonal variations of carbon and nutrient cycles in coastal areas were described. In particular the importance of the benthic environment in shallow water coastal areas for the burial of carbon and the reflux of nutrients was highlighted. The important role of benthic macrofauna for the benthic mineralisation of organic matter, the exchange of solutes along the sediment-water boundary and the importance of *in situ* techniques for an accurate quantification of benthic fluxes were introduced.

The following three chapters present the results of several research cruises which were carried out within the southern North Sea and the Baltic Sea. Diurnal to seasonal variations of benthic carbon and nutrient fluxes were studied both in the laboratory and by *in situ* experiments in the field. In the following paragraph the objectives and outline of the individual chapters are briefly described.

Chapter 2 and 3 present the results of a seasonal study about benthic carbon, nitrogen and silica fluxes measured *in situ* with the benthic lander NuSObs in the southern North Sea. So far, only a few studies addressed the benthic exchange of solutes over seasonal cycles with *in situ* techniques. In particular studies on temperate coastal shallow water sites such as the southern North Sea are rare, which are characterized by distinct spring and autumn phytoplankton blooms. In order to investigate the seasonal variability of benthic carbon and nutrient fluxes we studied a depositional site in the southern North Sea (Helgoland Mud Area). In depositional areas, accumulated sediments and benthic nutrient and carbon fluxes most likely reflect local processes in the overlying water column (e.g. particle export reaching the seafloor). Accumulated sediments are mostly fine grained and impermeable and therefore not affected by wave and current induced pore water flushing, narrowing benthic transport processes to diffusional and biological mediated transport processes.

In chapter 2 *in situ* measurements of benthic carbon and nitrogen fluxes in the southern North Sea are discussed. The impact of benthic macrofauna was investigated by detailed fauna analyses sampled from benthic chambers and chemical tracer flux studies. Calculated fauna respiration rates as well as different feeding types of benthic macrofauna were compared with measured oxygen and nitrogen fluxes. Estimations on the amount of organic bound carbon and nitrogen which settle annually at the seafloor and are recycled within surface sediments are discussed.

In chapter 3 the silica cycle was extensively studied over seasonal and spatial scales in the southern North Sea. One aim of this study was to compare different techniques that were used to measure silicic acid fluxes in the southern North Sea including *in situ* incubations carried out with the benthic lander NuSObs, *ex situ* incubations and pore water analyses. The importance of different functional types of benthic macrofauna on pore water profiles of silicic acid were studied with depth profiles of benthic macrofauna. Additionally, the seasonal variability of the biogenic silica cycle was investigated. Estimations about annual rain rates of biogenic silica (bSi) to the seafloor and the recycling efficiency of bSi in different types of surface sediments are discussed.

In chapter 4 benthic oxygen and nitrate fluxes were studied in coastal sediments which were inhabited by benthic microphytes. In microcosm experiments, sediment cores which were affected and not affected by benthic macrofauna were investigated over 12 hour light:dark cycles in the laboratory. The aim of this study was to monitor the temporal variability of benthic nitrate and oxygen fluxes over time scales of hours with the optical nitrate sensor SUNA V2 (SatlanticTM) and an oxygen optode (PyroscienceTM).

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Overview of manuscripts

Seasonal and spatial variations of benthic carbon and nitrogen fluxes in the Helgoland Mud Area (southern North Sea)

Chapter 2

Till Oehler, Roi Martinez, Ulrike Schückerl, Christian Winter, Ingrid Kröncke, Michael Schlüter

(submitted to *Limnology and Oceanography*)

The ideas for this manuscript were developed by me and Michael Schlüter. Planning and participation in research cruises were performed by me, Roi Martinez and Ingrid Dohrmann. Macrofauna data was provided by Ulrike Schückerl and Ingrid Kröncke. Nutrients, TOC, CN and bromide were analysed by myself with the support of Ingrid Stimac, Ingrid Dohrmann and Rita Fröhlking-Teichert. Grain size analyses were carried out by Christian Winter. I interpreted the data and wrote the manuscript by myself with contributions from all co-authors.

Seasonal dynamics of the biogenic silica cycle in surface sediments of the Helgoland Mud Area (southern North Sea)

Chapter 3

Till Oehler, Ulrike Schückerl, Michael Schlüter

(submitted to *Limnology and Oceanography*)

The ideas for this manuscript were developed by me and Michael Schlüter. Planning and participation of research cruises were carried out by me, Roi Martinez and Ingrid Dohrmann. Macrofauna data was provided by Ulrike Schückerl. Nutrients and bSi were analysed by myself with the support of Ingrid Stimac, Ingrid Dohrmann and Rita Fröhlking-Teichert. I interpreted the data and wrote the manuscript by myself with contributions from all co-authors.

Diurnal variations of benthic oxygen and nitrate fluxes measured with an oxygen optode and the nitrate sensor SUNA V2

Chapter 4

Till Oehler and Kasper Hancke

(in preparation)

The ideas of this manuscript were developed by Ronnie N. Glud. Laboratory experiments and sample collection was done by myself, with the support of Kasper Hancke and Annie Glud. I interpreted the data and wrote the manuscript with contributions from the co-author.

Chapter 2: Seasonal and spatial variations of benthic carbon and nitrogen fluxes in the Helgoland Mud Area (southern North Sea)

(submitted to *Limnology and Oceanography*)

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Abstract

Benthic carbon and nitrogen fluxes were quantified within the years 2012 to 2014 at different time series sites in the southern North Sea with the benthic lander NuSObs (Nutrient and Suspension Observatory). *In situ* incubations, sampling of macrofauna and pore water studies revealed considerable seasonal and spatial variations of carbon and nitrogen fluxes. In summer and autumn carbon fluxes were comparatively high (up to $-55.1 \text{ mmol m}^{-2} \text{ d}^{-1}$). At the end of the cold winter in 2012/2013 (water temperature $\sim 3 \text{ }^\circ\text{C}$) benthic carbon (2.0 to $-8.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) and nitrogen ($+0.2$ to $+0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$) fluxes were low and the pore water was depleted in ammonium. On the contrary, comparatively high carbon (6.1 to $-16.6 \text{ mmol m}^{-2} \text{ d}^{-1}$) and nitrogen ($+0.1$ to $+2.7 \text{ mmol m}^{-2} \text{ d}^{-1}$) fluxes were observed after the warm winter 2013/2014 (water temperature $\sim 7 \text{ }^\circ\text{C}$). Benthic macrofauna had a considerable impact on carbon fluxes, which was mostly related to large bodied species such as the suspension feeder *Ensis directus*. Tracer flux studies revealed that benthic fluxes were considerably enhanced by bioirrigation in autumn.

Estimated average annual rain rates of organic carbon and organic nitrogen to the seafloor are in the range of 5.0 to $11.8 \text{ mol C m}^{-2} \text{ a}^{-1}$ and 0.6 to $3.3 \text{ mol N m}^{-2} \text{ a}^{-1}$ respectively. Approximately 76 to 93 % of the organic bound carbon and 87 to 97 % of the organic bound nitrogen reaching the seafloor are recycled at the sediment-water interface. High rain rates to the sediment and high benthic fluxes suggest a close benthic-pelagic coupling.

Keywords: Benthic oxygen and nitrogen fluxes, In situ measurements, Benthic macrofauna, water column temperature, seasonal and spatial variations, benthic-pelagic coupling

1. Introduction

In shallow water regions, such as the coastal areas of the southern North Sea, nitrogen and carbon cycles are driven by a close benthic-pelagic coupling. Most of the organic matter which is produced via primary production in surface waters is transferred to the seafloor. Within surface sediments a major part of the organic matter is degraded and nutrients such as NH_4 or PO_4 are transported back into the water column, whereas only a small amount of organic carbon is buried within the sediment. The amount and the freshness of organic material reaching the seafloor can vary over seasonal and spatial scales and determine the structure of benthic communities and the geochemistry of the sediment (Berner 1980; Heip et al. 2001). In general, phytoplankton biomass production reaches a maximum in spring and autumn leading to an enhanced export of organic matter from the water column to the seafloor (Olesen and Lundsgaard 1995; Berelson et al. 2003). Physical and biogeochemical boundary conditions in the benthic environment (e.g. bottom water temperature, macrofauna, microbial activity) have a direct impact on mineralisation of organic matter, the transport of nutrients and vary considerably over seasonal cycles (Crill and Martens 1987; Thamdrup et al. 1998; Braeckman et al. 2014).

Oxygen is consumed directly or indirectly during the degradation of organic material and the total oxygen uptake (TOU) can be used as a proxy for benthic carbon mineralization of marine sediments (Canfield et al. 1993). Direct pathways include aerobic heterotrophic activity of benthic fauna and bacteria (Glud 2008). Indirect pathways include the oxidation of reduced solutes (e.g. Fe^{2+}), which are released into the pore water during the degradation of organic matter (Canfield et al. 1993). Accordingly high pore water nutrient concentrations build up within the sediment, leading to an efflux of nutrients into the water column. At the sediment water interface the influx of oxygen and efflux of mineralization products occurs via diffusion, but can be enhanced considerably by advective transport processes. In cohesive sediments (permeabilities $< 2 \cdot 10^{-11} \text{ m}^2$) advective pore water flushing by bottom water currents can be neglected (Huettel et al. 2014). Within these impermeable sediments benthic macrofauna plays an important role for an advective exchange of solutes between the sediment and the water column (Glud 2008).

The importance of benthic fauna on the benthic mineralization of organic matter and the exchange of solutes (e.g. nutrients) depends on the species functional traits, the size of the specimens and the sediment chemistry (Glud 2008). For example, bio-irrigators force burrow flushing and pore water transport (Kristensen et al. 2012) and have a pronounced effect on benthic respiration rates and the release of reduced solutes such as ammonium within anoxic sediments (Mermillod-Blondin et al. 2004; Braeckman et al. 2010). However, most of the studies which address the impact of benthic fauna on benthic nutrient cycles were carried out under controlled conditions

in the lab on single species (Glud 2008), whereas only few studies were carried out on whole benthic communities under *in situ* conditions (e.g. Forster et al. 1999). Considering the various physical and biogeochemical factors which influence the benthic environment, *in situ* studies are a prerequisite for a precise quantification of benthic carbon mineralisation rates and effluxes of nutrients (Viollier et al. 2003; Hammond et al. 2004).

In this study, benthic mineralisation of organic carbon and the reflux of nutrients (e.g. NH_4) from the sediments into the water column were investigated *in situ* with the benthic lander NuSObs (Nutrient and Suspension Observatory). For the southern North Sea benthic fluxes and pore water profiles of silicic acid, a less reactive species which is dominantly forced by abiotic first order dissolutions kinetics, were shown by Oehler et al. (submitted) at the same sampling sites. In this part we investigate the coupling between benthic macrofauna and benthic carbon and nitrogen fluxes over seasonal scales. Factors such as biomass and feeding type of benthic macrofauna, as well as the seasonal variability of faunal induced flushing of pore waters are considered. Therefore a temperate shallow water depositional site with fine grained organic rich sediments was investigated, at which strong seasonal variations and a pronounced impact benthic fauna can be expected. These results allow estimates about mass budgets of the carbon and nitrogen cycle of the southern North Sea, such as the amount of organic bound carbon and organic bound nitrogen which settle annually at the seafloor.

2. Material and Methods

2.1 Study site

The Helgoland Mud area is located in the southern German Bight and belongs to one of the few depositional areas in the North Sea (fig. 1). It stretches over 500 km² southeast of the island of Helgoland and consists mainly of impermeable organic rich sediments. Sediment deposition occurs due to a small scale eddy, which is driven by long-shore coastal currents, the discharge of the rivers Elbe and Weser and tidal dynamics (Hertweck 1983). Tidal currents can exceed 1 m s^{-1} within the upper 8 m of the water column (Forster et al. 1999). Hebbeln et al. (2003) gives a detailed geological description of the Helgoland Mud Area and reported sedimentation rates of 2.6 mm a^{-1} .

In the close vicinity of the Helgoland Mud area, biogeochemical and physical parameters of the water column, such as the temperature, nutrients and occurrence of phytoplankton blooms, are being measured since 1962 at the time series site Helgoland roads. Annual variations of the water column temperature are strong with yearly minimum temperatures of approximately -1 to 6 °C, maximum temperatures of about 16 to 20 °C and mean annual water temperatures of about 9 to 11

°C (Wiltshire and Manly 2004). Annual primary production was estimated to be $21.73 \text{ mol C m}^{-2} \text{ a}^{-1}$ (Howarth et al. 1993) with highest values in spring (e.g. $0.04 - 0.5 \text{ mol C m}^{-2} \text{ a}^{-1}$, Colijn et al. 1990) and lowest winter production reached in October/November ($<0.017 \text{ mol C m}^{-2} \text{ a}^{-1}$) (Beusekom and Diel-Christiansen 1994). In winter primary production is limited by the availability of light in the water column (Reid et al. 1990). Bottom water nitrate concentrations of around $40 \mu\text{mol l}^{-1}$ can occur due to the high freshwater input into the German Bight (Brockmann et al. 1988). In spring an exponential growth of phytoplankton occurs, as soon as light availability reaches a critical level (Sverdrup 1953; Gieskes and Kraay 1977). Within the German Bight the spring bloom occurs during the second half of April and is dominated by diatoms and limited by the availability of Si(OH)_4 in the water column (Radach et al. 1990; Joint and Pomroy 1993). In May to June the diatom bloom is followed by a second phytoplankton bloom which is dominated by flagellates (dominantly *Phaeocystis* sp.), whereas its size is dependent on the availability of N and P nutrients in the water column (Gieskes and van Bennekom 1973; Beusekom and Diel-Christiansen 2009). In summer one or two additional diatom blooms occur which are followed by flagellate blooms. The occurrence and species composition of these algal blooms are dominantly forced by the nutrient availability and nutrient ratios in the water column (Beusekom and Diel-Christiansen 2009). For example, long term measurements of plankton communities at Helgoland Reede revealed a ten-fold increase in flagellates between 1962 and 1984 accompanied with a change in nitrate concentrations (Reid et al. 1990).

Sediments of the German Bight contain one of the highest organic carbon contents (up to 1.9 %) of the North Sea and are rich in bioavailable nitrogen (de Haas et al. 1997; Kröncke et al. 2004). The high contents of labile organic matter result in high remineralisation rates within the sediments. Within the German Bight Forster et al. (1999) measured benthic oxygen influxes of up to $-42 \text{ mmol m}^{-2} \text{ d}^{-1}$ which belong to the highest values reported for the coastal waters of the North Sea. Their study suggested that bioirrigation is the main factor regulating the consumption of oxygen. In summer high mineralisation rates and low oxygen penetration depths result in a high efflux of ammonium and nitrate, which might contribute to more than 75 % of the nitrogen requirements of planktonic algae (Lohse et al. 1995).

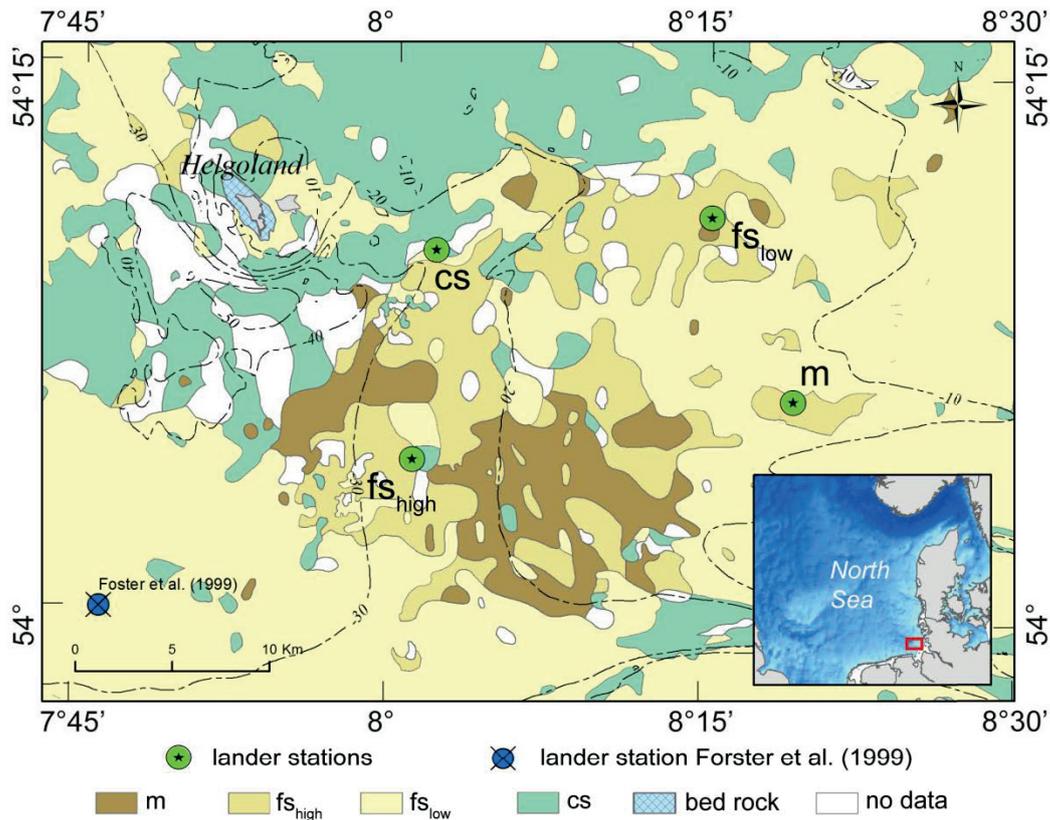


Figure 1: The benthic lander NuSObs (Nutrient and Suspension Observatory) was deployed on four different stations in the years 2012, 2013 and 2014. All stations differed in terms of fine grained sediment fraction (diameter $<63 \mu\text{m}$). On stations TS2 and TS3 seasonal studies were conducted. In the close vicinity of lander stations, Forster et al. (1999) observed high oxygen fluxes which were considerably influenced by benthic macrofauna.

2.2 Investigations of benthic fluxes, transport processes and macrofauna

The *in situ* sediment incubations were carried out with the benthic lander system NuSObs (Nutrient and Suspension Observatory). The lander (KUM, Kiel) was designed for harsh environments and strong tidal currents, because other lander systems had stability problems in the southern German Bight in prior studies (Forster et al. 1999). Two “Mississippi” type chambers (Witte and Pfannkuche 2000; Tengberg et al. 2004) were mounted to the lander frame and allowed us to measure a combination of (1) nutrient, oxygen and tracer fluxes, (2) sediment parameters (TOC, CN, grain size) and (3) to sample the benthic macrofauna within each chamber. The benthic lander was deployed on most stations for 24 to 48 hours at the seafloor.

After the positioning of the benthic lander, each chamber enclosing an area of 400 cm^2 was driven slowly by a motor into the sediment, without disturbing the sediment surface. Each chamber was equipped with an oxygen optode (AanderaTM/4330), a pH sensor (AMT/OEMTM) and a syringe sampler. Each syringe sampler consisted of seven sampling ports and one injection port. During the

incubation seven water samples (each having a volume of 50 ml) were obtained from each chamber every two to three hours. On some stations a potassium bromide tracer was injected during the start of the incubation into the overlying bottom water. Before the retrieval of the lander a shutter was moved underneath each chamber, which allowed us to sample the incubated bottom water, the sediment and the benthic macrofauna.

After the recovery of the lander the volume of the incubated bottom water was determined. Each obtained water sample from the syringe sampler was filtered and split into half. One half was frozen on board at -80 °C and the other half was stored in a refrigerator at 4 °C. After returning to the lab, nutrient analyses (ammonium, nitrate and nitrite) were carried out on the frozen samples with a segmented flow analyzer (Seal™ Analytical Autoanalyzer) (accuracy $\pm 2 \mu\text{mol l}^{-1}$). Bromide was measured on unfrozen samples via titration according to Grasshoff et al. (2009) .

Surface sediments were sampled from each chamber and analysed for grain sizes, porosities, total organic carbon contents (TOC) and C/N ratios. Grain sizes were determined with a coulter laser diffraction size analyzer. Samples for TOC measurements were treated with hydrochloric acid in order to remove carbonates and then measured with an ELTRA CS-2000 (Eltra™ Element Analyzers). C/N ratios were determined by a VARIO EL (Elementar™). Porosity was determined by weight loss after freeze drying.

The remaining sediment of each chamber during the cruises HE395, HE412 and HE417 was sieved on board over a 500 μm mesh size. Samples were fixed in 4 % buffered formaldehyde-seawater solution. In the lab, samples were stained with Bengal rose and all macrofauna was sorted and identified to the lowest possible taxonomic level, counted and biomasses were determined (wet weights). Each species was classified into functional feeding groups (surface deposit feeders, subsurface deposit feeders, suspension feeders, omnivores, hyperbenthos predators, predators, interface feeders) based on available literature (e.g. Pearson and Rosenberg 1978; Fauchald and Jumars 1979; Dauwe et al. 1998; Queirós et al. 2013).

Besides the two benthic chambers a multiparameter CTD (Sun&Sea™/CTD115M) and a 600 kHz ADCP (Teledyne RD Instruments™/Workhorse) were mounted to the lander frame. An oxygen optode (Aandera™/4330) was located about one meter above the seafloor.

2.3 Pore water and sediment samples

Pore water and sediment samples were collected with a multicorer (Barnett et al. 1984), equipped with eight acrylic tubes with an inner core diameter of 9.5 cm. After recovery all cores were sampled on board in a temperature controlled room under *in situ* temperatures. Within depth intervals of one to two centimeters in the sediment, about 4 ml of pore water were obtained by Rhizon sampling (Seeberg-Elverfeldt et al. 2005) within each depth. The overlying water was sampled with a syringe and subsequently filtered with a cellulose acetate filter (0.45 μm pore size). Pore water samples were frozen subsequently after recovery on the ship at $-80\text{ }^{\circ}\text{C}$. After returning the samples to the lab ammonium, nitrate and nitrite were measured with a segmented flow analyzer (Seal™ Analytical Autoanalyzer) (accuracy $\pm 2\ \mu\text{mol l}^{-1}$).

2.4 Computation of benthic carbon and nitrogen fluxes

Due to the shallow water depths of the coastal waters of the German Bight (<30 m) a substantial amount of primary produced organic matter might settle at the seafloor (Jørgensen et al. 1990; Beusekom et al. 1999). After deposition, organic bound carbon and organic bound nitrogen are either mineralized and transported back into the water column, or buried within the sediment. As a consequence, the sum of the burial of organic bound carbon and nitrogen and the reflux of dissolved carbon and nitrogen, yields the total rain rate of carbon and nitrogen to the seafloor, respectively (eq. 1.1, 1.2).

$$POC_{rain} = C_{flux} + C_{acc} \quad (1.1)$$

$$PON_{rain} = N_{flux} + N_{acc} \quad (1.2)$$

with

$POC_{rain}; PON_{rain}$: flux of organic carbon (POC) or of organic nitrogen (PON) reaching the seafloor ($\text{mol m}^{-2} \text{a}^{-1}$),

$C_{flux}; N_{flux}$: Carbon mineralisation rate (C_{flux}) or nitrogen effluxes (N_{flux}) across the sediment water interface measured during *in situ* incubations with the benthic lander ($\text{mol m}^{-2} \text{a}^{-1}$),

$C_{acc}; N_{acc}$: Carbon (C_{acc}) or nitrogen (N_{acc}) accumulation within the sediment ($\text{mol m}^{-2} \text{a}^{-1}$).

Sediment accumulation rates are calculated with equation (2):

$$C_{acc}; N_{acc} = (1 - \emptyset) * w * s * TOC; TON \quad (2)$$

with

$TOC; TON$: weighted percentage of particulate organic carbon (TOC) or organic nitrogen (TON) within the sediment,

\emptyset : porosity,

w : dry sediment density ($kg\ m^{-3}$),

s : sedimentation rate ($m\ a^{-1}$).

Sediment accumulation rates of carbon (C_{acc}) and nitrogen (N_{acc}) were calculated in $kg\ m^{-2}\ a^{-1}$ and then converted into $mol\ m^{-2}\ a^{-1}$ for equation 1.1 and 1.2. The benthic oxygen and nitrogen effluxes were calculated from the slopes of linear regressions of the change in concentration within the chamber for each solute versus time with the statistical software R. The slope of the regression line was multiplied with the height of the water column incubated in the chamber to calculate the flux of oxygen and nitrogen across the sediment water interface.

For the calculation of total oxygen uptake rates (TOU) a linear regression was only applied over the first 12 hours of the incubation. The calculated oxygen fluxes were then transferred into carbon equivalents using the Redfield ratio oxygen:carbon = 138:106 (Anderson and Sarmiento 1994). Burial rates were calculated by assuming sedimentation rates of $0.0026\ m\ yr^{-1}$ (Hebbeln et al. 2003) and a sediment density of $2650\ kg\ m^{-3}$ (Schulz and Zabel 2006). Porosity, organic carbon and organic nitrogen contents were calculated from average values of all measured values of respective sediment types.

The permeability of the sediment was calculated after the 15th percentile of the grain size distribution (d15) according to Soulsby (1997) and modified by Puls (2014, pers. comm.) (eq. 3):

$$K_P = \frac{0.0011 * D_{15}^2}{1.36 * 2.6} \quad (3)$$

Calculations on the hydraulic permeability of the sediments showed that most of the sediments are impermeable and wave and current induced pore water flows can be neglected (Huettel et al. 1996; Huettel and Rusch 2000). Only on station He395-56/CS the sediment type is semi-permeable and wave induced pore water flows might take place. Because our benthic chamber measurements

do not consider current and wave induced pore water flows (Viollier et al. 2003), oxygen and ammonium fluxes might be underestimated on that station.

2.5 Estimation of macrofaunal respiration

To estimate the macrofaunal respiration, biomasses were determined. Wet weights of each species were converted to ash free dry weight (AFDW) by using conversion factors (Brey 2001). Ash free dry weights were then converted to mg of organic carbon, assuming that for all species 50 % of the AFDW is carbon. Individual respiration rates were calculated according to the equation given in Mahaut et al. (1995) for shallow water macrofauna valid for the temperature range 15 to 20 °C:

$$R = 0.0174W^{0.844} \quad (4)$$

where R is the individual respiration rate (in day^{-1}) and W is the individual weight (in mg C). Respiration was corrected for temperature assuming a Q_{10} of 2 and then converted to oxygen consumption assuming a respiratory quotient of 0.85 (Hargrave 1973).

3. Results

In situ incubations with the benthic lander NuSObs were carried out during 5 cruises within the years 2012 to 2014 in the southern German Bight. The sampling sites (fig. 1, tab. 1) differed in terms of grain size, total organic carbon content and benthic macrofauna and could be classified into four different sediment types: (1) mud (m), (2) fine sand with a high content of fine grained sediment fractions ($f_{s_{\text{high}}}$), (3) a fine sand with a low content of fine grained sediment fractions ($f_{s_{\text{low}}}$), as well as (4) a coarse grained sediment type (cs). On time series station TS2 and TS3 the same site was revisited during different seasons in order to consider seasonal variations of benthic oxygen and nitrogen fluxes.

Station/ Acronym	Latitude	Longitude	Month year	W.T. (°C)	C	mf	Sed (Figge)	Permeability (m ²)	TOC (%)	C/N	O ₂ flux	NH ₄ ⁺ flux	NO ₂ ⁻ flux
He386-1/M	54°06'01.8"	8°19'04.1"	Aug 12	18	1	-	m	3.45E-14	1.7	14.3	6.6	7.2	0.07
					2	-	m	6.04E-14	1.1	16.8	17.4	10.7	0.08
He383-46/TS2	54°04'09.5"	8°01'07.7"	June 2012	14	1	-	fS _{high}	1.54E-13	0.8	22	25.1	3.8	0.03
					2	-	fS _{high}	1.06E-13	0.9	20.4	15.5	-	-
He395-38/TS2	54°04'13.2"	8°01'05.4"	March 2013	3	1	+	fS _{high}	1.05E-13	0.7	25.9	8.2	0.3	-
					2	+	fS _{high}	4.56E-14	0.8	21.4	2	0.2	-
He412-27/TS2	54°03'45.0"	8°01'00.6"	Nov 13	13	1	+	fS _{high}	6.02E-14	0.7	23.1	16.8	1.2	0.01
					2	+	fS _{high}	7.26E-14	0.7	22.1	21.5	2.3	0.04
He417-38/TS2	54°03'49.3"	8°00'56.5"	March 2014	6	1	+	fS _{high}	3.45E-14	1.4	14.2	6.1	0.1	-
					2	+	-	-	-	-	-	-	-
He386-33/TS3	54°11'04.2"	8°15'09.0"	Aug 12	18	1	-	fS _{low}	5.67E-13	0.6	31.1	33.2	3.3	0.07
					2	-	-	-	-	-	-	-	-
He412-38/TS3	54°11'04.8"	8°15'09.0"	Nov 13	11	1	+	fS _{low}	2.68E-13	0.4	31.7	47.2	7.6	0.02
					2	+	fS _{low}	1.05E-13	0.5	24.3	55.1	2.2	-
He417-54/TS3	54°11'02.4"	8°15'03.6"	March 2014	7	1	+	fS _{low}	7.70E-12	0.3	33.7	16.6	2.7	-
					2	+	fS _{low}	1.44E-12	0.5	32.1	-	-	-
He395-56/cs	54°10'02.4"	8°01'54.0"	March 2013	3	1	-	cs	1.12E-11	0.5	18.8	-3	0.6	-
					2	-	-	-	-	-	-	-	-

Table 1: The sampling sites at which the benthic lander NuSObs was deployed in different seasons in the years 2012 to 2014. Benthic oxygen (O₂ flux in mmol m⁻² d⁻¹) and nitrogen fluxes (NH₄ and NO₂ flux in mmol m⁻² d⁻¹) were measured *in situ* by benthic chamber incubations. Sediment samples were collected from respective benthic chambers after recovery of the lander. Abbreviations: C: chamber (1 or 2), W.T.: water temperature (°C), mf: available data about benthic macrofauna (+), Sed (Figge): sediment type which was classified after Figge (1981), TOC: total organic carbon (%), C/N: ratio between carbon (C) and nitrogen (N), (-) = no data.

3.1 Seasonal and spatial variations of oxygen fluxes

During each incubation oxygen was always consumed within the benthic chambers (fig. 2), as indicated by significantly linear decreasing oxygen concentrations with time ($r^2 = 0.80$ to 0.99). The initial decrease in oxygen concentrations quantifies the total O₂ exchange rate in between the water column and the sediment, including aerobic heterotrophic microbial and faunal mineralization of organic matter, fauna respiration and the oxidation of reduced solutes (Rasmussen and Jørgensen 1992; Glud 2008).

Our time series measurements revealed that oxygen fluxes follow the seasonal cycle with highest flux rates in June 2012, August 2012 and November 2013 and lowest flux rates in March 2013 and March 2014. Seasonal variations in flux rates were related to variations of the bottom water temperature. On time series station TS2 (fig. 2) we observed high oxygen fluxes in June 2012 (15.5 to 25.1 mmol m⁻² d⁻¹) and November 2013 (16.8 to 21.5 mmol m⁻² d⁻¹) and comparatively warm water temperatures of 14 °C and 13 °C, respectively (tab. 1). In March 2013 lowest oxygen fluxes of -2.0 mmol m⁻² d⁻¹ were measured in conjunction with lowest water column temperatures of 3 °C. In

March 2014 slightly higher oxygen fluxes ($8.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) and warmer water temperatures ($6 \text{ }^\circ\text{C}$) were observed. Time series station TS3 showed higher oxygen fluxes ($33.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) and higher water column temperatures ($18 \text{ }^\circ\text{C}$) in August 2012. Highest oxygen fluxes were observed in November 2013 (47.2 to $55.1 \text{ mmol m}^{-2} \text{ d}^{-1}$), which was followed by lower fluxes in March 2014 ($-16.6 \text{ mmol m}^{-2} \text{ d}^{-1}$). On both time series stations the sediment composition (TOC content, grain size distribution) did not show any seasonal variations.

Over spatial scales oxygen fluxes can be related to TOC contents in summer 2012. On station He386-1/M (fig. 2, red) lowest oxygen fluxes (6.6 to $17.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) and highest TOC contents (1.1 to 1.7 %) were observed. In comparison to station He386-1/M, oxygen fluxes were slightly higher (15.5 to $25.1 \text{ mmol m}^{-2} \text{ d}^{-1}$) on station He383-46/TS2 (fig. 2, blue) where lower TOC contents (0.8 to 0.9 %) were observed. The highest oxygen flux ($33.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed on station He386-33/TS3 which showed comparatively low TOC contents (0.5 %).

The spatial variability of macrofauna community structure and estimated respiration rates differed among stations and time. On time series site TS2 (Appendix A) increasing respiration rates of macrofauna species were found between March 2013 (2.11 to $3.07 \text{ mmol m}^{-2} \text{ d}^{-1}$) and November 2013 (6.12 to $8.75 \text{ mmol m}^{-2} \text{ d}^{-1}$), which decreased remarkably to $< 1 \text{ mmol m}^{-2} \text{ d}^{-1}$ in March 2014 (Fig. 8). The enhanced respiration in November 2013 coincided with an overall increase in biomass and abundance. While *Echinocardium cordatum* and *Notomastus latericeus* (chamber 1) just as anthozoa and *Nephtys hombergii* (chamber 2) contributed most to the oxygen consumption in March 2013, the increase in biomass of *Abra alba*, *Ophiura ophiura* and *Amphiura filiformis* attributed to the higher respiration rates in November 2013. On time series station TS3 (Appendix B) mainly large bodied species (*Ensis directus*, *Asterias rubens*, *Liocarcinus holsatus*) contributed to the large oxygen consumption. In November 2013, *Ensis directus* contributed in chamber 1 and chamber 2 to 57 % and 96 % of the total calculated respiration rates of $11.09 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $14.00 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively. In March 2013, it contributed in chamber 1 and chamber 2 to 86 % and 91 % of a total calculated respiration rate of 17.70 and $15.22 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively.

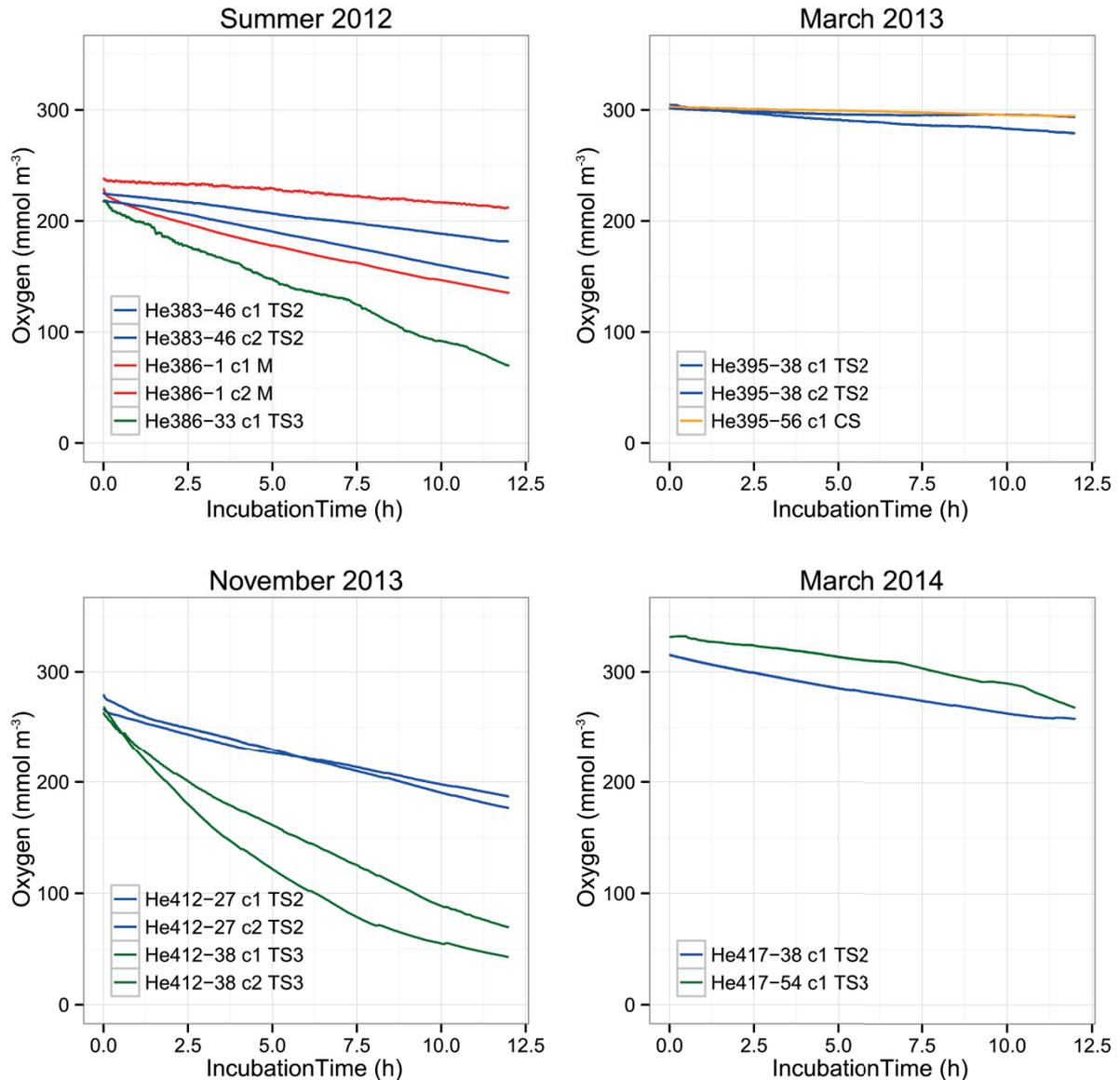


Figure 2: Oxygen flux measured *in situ* within the benthic chambers. Strong seasonal variations were observed with highest fluxes in summer 2012 and November 2013 and lowest fluxes in March 2013 and 2014. On some stations parallel measurements were carried out with two benthic chambers (c1=chamber 1, c2=chamber 2).

In order to account for possible faunal induced transport of solutes between the water column and the sediment (bioirrigation) a bromide tracer according to Forster & Graf (1995) was injected into the benthic chamber on three different sites (fig. 3). Enhanced transport along the sediment water boundary is indicated by a stronger decline in bromide concentrations with time. For a better visualization of the flux rates, bromide concentrations were normalized with respect to the initial concentration and are shown as percent versus time.

We observed a clear decrease in bromide concentrations in November 2013 (fig. 3, A+B, $r^2 = 0.55 - 0.85$, influx: 0.1 to $0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) which indicates significant exchange of chamber water and

pore water during that month. In contrast we did not observe any change in bromide concentrations during March 2013 (fig. 3, C, $r^2=0.35$), whereas the scatter is caused by the precision of the measurement.

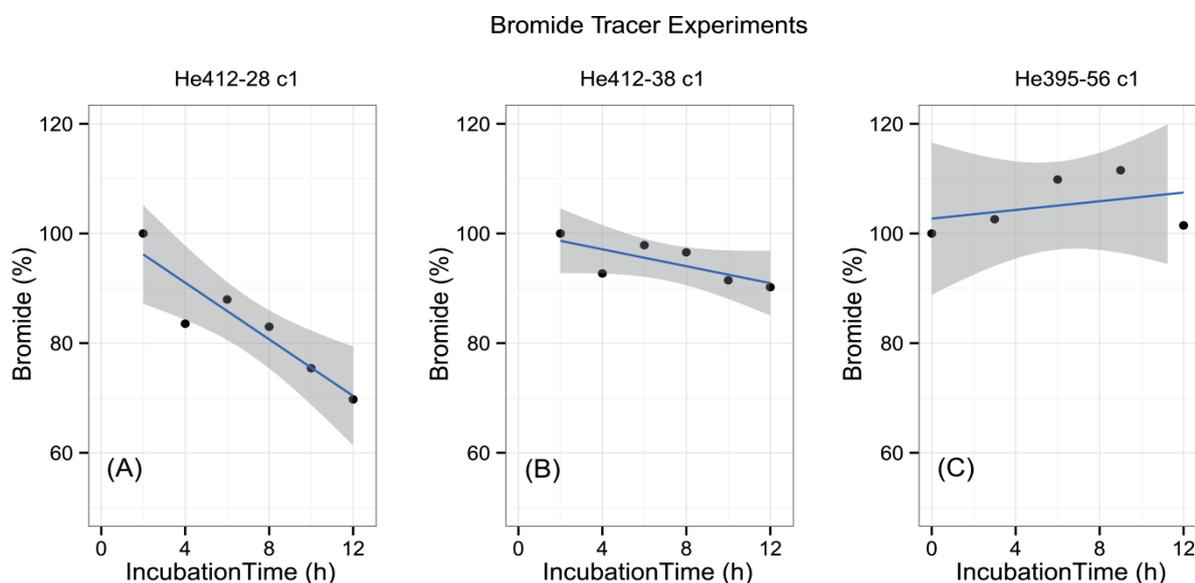


Figure 3: A bromide tracer was injected into the benthic chamber at three different sites. A significant bromide flux (A, B) in November 2013 indicates an exchange of chamber water and pore water. In March 2013 (C) no bromide flux was detectable.

3.2 Benthic nitrogen fluxes

Nitrogen fluxes of ammonium (fig. 4, A), nitrite (fig. 4, B) and nitrate (fig. 4, C) revealed a similar spatial and seasonal trend, as it was observed for oxygen. During chamber incubations we observed on every sampling site significantly linear increasing ammonium concentrations with time, which indicates an efflux of ammonium from the sediment into the water column. The sediments thus acted as a source of ammonium which is supported by pore water studies (fig. 5, see below). Nitrite (fig. 4, B) effluxes were observed on some stations in summer 2012 and November 2013. Significant nitrate fluxes were only observed in November 2013 (fig. 4, C).

On time series station TS2 (fig. 4, blue) we observed a strong seasonal pattern in ammonium and nitrite fluxes with highest effluxes of ammonium in summer 2012 ($3.8 \text{ mmol m}^{-2} \text{ d}^{-1}$), lower effluxes in November 2013 (1.2 to $2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$) and lowest effluxes in the cold winter March 2013 (0.2 to $0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$) and March 2014 ($0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$). Nitrite effluxes were observed to some extent in June 2012 and August 2012 as well as in November 2013. In March 2013 and March 2014 no significant nitrite fluxes were observed or nitrite concentrations were below analytical detection limit. On time series station TS3 (fig. 4, green) the seasonal variations were less distinct. No significant seasonal variations of ammonium effluxes between summer 2012 ($3.3 \text{ mmol m}^{-2} \text{ d}^{-1}$),

November 2013 (2.2 to $7.6 \text{ mmol m}^{-2} \text{ d}^{-1}$) and March 2014 ($2.7 \text{ mmol m}^{-2} \text{ d}^{-1}$) were observed. However we measured an efflux of nitrite in summer 2012 and November 2013, whereas in March 2014 no nitrite flux was detected.

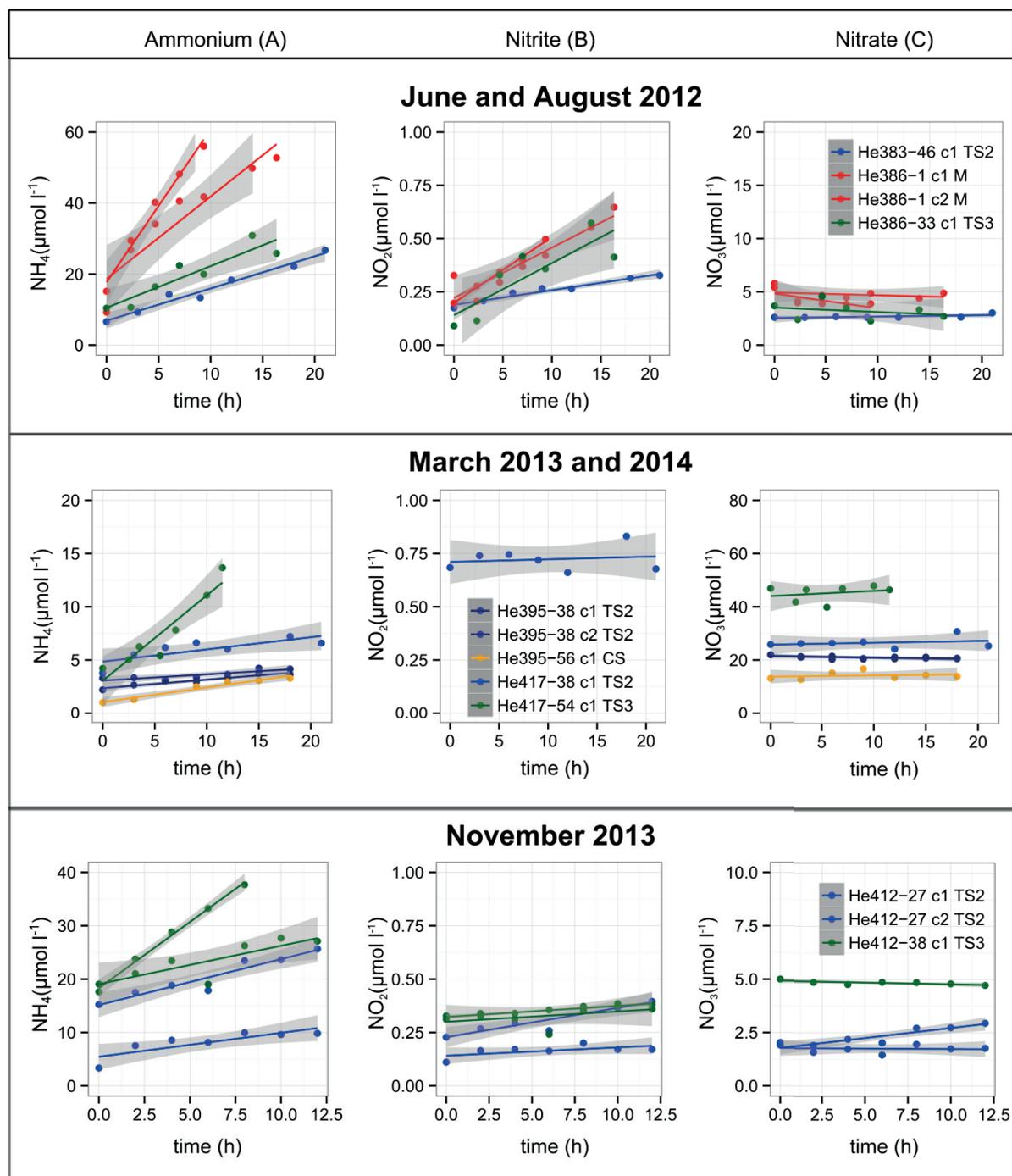


Figure 4: Ammonium (A), nitrite (B) and nitrate (C) concentrations within the benthic chambers vs incubation time. Ammonium concentrations always showed significantly linear increasing concentrations with time indicating an efflux of NH_4 out of the sediment into the bottom water. Nitrite concentrations either increased with time, showed no trend or were below detection limit. Nitrate concentrations stayed nearly constant during the chamber incubations.

Pore water concentrations of ammonium and bottom water concentrations of ammonium and nitrate showed a seasonal pattern. Highest ammonium concentrations were observed in summer 2012 and November 2013 ($\sim 20 \mu\text{mol l}^{-1}$) and lowest concentrations in March 2013 and 2014. In summer high ammonium pore water concentrations and high ammonium effluxes were observed on station He386-1/M (fig. 5, tab. 1). In March 2013 the pore water was depleted in ammonium and below detection limit within the upper 5 cm of the sediment at station He395-38/TS2. The low NH_4 pore water concentrations occurred in conjunction with low NH_4 fluxes during that season. In November 2013 pore water concentrations of ammonium were comparatively high. In March 2014 ammonium pore water concentrations were especially on station He417-54/TS3 extremely high. During this season highest nitrate bottom water concentrations of up to $40 \mu\text{mol l}^{-1}$ were observed on station He417-54/TS3. The pore water profile of nitrate indicated an influx of NO_3 into the sediment on that station (fig. 5, b).

In general, nitrate fluxes were not observed in incubation experiments or in pore water profiles. The nitrate pore water profile of station He383-46/TS3 (fig. 5, b) is shown as a typical profile in which no nitrate fluxes were indicated.

Comparing ammonium pore water profiles with silicic acid pore water profiles at the same stations (silicic acid profiles in Oehler et al., submitted), reveal that the pore water concentrations of ammonium ceased significantly within the upper 15 cm of the sediments in March 2013, whereas silicic acid concentrations were comparatively high during that season. A much stronger seasonal impact on ammonium pore water concentrations, when compared to silicic acid, was thus observed.

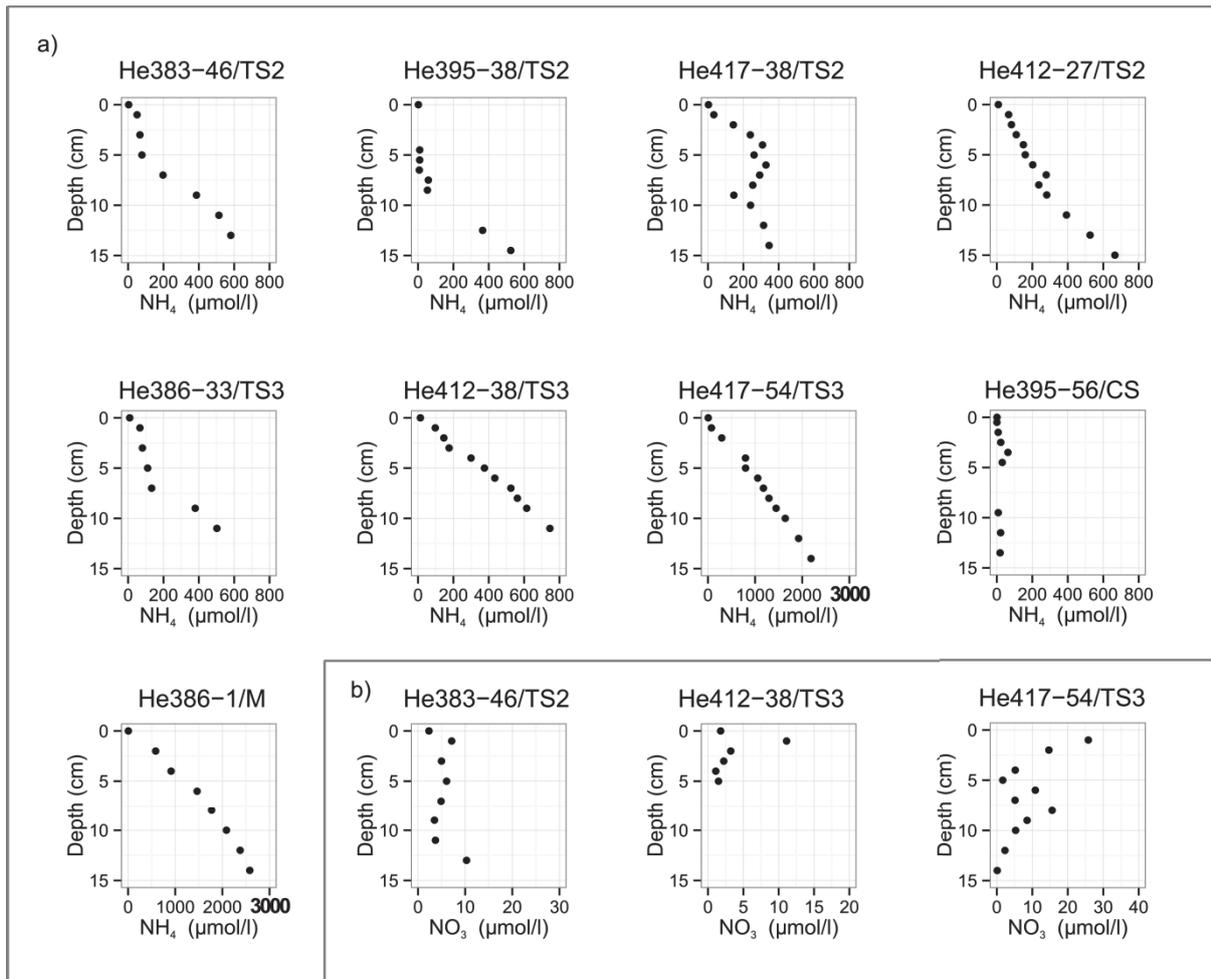


Figure 5: Pore water profiles of ammonium (a) and nitrate (b). Nitrate profiles are only shown from selected stations. Besides an influx on station He412-38/TS3 and He417-54/TS3, no nitrate fluxes were indicated in pore water profiles (e.g. He383-46/TS2).

The relationship between the remineralisation of organic matter and the concurrent release of ammonium is reflected in Redfield ratios (Redfield et al. 1963). In figure 6 the black line indicates the Redfield ratio of 106 moles of carbon vs 16 moles of nitrogen. Our *in situ* measured oxygen and ammonium fluxes followed to some extent the Redfield ratio. On some stations nitrogen fluxes were slightly lower. Furthermore outliers were observed on the muddy station He386-1/M, on which highest ammonium fluxes were observed (fig. 6, green marked). On this station the presence of fresh phytoplankton material was indicated during measurements of biogenic silica in the lab.

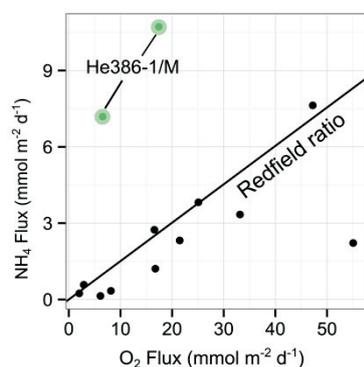


Figure 6: The oxygen flux and ammonium flux followed the Redfield ratio of 106:16:1 in which 106 moles of oxygen are required to release 16 moles of ammonium. The black line indicates the Redfield ratio (106/16). Outliers were observed on station He386-1/M (green dots) on which comparatively high ammonium fluxes were measured.

4. Discussion:

4.1 Seasonal and spatial variations in oxygen and nitrogen fluxes

In temperate coastal regions such as the southern German Bight, primary production in the water column and the benthic mineralisation of organic matter may vary significantly over seasonal and spatial scales. Distinct phytoplankton blooms occur in spring and at the end of summer, producing large amounts of organic material (Radach et al. 1990; Reid et al. 1990). Seasonal variations in physical and biological factors, such as the bottom water temperature and the macrofauna are known to have a crucial impact on the benthic mineralisation of organic matter and the associated reflux of nutrients (Thamdrup et al. 1998; Soetaert et al. 2000).

Over seasonal cycles variations in oxygen and to some extent in ammonium fluxes occurred in conjunction with variations in the water column temperature on time series station TS2 (fig. 7). The water column temperature can be a dominant factor regulating organic matter mineralization (Crill and Martens 1987; Thamdrup et al. 1998). Within the Belgian part of the southern North Sea an increase in water column temperature of about 10 °C, can double organic matter degradation rates in the sediment (Provoost et al. 2013) and highest oxygen consumption in summer were related to maximum water column temperatures (Braeckman et al. 2014). In this context temperature can regulate abiotic processes such as the diffusive exchange of solutes (e.g. oxygen, ammonium) along the sediment water interface (Yuan-Hui and Gregory 1974; Boudreau 1997), microbial oxygen consumption rates (Arnosti et al. 1998) or benthic faunal activities (Maire et al. 2007; Braeckman et al. 2010).

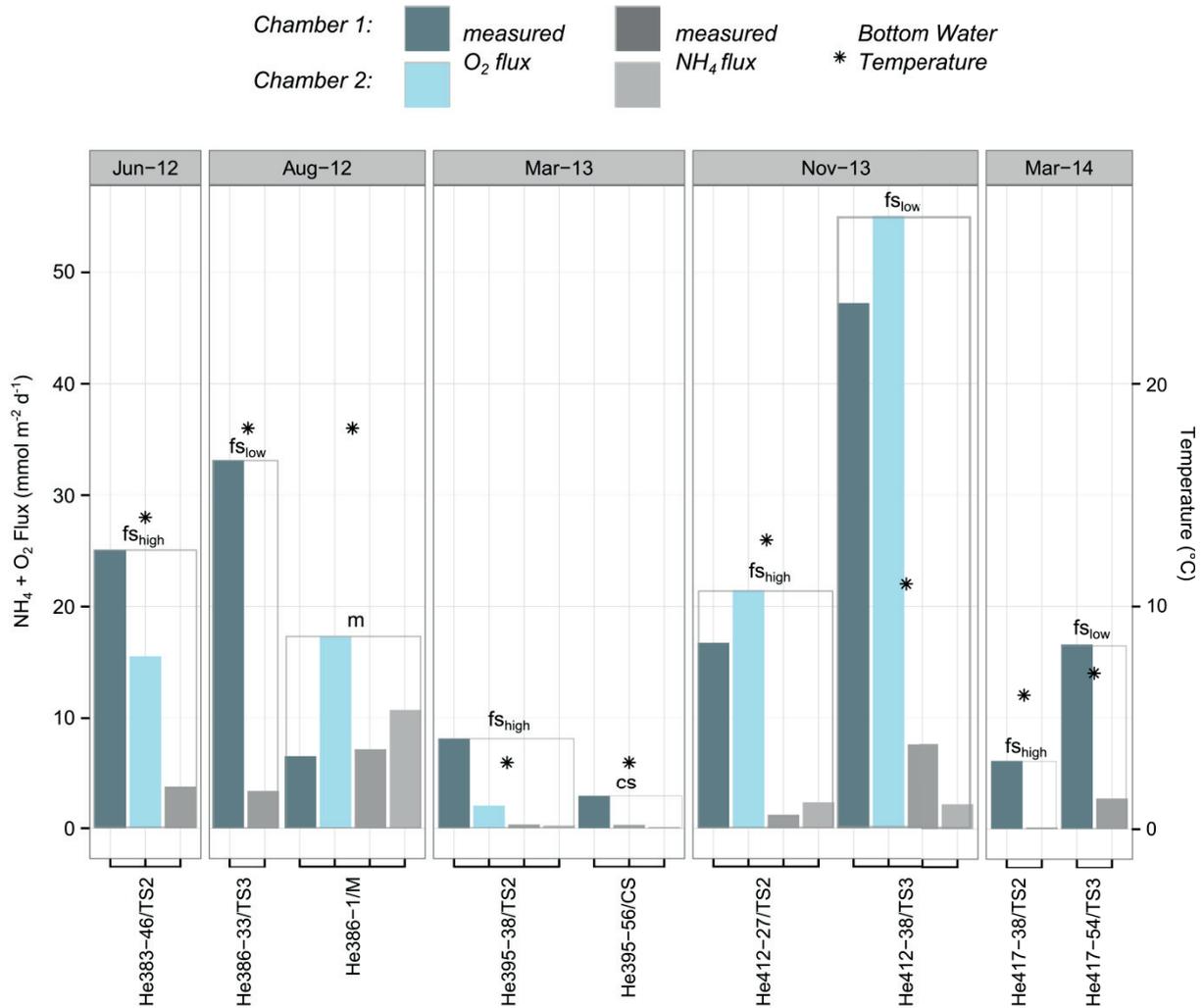


Figure 7: Oxygen (blue) and ammonium (grey) fluxes measured with the benthic lander NuSObs show significant seasonal and spatial variations. Seasonal variations correlate with the bottom water temperature (dots). On time series site TS2 fluxes were in general lower when compared to time series site TS3. All flux measurements carried out with chamber 1 are shown in darker colours (O₂=dark blue, NH₄=dark grey) and all fluxes measured with chamber 2 are shown in brighter colours (O₂=bright blue, NH₄=bright grey).

Besides the water column temperature, the timing of the annual deposition of organic matter (e.g. after a spring bloom) at the seafloor might be an important factor regulating benthic mineralisation rates. Spring phytoplankton blooms occur within the second half of April and in May to June in the German Bight (Beusekom and Diel-Christiansen 1994, 2009). High benthic mineralisation rates in summer 2012 (June and August) might be forced by the input of high quality particulate organic matter into the benthic environment. Especially ammonium effluxes tend to follow deposition of phytoplankton blooms, due to the subsequent degradation of labile nitrogen rich compounds of organic matter after deposition at the seafloor (Jensen et al. 1990; Grenz et al. 2000; Braeckman et al. 2014). High ammonium fluxes on station He386-1/M might be explained by the settling of fresh phytoplankton. Fresh phytoplankton was indicated from laboratory experiments on biogenic silica on that station. In August phytoplankton growth reaches in general another

maximum (Radach et al. 1990), whereas production declines to its annual low by October to November (Radach et al. 1990; Beusekom and Diel-Christiansen 1994, 2009). High benthic mineralisation rates in November 2013 indicate proceeding benthic mineralisation of organic matter, whereas primary production in the water column already ceased. Low benthic mineralisation rates in March might be related to the “harshness” of the winter. After the cold winter 2012/2013 benthic mineralisation rates of organic carbon were low, ammonium fluxes nearly absent and pore waters highly depleted in ammonium. After the warm winter 2013/2014 high benthic mineralisation rates of organic carbon, high ammonium fluxes and high ammonium pore water concentrations were observed. Variations might be related to a higher metabolic activity of benthic macrofauna in the water column and a higher food supply from the water column to the seafloor, as the better weather conditions might have triggered phytoplankton blooms earlier in the year.

Spatial variations in oxygen and ammonium fluxes might be related to the sediment type and the benthic macrofauna (see below). When compared to time series station TS2, higher oxygen fluxes on time series station TS3 occurred in conjunction with a lower fine grained sediment fraction ($d < 63 \mu\text{m}$) within the sediment. Furthermore considerable variations of benthic species and abundance were observed between TS2 and TS3 which might force spatial variations in benthic carbon and nitrogen fluxes.

In general no nitrate fluxes were measured during incubations or indicated in the pore water profiles. In winter, low to absent denitrification rates are caused by low water column temperatures. In summer denitrification is in general inhibited by due to a low oxygen and nitrate availability (Canfield et al. 2005). In oxygen deficient sediments denitrification is often reduced due to sulfide inhibition of nitrifying bacteria or inhibition of coupled nitrification-denitrification (Joye and Hollibaugh 1995; Eyre and Ferguson 2002). This is supported by Lohse et al. (1995), who showed that especially in summer, due to high mineralization rates and low oxygen penetration depths, only minor nitrate transformations occur and that the dominant contributor to the nitrogen flux is ammonium within the southern German Bight. In autumn, coupled nitrification-denitrification occurs in general due to a higher oxygen and nitrogen availability than in summer. Nitrification might have been observed on station He412-27/TS2 indicated by increasing nitrate concentrations with time and denitrification might have been observed on station He412-38/TS3 indicated by decreasing nitrate concentrations with time (fig. 4) in November 2013.

4.2 Impact of benthic macrofauna on benthic oxygen fluxes

Fauna-induced irrigation within the anoxic sediments of the Helgoland Mud Area should have a pronounced effect on benthic oxygen and ammonium fluxes. Inflow of oxygen rich water stimulates microbial mineralisation and oxidation of reduced solutes along burrow walls and transports reduced solutes such as NH_4 out of the sediment (Aller 2001; Glud 2008; Kristensen et al. 2012).

On time series station TS2 seasonal variations in oxygen and ammonium fluxes might be explained by seasonal variations in diversity, biomass and abundances of benthic macrofauna. Calculated respiration rates followed the seasonal cycle with lowest rates in March 2013 and March 2014 and highest rates in November 2013 (fig. 8). Especially due to the cold winter 2012/2013 measured oxygen fluxes of $2.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ (fig. 7) were in a similar range of the calculated respiration rates $2.11 \text{ mmol m}^{-2} \text{ d}^{-1}$ on station He395-38/TS2 (chamber 2) in March 2013. In November 2013 an increase in measured oxygen fluxes might partly be explained by the increase in calculated macrofauna respiration rates caused by increasing biomass of the benthic macrofauna. However calculated respiration rates considerably underestimated measured fluxes. Biomass does not consider faunal induced transport of solutes along the sediment-water boundary (e.g. bioirrigation) (Glud 2008). Bromide tracer flux studies (fig. 3) indicated an advective exchange of solutes along the sediment-water boundary. Differences between calculated respiration rates and measured oxygen fluxes might thus be explained by fauna mediated irrigation of the sediment (Glud 2008). The high water column temperatures in November 2013 probably attributed to a higher food supply governing burrowing and deposit-feeding activities and metabolic rates of macrofauna.

On station He395-38/TS2 the comparatively large difference in oxygen fluxes between chamber 1 and chamber 2 might be explained by small scale spatial variability of benthic macrofauna. In chamber 1 calculated respiration rates ($3.07 \text{ mmol m}^{-2} \text{ d}^{-1}$) were slightly higher when compared to chamber 2. Furthermore a community of *Echinocardium cordatum* was observed within chamber 1 which might have contributed to oxygen respiration rates due to their comparatively high biomass (Norkko et al. 2013). Small scale spatial variability between chamber 1 and chamber 2 in oxygen and ammonium fluxes might partly be explained by benthic macrofauna on other stations as well. On station He386-1/M differences in oxygen fluxes were most likely caused by a *Callianassa subterranea* which was observed in chamber 2, while in chamber 1 no fauna was visible. On station He412-38/TS2 spatial variations in benthic ammonium fluxes might be forced by benthic macrofauna as well. For example, higher ammonium fluxes in chamber 2 (fig. 7) were observed in conjunction with higher densities of the tube building interface feeder *Owenia fusiformis*, exchanging bottom water with pore water for respiratory and feeding purposes.

Spatial variations in oxygen fluxes between time series station TS2 and TS3 might be related to differences in species composition of macrofauna communities which were observed between both stations. While station TS2 was dominated by a comparatively high diversity and abundances of smaller species, fewer large bodied species were observed on station TS3, which might have an higher impact on benthic oxygen fluxes (Norkko et al. 2013). The suspension feeder *Ensis directus* dominantly forced oxygen fluxes on that station. Substantial amounts of particles might be mixed from the overlying the bottom water into the sediment by suspension feeders, thus leading to an enhanced carbon flux into the sediment when compared to station TS2 (Kristensen et al. 2012). Comparatively large differences between calculated respiration rates and measured oxygen fluxes (e.g. in November 2013) might be forced by the irrigating behaviour of *Ensis directus* which is supported by bromide tracer studies (fig. 3). Suspension feeders can considerably enhance benthic oxygen fluxes as they frequently pump oxygen rich bottom water into the sediment, stimulating microbial mineralisation (e.g. Forster and Graf 1995; Braeckman et al. 2010). Small scaled variability of oxygen fluxes between chamber 1 and 2 might as well be explained by *Ensis directus*, as its biomass was more than twice as high in chamber 2 when compared to chamber 1. In March 2014 calculated respiration rates ($17.70 \text{ mmol m}^{-2} \text{ d}^{-1}$) and measured oxygen fluxes ($16.60 \text{ mmol m}^{-2} \text{ d}^{-1}$) were comparatively similar to station TS3 (fig. 7 and 8). *Ensis directus* still contributed to the dominant part (86 %) of the total calculated oxygen respiration rates according to its biomass. Food supply and temperature are the most important factors regulating growth and conditions of *Ensis directus* (Witbaard et al, in press). We assume that *Ensis directus* reduced its metabolic activity to its lowest in March 2014 due to a lack of food supply and colder water temperatures compared to November 2013.

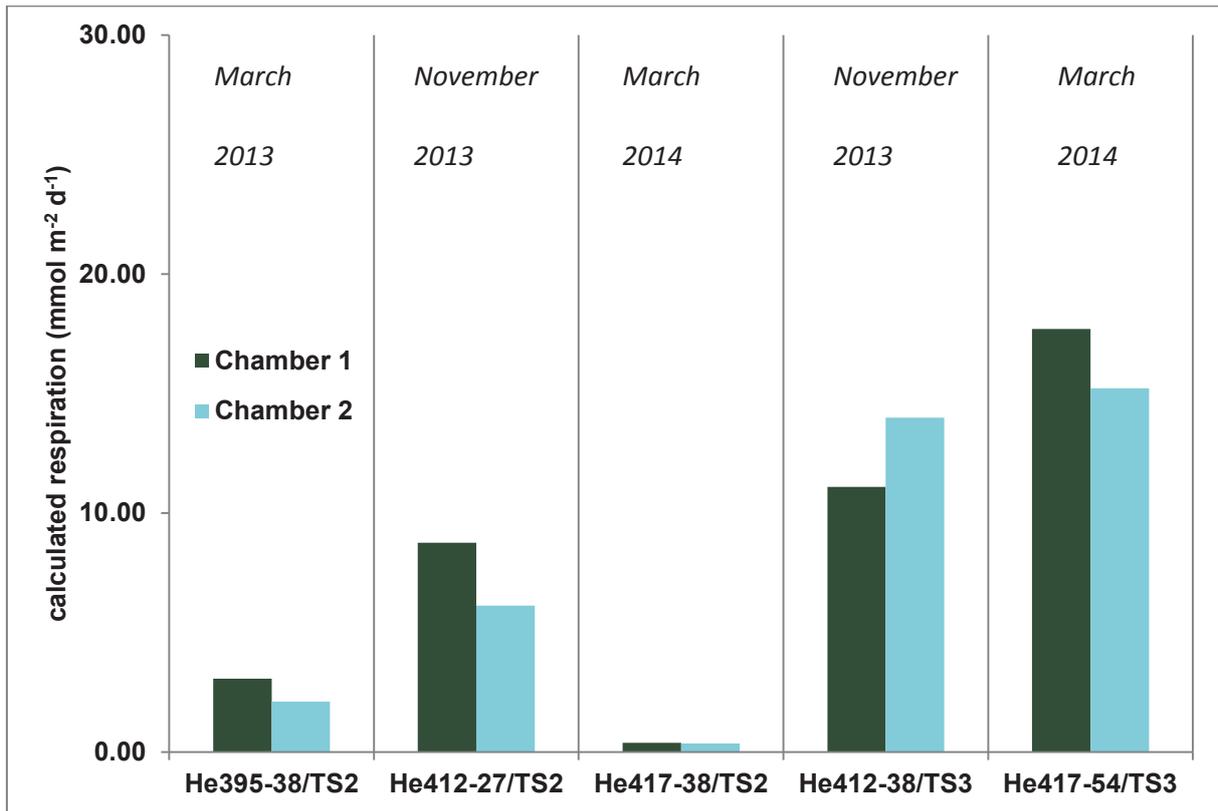


Figure 8: Calculated respiration rates according to benthic macrofauna which was sampled from the chambers. Calculation is based on weight according to Mahaut et al. (1995).

4.3 Carbon and nitrogen rain rates to the seafloor and recycling efficiency at the sediment-water interface

The amount of carbon (tab. 2, 4.1, C_{rain}) and nitrogen (tab. 2, 4.2, N_{rain}) which settle annually at the sediment water interface can be estimated from a mass balance consideration. Therefore the accumulation of carbon (table 2, 2.1, C_{acc}) and nitrogen (table 2, 2.2, N_{acc}) and the efflux of carbon (table 2, 3.1, C_{efflux}) and dissolved inorganic nitrogen (table 2, 3.2, N_{efflux}) at the sediment water interface has to be considered.

Total organic carbon and total organic nitrogen contents of sediments showed no significant variations over seasonal cycles (tab. 1). Accordingly average annual TOC and TON contents of respective sediment types ($f_{s_{high}}$, $f_{s_{low}}$, m) were considered for the calculation of sediment accumulation rates of carbon (C_{acc} , tab. 2, 2.1) and nitrogen (N_{acc} , tab. 2, 2.2). Carbon and nitrogen accumulation rates were in the range of 1.2 to 1.7 and 0.04 to 0.11 $mol\ m^{-2}\ a^{-1}$, respectively. The effluxes of carbon and nitrogen varied over seasonal scales. Therefore minimum, maximum and annual average effluxes (tab. 2, 3.1 and 3.2) of respective sediment types were considered for the calculation of carbon and nitrogen rain rates (tab. 2, 4.1 and 4.2). Estimated average carbon rain rates were in the range 5.0 to 11.8 $mol\ m^{-2}\ a^{-1}$. Assuming that approximately 22 $mol\ C\ m^{-2}\ a^{-1}$ are

produced by primary production within the German Bight (Howarth et al. 1993), about 20 to 50 % of that organic carbon would settle at the sediment water interface.

Station Acr (Sed) (1)	C_{acc} (2.1) ($mol\ m^{-2}\ a^{-1}$)	C_{efflux} (3.1) ($mol\ m^{-2}\ a^{-1}$)	C_{rain} (4.1) ($mol\ m^{-2}\ a^{-1}$)	Recy.(5) (%)
M (mud)	1.7	3.4 (min: 1.8, max: 4.9)	5.0 (min: 3.5, max: 6.5)	76
TS2 (fS_{high})	1.5	3.8 (min: 0.6, max: 7.0)	5.3 (min: 2.1, max: 8.6)	80
TS3 (fS_{low})	1.2	10.7 (min: 4.6, max: 15.4)	11.8 (min: 5.8, max: 16.6)	93
	N_{acc} (2.2) ($mol\ m^{-2}\ yr^{-1}$)	N_{efflux} (2.2) ($mol\ m^{-2}\ yr^{-1}$)	N_{rain} (2.2) ($mol\ m^{-2}\ yr^{-1}$)	
M (mud)	0.11	3.2 (min: 2.6, max: 3.9)	3.3 (min: 2.7, max: 4.0)	97
TS2 (fS_{high})	0.07	0.5 (min: 0.1, max: 1.4)	0.6 (min: 0.1, max: 1.5)	87
TS3 (fS_{low})	0.04	1.5 (min: 0.8, max: 2.8)	1.5 (min: 0.8, max: 2.8)	97

Table 2: Station acronyms and sediment types (1), carbon and nitrogen accumulation rates (2.1, 2.2), carbon and nitrogen accumulation effluxes (3.1, 3.2), rain rates of carbon and nitrogen to the seafloor (4.1, 4.2) and recycling efficiency of carbon and nitrogen (5) on different sediment types.

Within the relatively small area under study (2270 km²) no major spatial variations in primary production in the water column can be expected. Oehler et. al. (submitted) observed similar rain rates of biogenic silica to the seafloor on different sediment types within the same sampling sites. This is in contrast to spatial variations in carbon and nitrogen rain rates in this study (tab. 2, 4.1, 4.2). Comparatively high carbon fluxes on station TS3 might be overestimated from oxygen fluxes because oxygen might be used for fauna respiration (see section 4.2 *Impact of benthic macrofauna on benthic oxygen fluxes*).

Comparing the effluxes carbon (C_{efflux}) and nitrogen (N_{efflux}) at the sediment water interface with the total rain rate, gives the recycling efficiency (in percentages) of carbon and nitrogen on respective sediment types (tab. 2, 5). Recycling efficiencies of carbon increased gradually with decreasing organic carbon accumulation rates. The muddy sediment showed a lower recycling efficiency of about 76 %. On station TS2 (fS_{high}) 80 % of the organic carbon and on station TS3 (fS_{low}) 93 % of organic carbon reaching the seafloor are recycled. From a different perspective this indicates that the muddy sediment deposits act as an efficient sink for carbon. Organic bound nitrogen has a comparatively higher recycling efficiency of about 87 to 97 % on all three different sediment types and almost all of the organic nitrogen reaching the seafloor is recycled. In combination with a high rain rate of nitrogen to the seafloor, shallow sediments may be comparatively important sites for the reflux of nitrogen into the water column. Especially in summer, when the water column is depleted in nutrients, a high benthic reflux of nitrogen (up to 11 $mol\ N\ m^{-2}\ d^{-1}$) might be an important for the nitrogen requirements for the water column.

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Appendix

A) Dominant macrofauna species on time series station TS2 sampled from chamber 1 and chamber 2. Feeding type (feed. Type), wet weight (in $g\ m^{-2}$), abundance ($Ind\ m^{-2}$) and calculated respiration (Resp in $mmol\ m^{-2}\ d^{-1}$) after formula 4. Abbreviations: (SD = surface deposit feeders, SSD = subsurface deposit feeders, SF = suspension feeders, O = omnivores, HP = hyperbenthos predators, P = predators, IF = interface feeders)

Chamber 1					Chamber 2				
species	feed. Type	wet weight	abundance	Resp	species	feed. Type	wet weight	abundance	Resp
Cruise HE395-38/TS2 (March 2013)					Cruise HE395-38/TS2 (March 2013)				
<i>Echinocardium cordatum</i>	SD	154.20	25	1.28	Anthozoa	HP	31.49	25	0.80
<i>Notomastus latericeus</i>	SSD	36.71	400	1.02	<i>Abra alba</i>	SD	12.67	125	0.18
<i>Abra alba</i>	SD	17.72	75	0.23	<i>Nephtys hombergii</i>	P	11.99	25	0.40
<i>Nucula nitidosa</i>	SSD	11.85	450	0.17	<i>Kurtiella bidentata</i>	SF	7.89	1750	0.12
<i>Ophiura albida</i>	O	4.87	50	0.12	<i>Lagis koreni</i>	SSD	5.65	175	0.21
<i>Amphiura filiformis</i>	IF	2.26	50	0.06	<i>Notomastus latericeus</i>	SSD	5.45	125	0.20
<i>Abra nitida</i>	SD	1.81	75	0.03	<i>Nucula nitidosa</i>	SSD	5.22	325	0.08
<i>Nephtys hombergii</i>	P	1.58	125	0.07	<i>Amphiura filiformis</i>	IF	3.39	75	0.09
<i>Lagis koreni</i>	SSD	1.29	50	0.06	<i>Cylichna cylindracea</i>	P	0.67	25	0.03
<i>Tellimya ferruginosa</i>	SF	0.88	50	0.02	<i>Ophiura albida</i>	O	0.27	75	0.01
Total				3.07	Total				2.11
HE412-27/TS2 (November 2013)					HE412-27/TS2 (November 2013)				
<i>Abra alba</i>	SD	50.00	425	1.13	<i>Abra alba</i>	SD	48.48	400	1.10
<i>Ophiura ophiura</i>	O	44.12	150	1.49	<i>Amphiura filiformis</i>	IF	23.02	150	0.86
<i>Amphiura filiformis</i>	IF	34.53	225	1.21	<i>Notomastus latericeus</i>	SSD	13.26	525	0.86
<i>Nephtys hombergii</i>	P	21.50	25	1.30	<i>Ophiura albida</i>	O	11.84	50	0.49
<i>Nucula nitidosa</i>	SSD	19.54	600	0.51	<i>Nucula nitidosa</i>	SSD	10.59	325	0.30
<i>Ophiura albida</i>	O	11.43	100	0.48	<i>Abra nitida</i>	SD	10.38	600	0.30
<i>Phaxas pellucidus</i>	SF	10.60	75	0.30	<i>Kurtiella bidentata</i>	SF	8.64	1850	0.26
<i>Euspira nitida</i>	P	8.54	75	0.43	<i>Scalibregma inflatum</i>	SSD	6.97	300	0.50
<i>Notomastus latericeus</i>	SSD	8.33	325	0.58	<i>Ophiura ophiura</i>	O	6.41	25	0.29
<i>Abra nitida</i>	SD	5.72	475	0.18	<i>Lagis koreni</i>	SSD	4.80	325	0.37
<i>Lagis koreni</i>	SSD	4.73	150	0.36	<i>Nephtys hombergii</i>	P	3.82	50	0.30
<i>Kurtiella bidentata</i>	SF	4.09	875	0.14	<i>Glycera alba</i>	P	1.88	75	0.17
<i>Glycera alba</i>	P	3.30	50	0.27	<i>Ensis spp.</i>	SF	1.77	25	0.07
<i>Scalibregma inflatum</i>	SSD	2.26	475	0.19	<i>Cylichna cylindracea</i>	P	1.16	75	0.08
<i>Phyllodoce groenlandica</i>	P	0.93	25	0.09	<i>Ophelina acuminata</i>	SSD	0.96	100	0.09
<i>Owenia fusiformis</i>	IF	0.92	25	0.09	<i>Lanice conchilega</i>	IF	0.82	25	0.08
Total				8.75	Total				6.12
HE417-38/TS2 (March 2014)					HE417-38/TS2 (March 2014)				
<i>Nucula nitidosa</i>	SSD	10.90	275	0.19	<i>Amphiura filiformis</i>	IF	6.53	25	0.18
<i>Abra alba</i>	SD	9.14	50	0.17	<i>Nucula nitidosa</i>	SSD	5.52	250	0.11
<i>Owenia fusiformis</i>	IF	0.29	25	0.02	<i>Kurtiella bidentata</i>	SF	2.24	675	0.05
<i>Abra nitida</i>	SD	0.28	25	0.01	<i>Abra nitida</i>	SD	0.53	25	0.01
<i>Scoloplos armiger</i>	SSD	0.02	25	0.002					
Total				0.389	Total				0.36

B) Dominant macrofauna species on time series station TS3 sampled from chamber 1 and chamber 2. Feeding type (feed. Type), wet weight (in $g\ m^{-2}$), abundance ($Ind\ m^{-2}$) and calculated respiration (Resp in $mmol\ m^{-2}\ d^{-1}$) after formula 4. Abbreviations: (SD = surface deposit feeders, SSD = subsurface deposit feeders, SF = suspension feeders, O = omnivores, HP = hyperbenthos predators, P = predators, IF = interface feeders), *calculation based on $0.04m^2$

Chamber 1					Chamber 2				
species	feed. Type	wet weighth	abundance	Resp	species	feed. Type	wet weighth	abundance	Resp
HE412-38/TS3 (November 2013)					HE412-38/TS3 (November 2013)				
<i>Ensis directus</i>	SF	459.00	75	6.37	<i>Ensis directus</i>	SF	1107.75	175	13.40
<i>Asterias rubens*</i>	O	110	1	1.69	<i>Liocarcinus holsatus*</i>	O	6.98	1	0.30
<i>Nucula nitidosa</i>	SSD	30.17	750	0.64	<i>Nucula nitidosa</i>	SSD	1.81	100	0.06
<i>Abra alba</i>	SD	14.24	125	0.34	Anthozoa	HP	1.06	25	0.08
<i>Owenia fusiformis</i>	IF	10.52	400	0.62	<i>Glycera alba</i>	P	0.90	25	0.08
Anthozoa	HP	8.46	75	0.46	<i>Notomastus latericeus</i>	SSD	0.77	75	0.07
<i>Nephtys hombergii</i>	P	4.19	125	0.28	<i>Kurtiella bidentata</i>	SF	0.06	50	0.00
<i>Notomastus latericeus</i>	SSD	3.97	150	0.27	<i>Scoloplos armiger</i>	SSD	0.04	350	0.01
<i>Nereis longissima</i>	P	3.39	25	0.24	<i>Pholoe balthica</i>	P	0.03	25	0.004
<i>Corbula gibba</i>	SF	2.29	50	0.07	<i>Nephtys</i> spp.	P	0.02	25	0.00
<i>Scoloplos armiger</i>	SSD	1.30	1850	0.11					
Total				11.09	Total				13.995
HE417-54/TS3 (March 2014)					HE417-54/TS3 (March 2014)				
<i>Ensis directus</i>	SF	1798.78	175	15.29	<i>Ensis directus</i>	SF	1595.73	125	13.82
Anthozoa	HP	16.73	100	0.62	<i>Nucula nitidosa</i>	SSD	26.82	600	0.44
<i>Owenia fusiformis</i>	IF	16.08	50	0.67	<i>Abra alba</i>	SD	17.88	125	0.31
<i>Nucula nitidosa</i>	SSD	11.99	225	0.22	Anthozoa	HP	6.76	50	0.29
<i>Abra alba</i>	SD	11.73	100	0.22	<i>Notomastus latericeus</i>	SSD	4.64	100	0.24
<i>Notomastus latericeus</i>	SSD	10.83	125	0.48	<i>Owenia fusiformis</i>	IF	1.03	25	0.07
<i>Nephtys hombergii</i>	P	2.88	50	0.16	<i>Nephtys hombergii</i>	P	0.84	50	0.06
<i>Corbula gibba</i>	SF	1.66	75	0.04	<i>Scoloplos armiger</i>	SSD	0.03	25	0.00
Total				17.70	Total				15.22

Chapter 3: Seasonal dynamics of the biogenic silica cycle in surface sediments of the Helgoland Mud Area (southern North Sea)

(submitted to *Limnology and Oceanography*)

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Abstract

In coastal waters and the ocean silicic acid ($\text{Si}(\text{OH})_4$) is a key nutrient for primary producers (e.g. diatoms) and other siliceous organisms, dominantly because it is required for the formation of frustules and other hard parts made of biogenic silica (bSi). Especially in shallow waters like the southern North Sea, dissolution of bSi in surface sediments and the reflux of silicic acid from the sediments into the surface water is an important feedback mechanism for sustaining primary production in the water column. We investigated benthic fluxes of silicic acid and the recycling of bSi in surface sediments of the Helgoland Mud Area (southern North Sea) over seasonal cycles. For this purposes, a benthic lander system for *in situ* studies, *ex situ* incubations and pore water studies were applied. Our *in situ* measurements revealed low silicic acid fluxes in winter and high fluxes in summer (+0.3 to +1.3 $\text{mmol m}^{-2} \text{d}^{-1}$ in March 2013 and 2014, +2.0 to +4.0 $\text{mmol m}^{-2} \text{d}^{-1}$ in November 2013 and +3.6 to +8.3 $\text{mmol m}^{-2} \text{d}^{-1}$ in June and August 2012). The relevance of biological mediated transport for the benthic $\text{Si}(\text{OH})_4$ flux was underlined by comparing *in situ* and *ex situ* sediment incubations, pore water studies, as well as depth profiles of benthic macrofauna. Mass budget calculations indicate that about 1.7 to 2.2 mol bSi m^{-2} settle annually at the seafloor, of which about 60 to 81 % are recycled within surface sediments and transported back into the water column.

Keywords: North Sea, Biogenic silica cycle, Benthic fluxes, Seasonality, In situ measurement

1. Introduction

In aquatic environments, dissolved silicic acid ($\text{Si}(\text{OH})_4$) is an important component with respect to primary production and considerations of food-web interactions. As a key nutrient it controls the growth of diatoms and is used by some sponges, radiolarians, silicoflagellates, species of choanoflagellates and potentially by picocyanobacteria (Tréguer and De La Rocha 2013). These organisms produce amorphous biogenic silica (bSi), which serves primarily as structural material. The availability of $\text{Si}(\text{OH})_4$ in the water column is controlled by external sources (e.g. river runoff), uptake by siliceous plankton, as well as recycling of biogenic silica in the water column and surface sediments (e.g. Gehlen et al. 1995; Tréguer & De La Rocha 2013).

Biogenic silica is undersaturated with respect to $\text{Si}(\text{OH})_4$ concentrations in the water column or in pore waters of surface sediments (e.g. Hurd 1973). Consequently, a significant part of bSi is dissolved during the transfer through the water column to the seafloor and in surface sediments. This causes rather low preservation and burial rates, compared to the rain rate of bSi reaching the seafloor (Dixit et al. 2001; Rickert et al. 2002; Tréguer and De La Rocha 2013).

Comparing different regions of the world ocean, DeMaster (2002) identified largest long-term burial rates of bSi for continental margins, the North Pacific, the equatorial Pacific and the Southern Ocean. For example, biogenic silica contents of more than 70 %, silicic acid fluxes of 0.095 to 0.767 $\text{mol m}^{-2} \text{a}^{-1}$ (Deep Sea) and burial rates of $> 0.84 \cdot 10^{12} \text{ mol a}^{-1}$ were reported for the Southern Ocean (Schlüter et al. 1998; DeMaster 2002; Geibert et al. 2005). Although for coastal regions like the Amazon Shelf or Monterey Bay high fluxes of 0.46 $\text{mol m}^{-2} \text{a}^{-1}$ or 2.28 $\text{mol m}^{-2} \text{a}^{-1}$ were observed (Tréguer and De La Rocha 2013), still little is known about the benthic silica cycle in temperate coastal, shallow water environments. Due to shallow water depths such environments are characterized by a close coupling between surface waters and sediment processes, as well as by seasonal variations. Especially after phytoplankton blooms at the end of spring and during summer, silicic acid is often depleted within the water column and a limiting nutrient for primary production. During this time the benthic reflux of silicic acid from the sediment into the water column might be remarkably important for phytoplankton blooms and food webs.

Considering the North Sea, the benthic silica cycle was studied by e.g. Helder & Andersen (1987), Rutgers van der Loeff et al. (1980), Vanderborcht et al. (1977), Ehrenhauss et al. (2004), Gehlen et al. (1995), Nedwell et al. (1993) or Raaphorst et al. (1990). Most of the data sets were derived from the Wadden Sea, whereas only a few studies considered and compared permanently water covered regions of the southern North Sea (e.g. Gehlen et al. 1995). These data sets were derived by *ex situ* incubation experiments or *ex situ* pore water studies. Investigations of benthic fluxes by *in situ* techniques like benthic lander systems, a prerequisite for accurately quantified benthic nutrient

fluxes (Viollier et al. 2003; Hammond et al. 2004), are still limited for the North Sea. Such *in situ* studies mainly addressed the quantification of the sediment oxygen demand in the North Sea (Forster et al. 1999; Ståhl et al. 2004; Janssen et al. 2005b).

We considered the benthic silica cycle in the southern North Sea, by *in situ* and *ex situ* studies of benthic fluxes as well as by pore water and sediment investigations during several cruises with *RV Heincke* in the years 2012 to 2014. Major objectives of our study were to identify seasonal patterns and the significance of biological mediated transport processes for the flux of Si(OH)_4 through the sediment-water interface. Other nutrient (e.g. NH_4 , NO_3) and carbon fluxes, as well as detailed analyses of benthic macrofauna are shown elsewhere (Oehler et al., submitted). Our study site (fig. 1) represents an exceptional depositional environment with mostly impermeable to semi-permeable sediments. We chose the Helgoland Mud Area because sediments are not frequently reworked and relocated by tidal currents and storms, as it is the case for most of the sandy sediments of the North Sea. Therefore accumulated sediments and benthic nutrient fluxes reflect local processes in the overlying water column (e.g. primary production or particle export reaching the seafloor). Furthermore the impermeable sediments are not affected by wave induced pore water flushing which narrows benthic transport processes to diffusional and biological mediated transport processes. This allows us to estimate the impact of benthic fauna on pore water chemistry and benthic fluxes of silicic acid. Our results may support food web studies or ecological modelling, as we identified the different time scales in which particulate and dissolved silica cycle in between the benthic and pelagic environment.

2. Material and Methods

2.1 Study site

For investigations of benthic fluxes in the southern North Sea, we selected the Helgoland Mud Area and its surroundings (fig. 1). This area with an extent of 500 km² and an average water depth of 20 m is located south east of the island Helgoland. It is one of the few depositional areas in the North Sea (Hebbeln et al. 2003). Sediment deposition is forced by a small scale eddy, which is driven by long-shore coastal currents, the discharge of the rivers Elbe and Weser and tidal dynamics (Hertweck 1983).

Within the Helgoland Mud Area about 30 meters of Holocene sediments have filled a morphological depression (von Haugwitz et al. 1988). The surface sediments consist in the west of clayey silt and become more sandy towards the east (Hertweck 1983). Sediment records and paleo-environmental reconstructions showed a drastic change in sedimentation around the year 1250, when sedimentation rates changed from > 13 to 1.6 mm a^{-1} (Hebbeln et al. 2003). Based on ²¹⁰Pb

dating, present day average sedimentation rates of 7.7 mm a^{-1} (min = 2 mm a^{-1} , max = 18 mm a^{-1}) were estimated by Dominik et al. (1978) and 2.6 mm a^{-1} were estimated by Hebbeln et al. (2003).

Phytoplankton blooms are regulated by the availability of light and nutrients in the water column. During winter the water column is enriched in nutrients but primary production limited due to the low irradiation of light. During spring, phytoplankton blooms start to grow exponentially as soon as light radiation reaches a critical level (Sverdrup 1953; Gieskes and Kraay 1977). Within the German Bight spring phytoplankton blooms start to grow during the second half of April and occur in two different stages. The first spring bloom is dominated by diatoms and is in general limited by silicic acid availability. The second spring bloom is dominated by flagellates and its size is regulated by the amount of nitrogen and phosphorus nutrients which are left in the water column after the first diatom bloom (Gieskes and van Bennekom 1973; Radach et al. 1990; Joint and Pomroy 1993). During summer most nutrients are delivered into the coastal zone due to the mineralization of organic matter and continental freshwater inputs (Beusekom and Diel-Christiansen 2009). In general, one or two more additional diatom blooms occur which are mostly followed up by non-diatom (flagellate) blooms (Radach et al. 1990). In August phytoplankton production reaches another maximum, which is followed by a decrease to lowest production in October-November (Radach et al. 1990; Beusekom and Diel-Christiansen 1994).

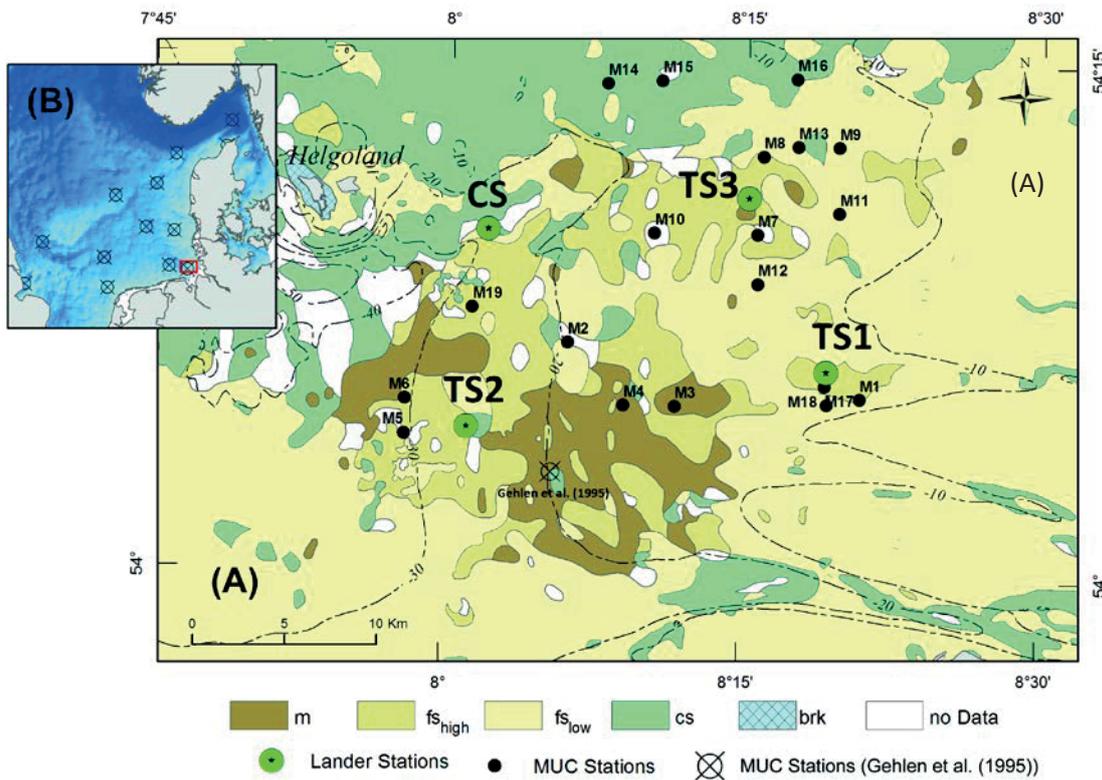


Figure 1: A) Study sites in the Helgoland Mud Area (500 km²) located in the (B) North Sea. The average water depth is ~20 m. At time series site TS1, TS2, and TS3, as well as on station CS (stars) we deployed the benthic lander NuSObs for *in situ* incubations. The sediment classification is according to Figge (1981): m=mud, fs_{high} = fine sand with high content (>50 %) of fine grained fractions ($d < 63 \mu m$), fs_{low} = fine sand with low content (<50 %) of fine grained fraction ($d < 63 \mu m$), cs=coarse grained sediment, brk=bed rock. B: Sites (circles with crosses) where the benthic silica cycle was investigated by Gehlen et al. (1995).

2.2 *In situ* and *ex situ* flux measurements

Figure 1 shows the study area, the sediment types and the sites at which the benthic lander NuSObs was deployed and sediment cores were sampled. Different sediment types, from muddy to sandy sediments were investigated. To consider seasonal variations, three time series sites (TS1, TS2, TS3) were revisited in the years 2012, 2013 and 2014 during various seasons with the research vessel *RV Heincke* (fig. 1, tab. 1).

For *in situ* flux studies we developed and applied the benthic lander system NuSObs (Nutrient and Suspension Observatory). The lander was equipped with two “Mississippi” type chambers each enclosing a sediment area of 400 cm² (Witte and Pfannkuche 2000; Tengberg et al. 2004). After the deployment of the lander, both chambers were moved by a motor into the sediment without disturbing the sediments surface. Each chamber was equipped with a syringe sampler (7 times 50 ml syringes for each chamber), an oxygen Optode (Aanderaa™, Optode 4330), as well as a pH sensor (AMT/OEM™). The syringe sampler was pre-programmed to obtain water samples from the chamber every 2 to 3 hours. By this mean, a time series of silicic acid concentrations within the chamber was

obtained. Incubations were in general carried out over a time interval of 12 to 24 hours. *In situ* incubations by benthic chamber systems consider the mass flux of dissolved constituents like Si(OH)_4 transported by molecular diffusion or biological mediated transport (e.g. bioirrigation) along the sediment water interface.

Station/Acronym	Latitude	Longitude	Month Year	Sed. Type (Figge)	\emptyset	bSi	F_s	F_{pw}	$F_{(c1/c2)}$
A) In situ incubations and time series stations									
He386-1/TS1	54° 06' 01.8"	8° 19' 04.1"	August 2012	m	0.8	3.7	-	-	3.6/5.5
He395-52/TS1	54° 06' 02.9"	8° 19' 10.9"	March 2013	m	0.8	3.6	1.6	-	-
He383-46/TS2	54° 04' 09.5"	8° 01' 07.7"	June 2012	f _{high}	0.7	1.7	5	-	5.5/-
He395-38/TS2	54° 04' 13.2"	8° 01' 05.4"	March 2013	f _{high}	0.6	1.4	-	-	1.1/-
He412-27/TS2	54° 03' 45.0"	8° 01' 00.6"	November 2013	f _{high}	0.6	2.2	2.4	-	4.0/3.3
He417-38/ TS2	54° 03' 49.3"	8° 00' 56.5"	March 2014	f _{high}	0.9	2.4	-	-	0.3/0.4
He386-33/TS3	54° 11' 04.2"	8° 15' 09.0"	August 2012	f _{low}	0.5	1.1	5.5	-	8.3/-
He395-62/TS3	54° 11' 06.7"	8° 15' 09.7"	March 2013	f _{low}	0.4	1.5	0.8	-	-
He412-38/TS3	54° 11' 04.8"	8° 15' 09.0"	November 2013	f _{low}	0.6	1.3	3.6	0.6	2.5/2.0
He417-54/ TS3	54° 11' 02.4"	8° 15' 03.6"	March 2014	f _{low}	0.5	0.8	-	-	1.1/-
He395-56/CS	54° 10' 02.4"	8° 01' 54.0"	March 2013	cs	0.4	0.6	-	0.1	1.3/-
B) Ex situ incubations and/or pore water studies									
He386-15/M2	54° 06' 46.1"	8° 06' 06.1"	August 2012	f _{high}	0.6	1.7	4.5	0.8	-
He386-21/M5	54° 04' 00.1"	7° 57' 57.6"	August 2012	f _{high}	0.6	1.1	-	0.4	-
He386-23/M6	54° 05' 03.5"	7° 57' 56.9"	August 2012	f _{high}	0.7	2.1	4.6	1.1	-
He386-4/M17	54° 05' 39.1"	8° 19' 07.3"	August 2012	f _{high}	0.7	2.7	-	-	-
He386-11/M19	54° 07' 45.1"	8° 01' 16.7"	August 2012	f _{high}	0.7	1.5	-	-	-
He386-20/M20	54° 04' 10.9"	8° 01' 06.6"	August 2012	f _{high}	0.6	1.8	-	-	-
He386-17/M3	54° 04' 57.7"	8° 11' 35.9"	August 2012	f _{low}	0.5	1.4	2.5	0.9	-
He386-27/M7	54° 10' 01.9"	8° 15' 34.9"	August 2012	f _{low}	0.6	1.4	3	0.9	-
He386-29/M8	54° 12' 16.2"	8° 15' 51.1"	August 2012	f _{low}	0.4	0.6	1.5	-	-
He386-42/M9	54° 12' 37.1"	8° 19' 41.9"	August 2012	f _{low}	0.5	0.9	-	0.5	-
He386-46/M11	54° 10' 39.7"	8° 19' 43.7"	August 2012	f _{low}	0.4	0.9	1.2	0.3	-
He386-47/M12	54° 08' 33.0"	8° 15' 40.3"	August 2012	f _{low}	0.6	2	1.2	-	-
He386-8/M1	54° 05' 15.7"	8° 20' 57.1"	August 2012	cs	0.4	0.2	2.3	-	-
He386-19/M4	54° 04' 59.9"	8° 08' 58.9"	August 2012	cs	0.6	2.2	10.1	0.8	-
He386-45/M10	54° 09' 59.4"	8° 10' 23.9"	August 2012	cs	0.4	0.4	-	0.4	-
He386-56/M13	54° 01'36.0"	8° 17' 31.2"	August 2012	cs	0.4	0.4	6.3	-	-
He386-57/M14	54° 01'16.8"	8° 07' 36.0"	August 2012	cs	-	0.3	4.9	-	-
He386-58/M15	54° 01'27.6"	8° 10' 33.6"	August 2012	cs	0.4	0.4	4.4	-	-
He386-59/M16	54°01'31.2"	8° 17' 27.6"	August 2012	cs	0.5	0.2	1.7	-	-
He386-5/M18	54° 05' 6.0"	8° 19' 13.1"	August 2012	-	0.8	0.5	-	-	-

Table 1: Location of sampling sites, month of sampling, as well as benthic $\text{Si}(\text{OH})_4$ fluxes and sediment composition derived for these locations. A: Sites at which *in situ* incubations (bold) and/or seasonal studies were carried out. B: Sites where fluxes were derived by *ex situ* incubations and/or by pore water studies. Abbreviations: Sed. Type = sediment type, \emptyset = porosity, bSi = biogenic silica content of surface sediments (wt%), F_s = ex situ incubation ($\text{mmol m}^{-2} \text{d}^{-1}$), F_{pw} = pore water flux calculations ($\text{mmol m}^{-2} \text{d}^{-1}$) according to equation (2), $F_{(c1/c2)}$ = benthic chamber incubations ($\text{mmol m}^{-2} \text{d}^{-1}$) with c1 = chamber 1 and c2 = chamber 2 and (-) = no data available.

During the retrieval of the lander the incubated sediment and the bottom water was recovered by closing a lid underneath the chamber (fig. 2). In addition to the detection of the penetration of the chamber into the sediment this allows to quantify the volume of the incubated water which is a

prerequisite for a precise flux calculation. The sediment was sampled for sedimentological and geochemical analysis.

The efflux of silicic acid from the sediment was calculated by linear regression of the concentration of silicic acid versus time applying the statistical software R. The slope of the regression line was multiplied with the height of the water column, incubated in the chamber to calculate the flux of silicic acid across the sediment water interface.

Besides the two benthic chamber systems, the NuSObs lander was equipped with an 600 kHz ADCP (Teledyne RD Instruments™) and a multiparameter CTD 115M (Sun&Sea™). The physical boundary conditions of the bottom waters such as pressure, temperature and conductivity, chlorophyll-a (Cyclops-7, Turner™), turbidity (Seapoint™) and oxygen (4330 Oxygen Optode, Aanderaa™) were monitored during each deployment.

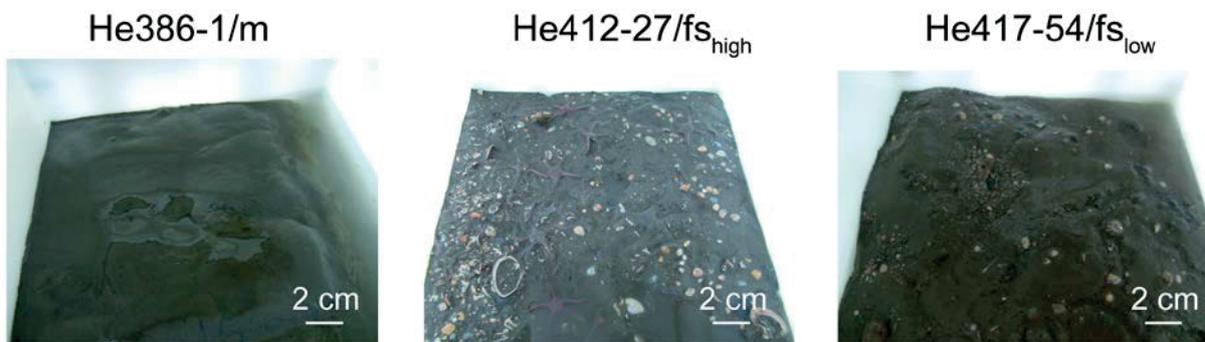


Figure 2: Photographs of different sediment types which were incubated and recovered by the chambers of the benthic lander NuSObs. All photographs were taken after NuSObs was recovered and the bottom water was released from the benthic chambers.

For *ex situ* shipboard flux measurements, sediment cores were incubated at *in situ* temperatures in a temperature regulated room of the research vessel. The incubation and sampling started immediately after recovery of the core. For *ex situ* flux studies, the overlying water of the sediment core was sampled every one to two hours. The maximum incubation time was 9 hours. The water samples were filtered with a cellulose acetate filter (pore size = 0.45 μm) and subsequently stored at 4 °C in a refrigerator. Within a few days the $\text{Si}(\text{OH})_4$ concentration was analyzed by the segmented flow analyzer (Seal™ Analytical Autoanalyzer). As for the chambers, the silicic acid efflux was calculated from the increase of the $\text{Si}(\text{OH})_4$ concentration versus time.

2.3 Sediment sampling and analysis

Surface sediments were sampled with a multi corer equipped with 8 cores (inner diameter of 9.5 cm) made of acrylic glass (Barnett et al. 1984). Generally, the cores recovered the upper 10 to 30 cm of the surface sediment. Subsequently to the recovery, the cores were sampled on board of the ship in a temperature regulated room adjusted to ambient bottom water temperature. The overlying water was sampled by a syringe and filtered with a cellulose acetate filter (0.45 μm pore size). Pore water samples (~ 4 ml from each depth) were collected with Rhizons with a vertical resolution of one to two centimeters within the sediment (Seeberg-Elverfeldt et al. 2005). The water and pore water samples were filtered and stored at 4 °C in a refrigerator. The concentration of silicic acid was analyzed by a segmented flow analyzer (Seal™ Analytical Autoanalyzer) within a few days. The accuracy of the analysis is $\pm 2 \mu\text{mol l}^{-1}$.

Sediment samples were taken from the same depths as the pore water samples for measurements of porosity, biogenic silica content, as well as grain sizes. Grain sizes were determined with a coulter counter particle laser (diffraction) meter. The sediment was categorized according to Figge (1981) into mud (m), fine sand ($f_{\text{S}_{\text{high}}}$, $f_{\text{S}_{\text{low}}}$) and sediments which are coarser than fine sand (cs). This sediment classification considers differences of fine grained particles ($d < 63 \mu\text{m}$), which is for benthic biological processes of importance. In this context mud (m) is classified as sediment containing more than 80 % of fine grained material ($< 63 \mu\text{m}$). $f_{\text{S}_{\text{high}}}$ is fine sand containing more than 50 % and $f_{\text{S}_{\text{low}}}$ is fine sand containing less than 50 % of fine grained material ($d < 63 \mu\text{m}$) (tab. 1). Porosity was calculated assuming a sediment density of 2.65 g cm^{-3} (Breitzke 2006) and determining the water content by the weight loss after freeze drying. The biogenic silica content of the sediment was determined by leaching the sediment sample according to Müller & Schneider (1993).

To assess the influence of macrofauna species on the sedimentary environment via e.g. actively reworking and irrigating the sediment or transport oxygen and organic matter deeper into the sediment, macrofauna species were sampled at time series site TS2 in 2013 and 2014 from sediment cores. The upper 20 to 30 cm of the sediment were sliced in 5 cm horizons (0-5, 5-10, 10-15, 15-20, 20-25 cm) and sieved on board over 500 μm mesh size which retained nearly all individuals of those taxa generally regarded as members of the macrofauna. Samples were fixed in 4 % buffered formaldehyde-seawater solution. In the lab, samples were stained with Bengal rose and all macrofauna was sorted and identified to the lowest possible taxonomic level, counted and biomasses were determined (wet weights). Prior to data analysis, mean species abundance and biomass were determined and standardized to 1 m^2 . Each species was classified into functional feeding groups (surface deposit feeders, subsurface deposit feeders, suspension feeders, omnivores, predators, interface feeders) and functional types (surficial modifier, biodiffuser, upward conveyor, upward-downward conveyor) based on available literature (e.g. Fauchald and Jumars 1979; Queirós

et al. 2013). Macrofauna species which contributed most to the community structure of each station were identified by using the SIMPER routine implemented in PRIMER v6 (Clarke and Gorley 2006).

2.4 Computation of benthic fluxes and recycling efficiencies

Biogenic silica which is reaching the sediment water interface is either dissolved and transported back into the water column in the form of silicic acid, or is being buried within the sediment. Consequently, the rain rate of biogenic silica (bSi_{rain}) reaching the seafloor is equal to the sum of the reflux of silicic acid ($Si(OH)_4_{flux}$) back into the water column and the mass accumulation of bSi in the sediment (Schlüter et al. 1998; Ragueneau et al. 2009; Tréguer and De La Rocha 2013):

$$bSi_{rain} = Si(OH)_4_{efflux} + bSi_{acc} \quad (1.1)$$

with

bSi_{rain} : rain rate of biogenic silica from the water column to the seafloor ($mol\ m^{-2}\ a^{-1}$),

$Si(OH)_4_{flux}$: efflux of silicic acid across the sediment water interface ($mol\ m^{-2}\ a^{-1}$),

bSi_{acc} : accumulation rate of biogenic silica within the sediment ($mol\ m^{-2}\ a^{-1}$)

$$bSi_{acc} = (1 - \emptyset) * w * s * bSi \quad (1.2)$$

\emptyset : porosity (-),

w : dry sediment density ($kg\ m^{-3}$),

s : sedimentation rate ($m\ a^{-1}$),

bSi : weighted percentage of biogenic silica (wt%).

For equation 1.1 the accumulated biogenic silica (bSi_{acc}) within the sediment is converted from $kg\ m^{-2}\ a^{-1}$ into $mol\ m^{-2}\ a^{-1}$. The ratio between the silicic acid flux ($Si(OH)_4_{flux}$) and the total bSi rain rate (bSi_{rain}) is an indicator for the efficiency of a sediment to recycle biogenic silica at sediment water interface and transport it back into the water column in the form of silicic acid. For the calculation of the mass accumulation rates of biogenic silica within the sediment, average porosities and average biogenic opal concentrations for respective sediment types were chosen. Furthermore we selected a sedimentation rate of $0.0026\ m\ a^{-1}$ (Hebbeln et al. 2003) and a bulk dry sediment density of $2650\ kg\ m^{-3}$. The efflux of silicic acid ($Si(OH)_4_{flux}$) from the sediment to the water column was directly measured by *in situ* and *ex situ* incubations.

Based on pore water profiles, the diffusive flux of solutes along the sediment-water interface was calculated. Several $\text{Si}(\text{OH})_4$ pore water profiles are characterized by an exponential curvature close to the sediment water interface and a constant, asymptotic concentration at sediment depths (Vanderborght et al. 1977; Raaphorst et al. 1990; Gehlen et al. 1995). For the calculation of fluxes across the sediment-water-interface, different types of models or fitting function were developed (Hurd 1973; Gehlen et al. 1995). We applied an exponential decay equation (2) fitted to the measured silicic acid profile (Gehlen et al. 1995; van Raaphorst et al. 1990):

$$F_0 = \phi D_{eff} \delta^{-1} (S_0 - S_b) \quad (2)$$

$$\delta = (D_{eff}/K_{Si})^{1/2}$$

with

F_0 : Diffusive flux of silicic acid across the sediment water interface ($\text{mmol m}^{-2} \text{d}^{-1}$),

D_{eff} : Molecular diffusion coefficient corrected for temperature and tortuosity ($\text{m}^2 \text{s}^{-1}$) (Boudreau 1997);

δ : Depth constant (m);

S_0 : Bottom water concentration of silicic acid (mmol m^{-3}),

S_b : Asymptotic concentration of silicic acid at sediment depth (mmol m^{-3}),

K_{Si} : First order reaction rate (s^{-1})

The exponential decay equation (eq. 2) was fitted to the measured silicic acid profile by adjusting the depth constant δ . The best fit was obtained by minimizing the sum of the least squares of the residuals (difference between measured and calculated concentration) applying the statistical software R. The depth constant δ reflects the ratio between the transport by molecular diffusion (D_{eff}) and the reaction rate (K_{Si}) of bSi. A detailed description of equation (2) is provided by Gehlen et al. (1995).

3. Results

3.1 *In situ* benthic chamber- and *ex situ* shipboard flux measurements

The time series sites (*TS1*, *TS2*, *TS3*, *fig.1*) cover different sediment types from mud (m) to fine sand (fs) deposits. During the *in situ* incubations (about 12 to 24 hours at the seafloor), the increase of the Si(OH)_4 concentration versus time within the benthic chamber is nearly linear (*fig. 3*). The slope of the increase of Si(OH)_4 over time indicates the efflux of silicic acid. This efflux is caused by dissolution of particulate biogenic silica and by transport processes like molecular diffusion or biological mediated transport (e.g. bioirrigation). The benthic fluxes of Si(OH)_4 through the sediment water interface derived by *in situ* as well as *ex situ* incubations are summarized in table 1.

On site *TS1* we carried out *in situ* incubations with the benthic lander NuSObs in August 2012 and *ex situ* incubations in March 2013 (*fig. 3*). In August 2012 fluxes ranged from +3.6 to +5.5 $\text{mmol m}^{-2} \text{d}^{-1}$ and were significantly higher compared to March 2013 (+1.6 $\text{mmol m}^{-2} \text{d}^{-1}$, determined *ex situ*). The sediment type (mud) and relatively high bSi contents (3.6 to 3.7 wt%) did not change significantly in between both seasons.

We studied the seasonal dynamics at station *TS2* and carried out *in situ* and *ex situ* incubations in June 2012, March 2013, November 2013 and March 2014 (*tab. 1*). The sediment type consisted of a fine sand with a high content of fine grained fractions (fs_{high}). The efflux of silicic acid followed a clear seasonal cycle with high effluxes in June 2012 (+5.5 $\text{mmol m}^{-2} \text{d}^{-1}$), low effluxes in March 2013 (+1.1 $\text{mmol m}^{-2} \text{d}^{-1}$), high effluxes in November 2013 (+3.3 to +4.0 $\text{mmol m}^{-2} \text{d}^{-1}$) and very low effluxes in March 2014 (+0.3 to +0.4 $\text{mmol m}^{-2} \text{d}^{-1}$). *Ex situ* incubations were carried out on time series station *TS2* in June 2012, March 2013 and November 2013. In June 2012 and November 2013 determined silicic acid effluxes were slightly lower as compared to the *in situ* determined flux rates. In March 2013 a significant change in silicic acid concentration with time in the *ex situ* incubated core was not observed.

Time series station *TS3* was investigated by *in situ* incubations in August 2012, March 2013 and March 2014 and by *ex situ* incubations in August 2012, March 2013 and November 2013. Similar to time series station *TS2* the silicic acid effluxes followed the seasonal cycle with high flux rates in August 2012 (+8.3 $\text{mmol m}^{-2} \text{d}^{-1}$), low flux rates in March 2013 (+0.8 $\text{mmol m}^{-2} \text{d}^{-1}$, determined *ex situ*) and March 2014 (+1.1 $\text{mmol m}^{-2} \text{d}^{-1}$), as well as intermediate flux rates in November 2013 (+2.0 to +2.5 $\text{mmol m}^{-2} \text{d}^{-1}$). The sediment type did not vary in between the different seasons and consisted of a fine sand (fs_{low}) with lower porosities (0.4 to 0.6) and lower bSi contents (0.8 to 1.5 wt%), when compared to station *TS2*.

In situ incubations at site He395-56/CS (CS: coarse sediment) by the NuSObs lander were carried out in March 2013. Silicic acid effluxes were low ($+1.3 \text{ mmol m}^{-2} \text{ d}^{-1}$). The coarse grained sediments (cs) had a low bSi content of 0.6 wt%.

Ex situ flux measurements revealed a similar efflux of silicic acid (fig. 3, e), as *in situ* flux measurements (fig. 3, a-d). The fluxes determined *ex situ* support the seasonal pattern detected by the *in situ* incubations. High *ex situ* measured fluxes were observed in June 2012 and August 2012 ($+1.2$ to $+10.1 \text{ mmol m}^{-2} \text{ d}^{-1}$, average efflux of: $+3.9 \text{ mmol m}^{-2} \text{ d}^{-1}$), moderate fluxes in November 2013 ($+2.4$ to $+3.6 \text{ mmol m}^{-2} \text{ d}^{-1}$) and low fluxes in March 2013 ($+0.8$ to $+1.6 \text{ mmol m}^{-2} \text{ d}^{-1}$). In March 2013 we did not measure any significant increase in silicic acid concentrations in the bottom water on stations He395-38/TS2 and He395-56/CS. The comparison between *ex situ* and *in situ* fluxes (fig. 3) are discussed below.

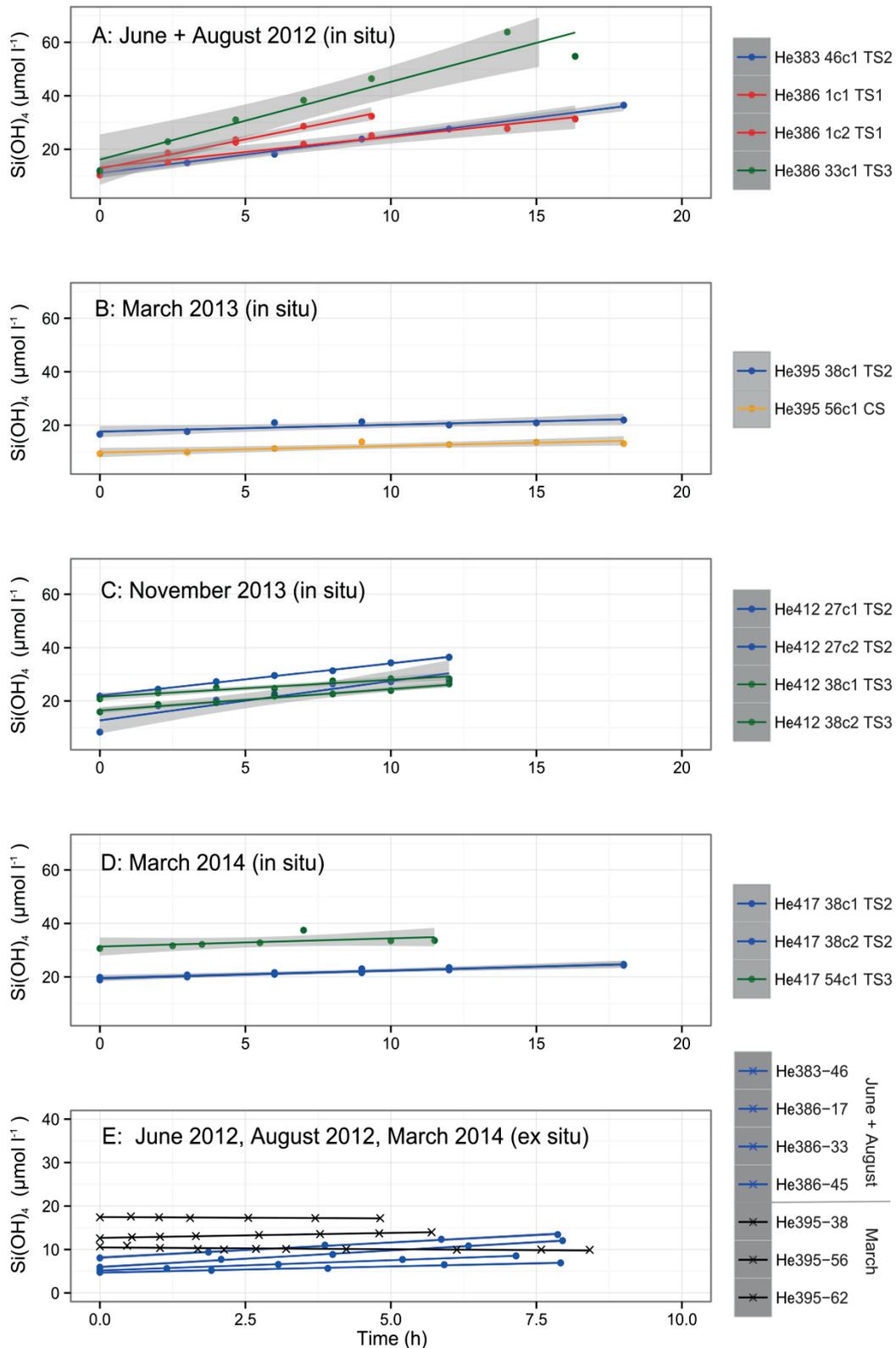


Figure 3: *In situ* flux measurements derived by the benthic lander NuSObs in June and August 2012 (A), March 2013 (B), November 2013 (C) and March 2014 (D) and *ex situ* measured fluxes (E). A significant linear increase in silicic acid concentration with time was observed during the incubations. High fluxes were observed in the summer and autumn season, whereas low fluxes were derived during winter. E: Examples for fluxes derived by *ex situ* incubations (the blue dots show measurements carried out in June and August 2012 and the black crosses show data collected in March 2013).

3.2 Pore water profiles of Si(OH)_4 and biogenic silica contents of surface sediments

In situ sediment incubations by benthic chambers allow quantification of total fluxes along the sediment water interface and summarize the transport of dissolved constituents like e.g. Si(OH)_4 , O_2 , NO_3 via molecular diffusion and by biological mediated transport (e.g. bioirrigation). In contrast, flux calculations based on pore water profiles consider only diffusive fluxes (e.g. Glud 2008). Nevertheless an advantage of pore water studies is the capability to identify reaction and transport processes (e.g. bioirrigation) by interpretation of the curvature of concentration versus depth profiles (Boudreau 1997). Examples of pore water profiles measured for sediments of the Helgoland Mud Area are shown in figure 4.

Considering the shape of the pore water profiles (fig. 4) a steady increase of silicic acid concentrations with sediment depth close to the sediment water interface and an asymptotic Si(OH)_4 concentration at depth was observed on some stations. The exponential curvature of pore water profiles (fig. 4) is typical for a diffusive transport of silicic acid within the sediment (Lerman 1978; Berner 1980). To calculate benthic silicic acid fluxes from pore water profiles, we only considered these pore water profiles. The calculated diffusive fluxes are in the range of +0.1 to +1.1 $\text{mmol m}^{-2} \text{d}^{-1}$ (tab. 1). In August the median diffusive flux of Si(OH)_4 is +0.7 $\text{mmol m}^{-2} \text{d}^{-1}$. One exceptional site was station HE396-56/CS with low asymptotic pore water concentrations of 220 $\mu\text{mol l}^{-1}$, being located on a coarse grained sediment type. Similar profiles were observed by other authors in coarse grained sediment types in the North Sea (e.g. Gehlen et al. 1995), which are typical for non-depositional environments.

In most of the remaining pore water profiles a two layer pattern with varying silicic acid concentrations within the upper 3 to 9 centimeters of the sediment, followed by a nearly asymptotic pore water profile at depth were observed. The shape of these pore water profiles is typical for advective transport processes in the upper sediment column and a diffusive transport below. The advective transport of pore water at the core top could be forced by physical mixing processes including wave induced transport or bioirrigation (Vanderborght et al. 1977; Huettel et al. 2014). Wave induced pore water flows are known to take place in sediments where permeabilities exceed a certain threshold of 10^{-12} m^2 (Huettel et al. 1996; Huettel and Rusch 2000). Based on the measured grain size distribution, we computed the hydraulic permeability of the sediments according to Soulsby (1997). The permeability of most surface sediments is below 10^{-12} m^2 . We consider these unsorted sediments as impermeable ($<10^{-12}$) with respect to e.g. wave induced transport (Vanderborght et al. 1977; Huettel et al. 2014). We assume that advective flux profiles are most likely forced by biologically induced transport processes (for example He386-33/TS3, see fig. 4 and fig 2).

Biogenic silica contents (bSi) of surface sediments varied between 0.2 wt% to 3.7 wt% (tab. 1). These values are in a similar range as observed for sediments in the North Atlantic and other coastal

regions (DeMaster et al. 1983; Schlüter and Sauter 2000; Berelson et al. 2003). Higher median bSi contents were related to sediment types with a higher fraction of fine grained material (Figge, 1981): $m = 3.6 \text{ wt\%}$, $n=2$; $f_{s_{\text{high}}} = 1.9 \text{ wt\%}$, $n=10$; $f_{s_{\text{low}}} = 1.2 \text{ wt\%}$, $n=10$; $cs = 0.6 \text{ wt\%}$, $n=8$.

A) Pore water profiles (time series sites/lander stations)

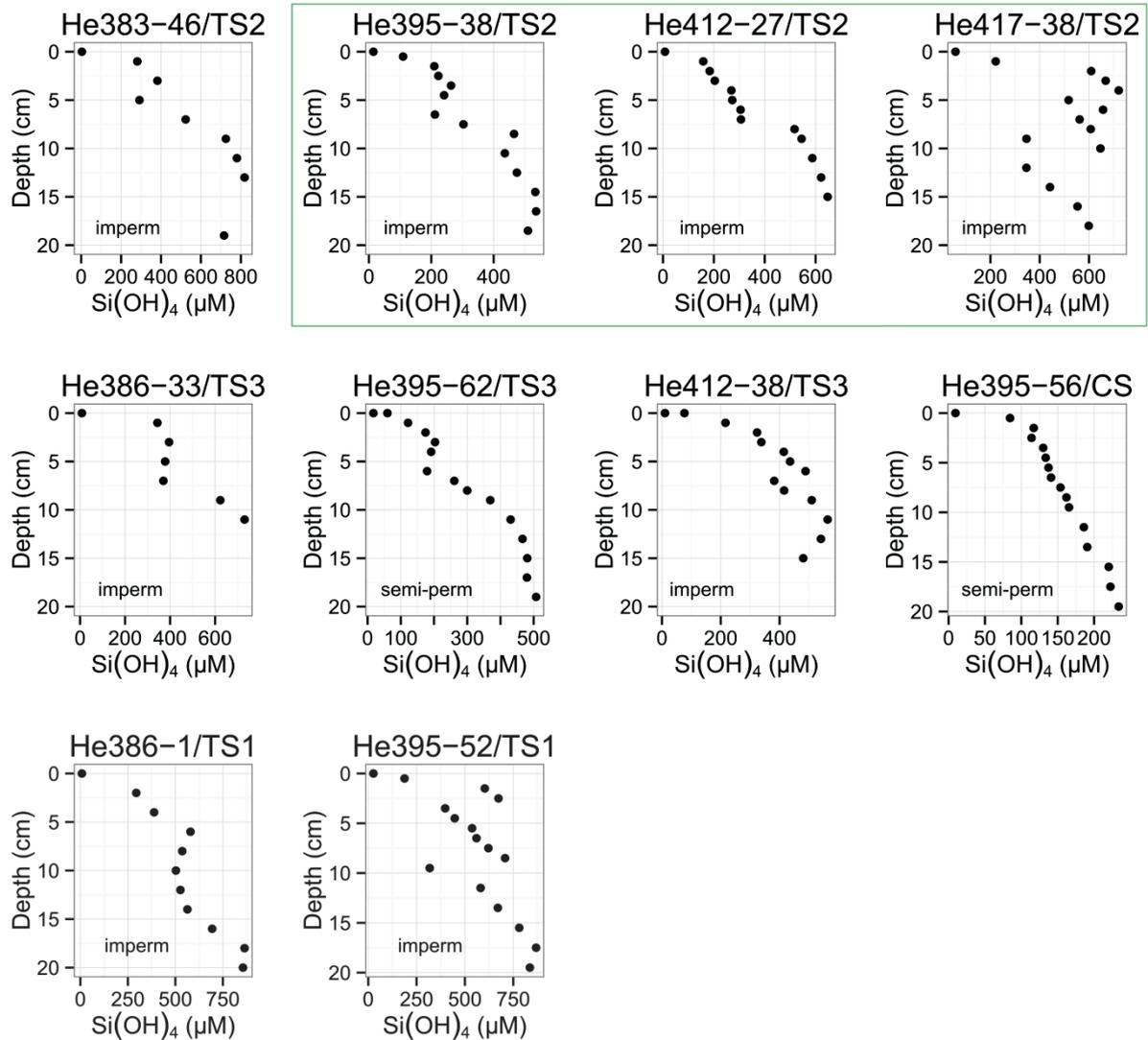


Figure 4 A: Pore water profiles sampled in the southern North Sea. Pore water profiles of time series sites and/or lander stations TS1, TS2, TS3, CS (fig.1) are shown. On station He395-38/TS2, He412-27/TS2 and He417-38/TS2 (green box) depth profiles of benthic macrofauna were sampled. According to the grain size distribution of the sediment the hydraulic permeability was calculated and categorized: imperperm = impermeable sediments, semi-perm = semipermeable, perm = permeable.

B) Pore water profiles (no time series sites/lander stations)

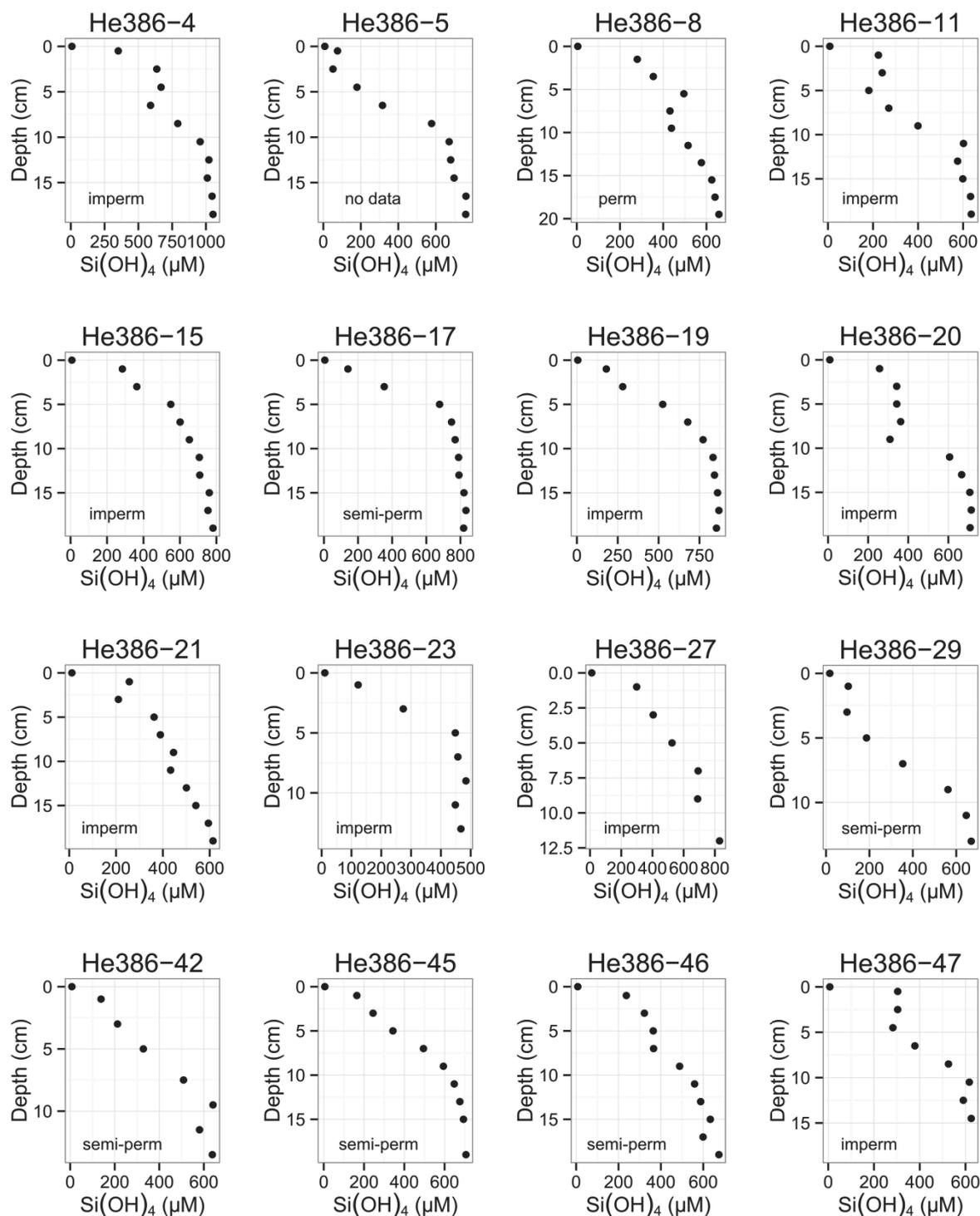


Figure 4 B: Pore water profiles measured at non-time series sites in the southern North Sea. According to the grain size distribution of the sediment the hydraulic permeability was calculated and categorized: imperm = impermeable sediments, semi-perm = semipereable, perm = permeable.

3.3 Vertical distribution of dominant macrofauna species

To assess the biological mediated transport of particles, depth profiles of macrofauna were analysed on time series station TS2 (fig. 5, Appendix A). Thereby different functional types are distinguished. Surficial modifiers (S) are organisms whose activities are restricted to the uppermost sediment layers (< 1 to 2 cm). The activities of biodiffusers (b) result in a random diffusive transport of particles over small distances. Upward conveyors (UC) feed vertically within the sediment with their head located at depth, while downward conveyors (DC) are head-up oriented feeders which transport particles vertically from the sediment water interface to depth (Solan and Wigham 2005). The SIMPER results characterize each station by the most abundant species. In general, highest species numbers and abundance (ind./m²) were found in the first 5 cm of the sediment. The community structure was dominated by surficial modifiers (*Nucula nitidosa*, *Kurtiella bidentata*), biodiffusers (*Scoloplos armiger*, *Amphiura filiformis*, *Scalibregma inflatum*) and upward/downward conveyors like *Spiophanes bombyx* and Capitellidae. A clear seasonal pattern was found. Lowest abundances occurred in March 2013, which increased in November 2013 and remained stable in March 2014 after the warm winter. The functional diversity decreased from November 2013 to March 2014 (fig. 5, Appendix A).

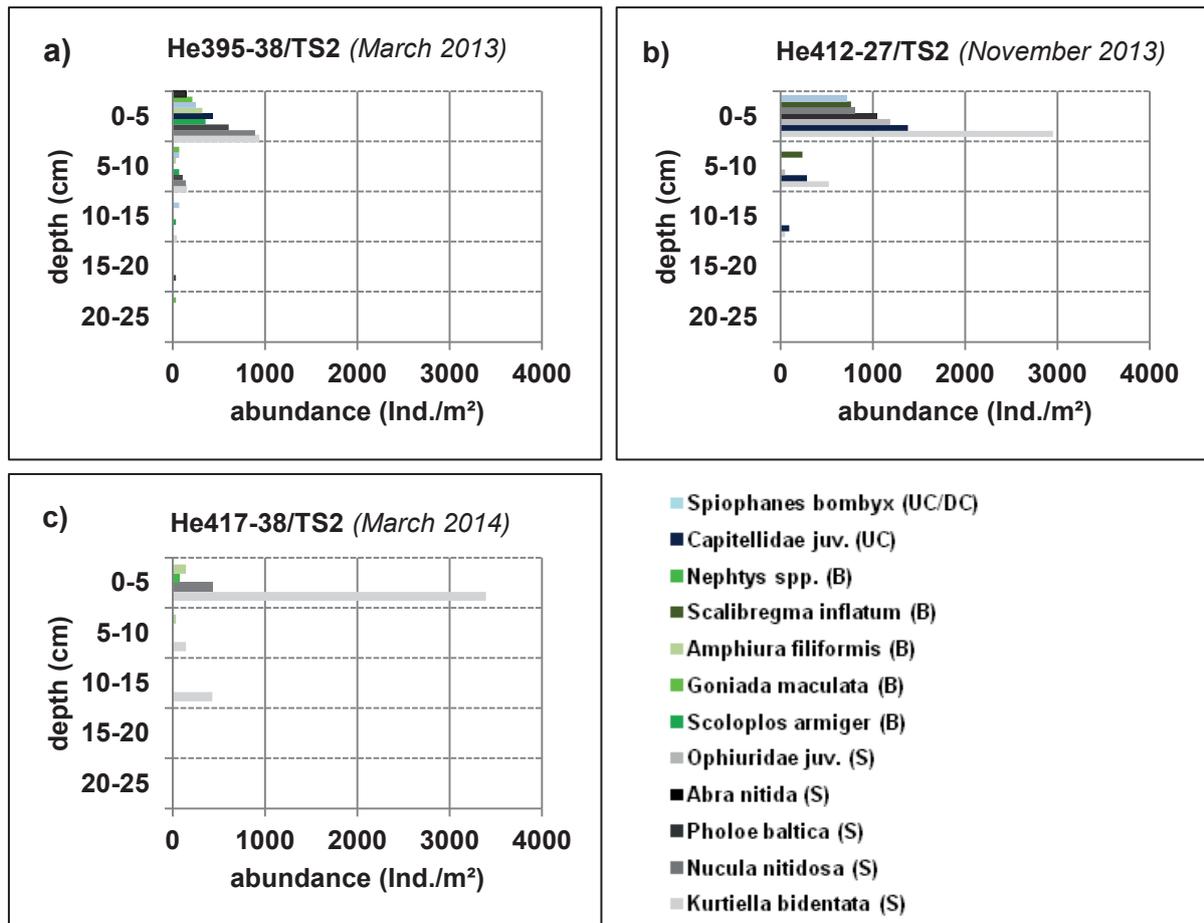


Figure 5: Vertical distribution of dominant macrofauna species (Ind./m²) within the sediment at stations TS2 (HE395-38/TS2 (a), HE412-27/TS2 (b) and HE417-38/TS2 (c)) sampled in 2013 and 2014. Abbreviations: S = surficial modifier, B = biodiffuser, UC = upward conveyor, UC/DC = upward-downward conveyor.

4. Discussion

Our *in situ* and *ex situ* benthic flux data derived for different seasons between 2012 to 2014 allow a comparison of methods applied for the quantification of benthic fluxes, the identification of seasonal variations, estimates about the preservation efficiency of bSi in sediments and the calculation of spatial budgets about the reflux of Si(OH)₄ into the bottom water.

4.1 Comparison of techniques applied for benthic flux measurements

Considering results derived by sediment incubations, fluxes determined *ex situ* were in general lower than fluxes measured *in situ*. On stations He395-38/TS2 and He395-56/CS no significant fluxes were measured in *ex situ* incubations, while a significant flux was observed in *in situ* incubations. On three stations (He383-46/TS2, He412-27/TS2, He386-33/TS3) *in situ* flux measurements showed approximately 10 to 30 % higher flux rates than those derived by the *ex situ* incubations. These results are in accordance to studies by Hammond et al. (2004), who investigated benthic fluxes (e.g.

Si(OH)₄, PO₄ or NO₃) by *ex situ* and *in situ* incubations of sediments derived from water depths of 100 m to 3300 m at the California margin. Compared with the *in situ* derived fluxes, Hammond et al. (2004a) observed a systematical reduction of 15 to 30 % in *ex situ* studies. Hammond et al. (2004a) observed largest offsets between *in situ* and *ex situ* incubations in shallow water sites, where most of the benthic fauna is present. Differences in flux rates were caused by a reduction in irrigating activity of benthic fauna in recovered cores.

Advantages of *in situ* studies are the larger area incubated by a benthic chamber (area 400 cm²) when compared to e.g. Multicorer tubes (area 70 cm²). Therefore, probability to assess the activity by macro-benthos, when compared to Multicorer samples is considerably higher. Furthermore artifacts which are related to changes in faunal behavior may be less under *in situ* conditions, compared to shipboard incubations at which the benthic community was exposed to a stressful recovery process (Glud 2008). Consequently, *in situ* benthic chamber incubations represent benthic fluxes, affected by biological mediated transport like bioirrigation, more accurate than *ex situ* incubations and are better suited for process oriented studies like quantification by bioirrigation by tracer injection. This underlines the advantage of *in situ* techniques in shallow water sediments, which are in general inhabited by abundant benthic macrofauna (Glud 2008).

Compared with sediment incubations, the benthic fluxes calculated from pore water profiles are considerably lower. On the average, the pore water derived fluxes are by factor of more than 7 lower than those measured in incubation experiments (ratio of lower fluxes for all stations: average= 6.5, min=2.9, max=15.6).

The discrepancy was observed by Gehlen et al. (1995) in the Helgoland Bight and in the Skagerrak (fig. 1, B) as well and seems to be attributed to an enhanced transport by irrigating fauna, which is not considered in pore water calculations. Depth profiles of the abundance of benthic macrofauna (fig. 5) suggest that the shape of the silicic acid pore water profile was affected by the functional type of macrofauna within different sediment layers. On station He395-38/TS2 and He412-27/TS2 distinct changes in the silicic acid pore water profile at a depth of 5 to 10 cm might be explained by the upward and downward conveyor (fig. 5, UC/DC) *Spiophanes bombyx* or biodiffusers (fig. 5, B) such as *Goniada maculata* or *Amphiura filiformis* which were observed within this sediment depth. Surficial modifiers (fig. 5, S) most likely did not affect the pore water composition, as their activity is restricted to the uppermost two centimeters of the sediment (Queirós et al. 2013). Surficial modifiers which were observed on station He417-38/TS2 down to sediment depths of 20 centimeters might be related to sampling artifacts, as benthic fauna can be forced into the sediment while being sampled with a multicorer device.

4.2 Seasonal variability of benthic fluxes

For the southern North Sea, our *in situ* and to some extent *ex situ* measurements revealed a significant seasonal cycle with silicic acid effluxes of +3.6 to +8.3 $\text{mmol m}^{-2} \text{d}^{-1}$ (June and August 2012), +2.0 to +4.0 $\text{mmol m}^{-2} \text{d}^{-1}$ (November 2013) and +0.3 to +1.3 $\text{mmol m}^{-2} \text{d}^{-1}$ (in March 2013 and 2014, respectively: +1.1 to +1.3 $\text{mmol m}^{-2} \text{d}^{-1}$ and +0.3 to +1.1 $\text{mmol m}^{-2} \text{d}^{-1}$). Such variations could be caused by chemical processes related to solubility and kinetics, as well as biological mediated transport which could cause a considerable undersaturation of Si(OH)_4 in the sediment due to flushing by bottom water (Aller and Yingst 1985; Marinelli 1992).

In figure 6, water column temperatures (stars), sediment types, as well as Si(OH)_4 fluxes measured by *in situ* and *ex situ* incubations on time series and lander sites (tab. 1, A), are shown. The datasets suggest a relationship between silicic acid fluxes and the bottom water temperatures. Fluxes measured in July 2012 at site *TS2* (bottom water temperature (T_{BW}) 14 °C) are about 5 times higher as those observed in March 2013 ($T_{\text{BW}} = 3$ °C) and of similar magnitude than November 2013, for $T_{\text{BW}} = 11$ to 13 °C. A similar pattern was observed for site *TS1* and *TS3*. The bottom water temperature has an effect on the molecular diffusion coefficient and might decrease flux rates by about 1.6 times for a temperature drop from 15 °C to 5 °C (Berner 1980). Furthermore the solubility of a solid phase and the reaction rate is affected by the temperature. A temperature drop from 15 °C to 5 °C would decrease the solubility of amorphous silica by about 20 % and decrease the reaction rate by 3.5 (Wollast 1974; Gehlen et al. 1995). Seasonal variations of dissolution rates might further be enhanced by the settling of diatoms at the sediment surface after phytoplankton blooms during the second half of April and at the end of summer (Joint and Pomroy 1993). Dissolution of biogenic silica at the sediment surface and within the sediment might thus partly explain temperature related seasonal variations in silicic acid fluxes.

Furthermore, benthic macrofauna seems to play an important role in the effluxes of silicic acid, as indicated by *ex situ* incubations, *in situ* incubations and pore water flux calculations. Within the North Sea the effect of bioirrigation on benthic nutrient cycling was studied by Gehlen et al. (1995) and Forster et al. (1999). For example, Gehlen et al. (1995) showed in *ex situ* flux measurements that benthic silicic acid fluxes can be enhanced by a factor of 1.1 to 3.4 by bioirrigation. Benthic macrofaunal enhanced fluxes of dissolved silica are positively correlated with the density of burrow or tube structures (Aller 1982) and with the activity of burrow inhabitants (Marinelli 1992). Accordingly higher abundances of upward/downward conveyors (fig. 5, UC/DC) in November 2013 might contribute to higher silicic acid effluxes, while seasonal variations of surficial modifiers (fig. 5, S) (e.g. *Kurtiella bidentata*) are probably less important. Furthermore higher bottom water temperatures and better food supply might enhance metabolic activities of benthic macrofauna in November compared to March.

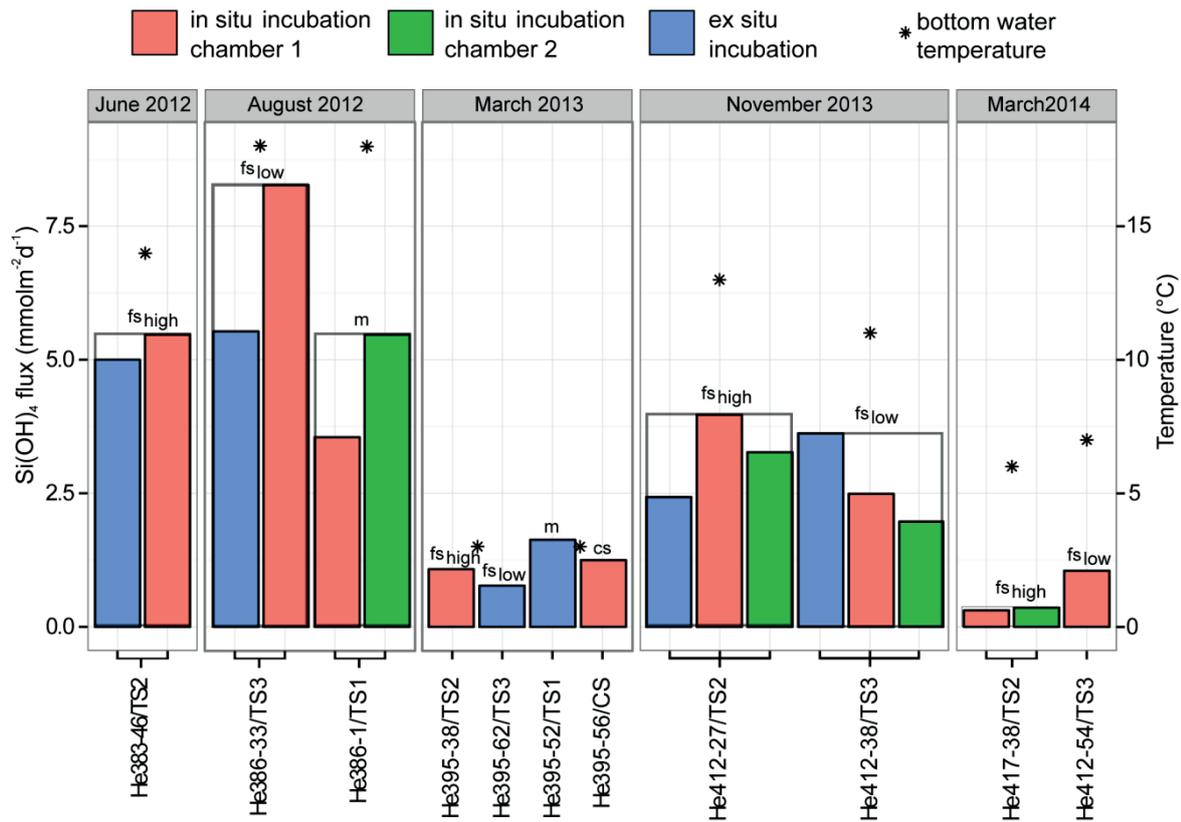


Figure 6: Seasonal variations of benthic Si(OH)_4 fluxes. In blue *shipboard flux measurements* carried out on time series stations are shown. *In situ* flux measurements are shown in red (chamber 1) and green (chamber 2). The bottom water temperature on each respective station is indicated by stars (*).

4.3 Recycling efficiency of silicic acid into the bottom water

In shallow coastal waters like the North Sea (water depth of about 30 m) a close coupling between pelagic and benthic processes is obvious, due to the short residence time of particles (e.g. aggregates or phyto- and zooplankton) in the water column. Therefore, the remineralisation and dissolution of particles in the water column during the transfer to the seafloor should be rather low, when compared with continental margins or the open ocean.

Assuming sedimentation rates of 0.0026 m a^{-1} (Hebbeln et al. 2003) we calculated the mass accumulation of biogenic silica (tab 2, 2) for the study area (eq. 1.2). For this purpose, we applied average biogenic silica content and porosity for each sediment type, since the content of biogenic silica as well as grain size distribution or porosity did not show major variations over the period of investigation (tab. 1). For muddy and fine sand deposits bSi accumulation rates of 0.7 to $0.9 \text{ mol m}^{-2} \text{ a}^{-1}$ are almost similar. In contrast, the bSi mass accumulation in coarse sand sediments is considerably lower (tab. 2, 2). This might be due to different depositional conditions (e.g. bottom water current speed) at sites with coarse grained sediments, compared to sites where fine grained sediments deposit.

To quantify the total rain rate of bSi reaching the seafloor, the efflux of silicic acid through the sediment water interface has to be considered. This quantity reflects the amount of bSi dissolved within the sediments. In contrast to the sediment composition, the efflux of silicic acid has a seasonal pattern as discussed before (fig. 6). Therefore, we calculated a weighted average efflux of $\text{Si}(\text{OH})_4$ as well as minimum and maximum efflux rates with respect to the seasonal cycle from *in situ* and *ex situ* incubations (tab. 2, 3). Within the target area, the calculated bSi rain rates (tab. 2, 4) are comparatively similar (average 1.7 to 2.2 $\text{mol Si m}^{-2} \text{a}^{-1}$) for the different sediment types. This seems likely, since local differences in primary production in surface waters within the study area of about 2270 km^2 are not to be expected. Based on benthic flux data and the burial of bSi, we calculated a mass budget for the whole area of investigation by multiplying each flux with the spatial coverage (km^2) of the respective sediment type and summing up all fluxes. This results in a total rain rate of biogenic silica (bSi_{rain} rate) of $3.8 * 10^9 \text{ mol Si a}^{-1}$ (min $2.0 * 10^9 \text{ mol Si a}^{-1}$, max $7.8 * 10^9 \text{ mol Si a}^{-1}$) for the entire area under study.

The efficiency of different sediment types to recycle biogenic silica is shown in table 2 (5). In coarse grained sediments a fraction of about 81 % of the deposited biogenic silica is transported back into the water column. Considerably lower recycling efficiencies (60 to 61 %) were observed in the fine grained sediments. This suggests that in coarse grained sediments biogenic opal is efficiently recycled, whereas in finer grained sediments higher amounts of biogenic silica are preserved. Lower preservation efficiencies in permeable sediments might be caused by higher dissolution rates and effluxes due to advective transport processes such as bioirrigation or wave induced pore water flushing (Vanderborght et al. 1977; Huettel et al. 2014).

Sed. Type (1)	$b\text{Si}_{acc}$ (2) ($\text{mol m}^{-2} \text{a}^{-1}$)	$\text{Si}(\text{OH})_4$ efflux (3) ($\text{mol m}^{-2} \text{a}^{-1}$)	$b\text{Si}_{rain}$ (4) ($\text{mol m}^{-2} \text{a}^{-1}$)	Recycling. (5) (%)
m	0.9	1.3 (min 0.6, max 2.0)	2.2 (min 1.4, max 2.9)	60
fs _{high}	0.7	1.1 (min 0.1, max 2.0)	1.9 (min 0.8, max 2.7)	61
fs _{low}	0.7	1.0 (min 0.3, max 3.0)	1.7 (min 0.9, max 3.7)	60
cs	0.4	1.6 (min 0.5, max 3.7)	2.0 (min 0.8, max 4.1)	81

Table 2: Estimates about the recycling efficiency of silicic acid and the total rain rate of biogenic silica reaching the sediment. Column (1) the sediment type, (2) bSi accumulation rate ($b\text{Si}_{acc}$), (3) $\text{Si}(\text{OH})_4$ efflux along the sediment water interface based on seasonal averaged values, (4) bSi rain rate, (5) recycling efficiency in terms of the percentage dissolved and release of $\text{Si}(\text{OH})_4$ into bottom water. On an average about 60 % of the rain rate of bSi reaching the sediment is recycled.

High rain rates of biogenic silica considerably exceed those of most other regions such as the North Atlantic, North Pacific or the Indian Ocean (Tréguer and De La Rocha 2013), while biogenic silica contents of surface sediments are rather low (0.2 to 3.7 wt %) and similar to other coastal areas

such as the amazon shelf (~0.2 to 0.4 wt %, DeMaster et al. 1983) or the Monterey Bay (<1 wt %, Berelson et al. 2003). However, asymptotic silicic acid concentrations of pore water profiles as well as benthic fluxes are rather similar to those observed for bSi rich sediments in the Southern Ocean or North Pacific. High rain rates of readily soluble biogenic silica to the sediment, coupled with a high reflux of silicic acid emphasize the importance of benthic-pelagic coupling in shallow water ecosystems.

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Appendix

A) Dominant macrofauna species based on mean abundance (Ind./m²) according to SIMPER Analysis that contributed (contrib (%)) most to the community structure of each station. Mean biomass is given in wet weight (g/m²). Feeding types: SF = suspension feeder, SSD = subsurface deposit feeder, P = predator, IF = Interface feeder, O = omnivorous, SD = deposit feeder. Functional types: S = surficial modifier, B = biodiffuser, UC = upward conveyor, UC/DC = upward-downward conveyor

Species	mean abundance (Ind./m ²)	contrib (%)	mean biomass (g/m ²)	feeding type	functional type
He395-38/TS2 (March 2013)					
<i>Kurtiella bidentata</i>	1107	21.19	2.86	SF	S
<i>Nucula nitidosa</i>	1036	18.63	14.29	SSD	S
<i>Pholoe baltica</i>	750	14.55	1.43	P	S
<i>Scoloplos armiger</i>	464	8.27	1.43	SSD	B
Capitellidae juv.	429	7.79	1.43	SSD	UC
<i>Amphiura filiformis</i>	357	5.45	12.86	IF	B
<i>Spiophanes bombyx</i>	393	4.97	1.43	IF	UC/DC
<i>Goniada maculata</i>	321	3.78	1.43	P	B
<i>Spiophanes bombyx</i>	143	3.32	5.71	SD	S
He412-27/TS2 (November 2013)					
<i>Kurtiella bidentata</i>	3524	23.16	5.71	SF	S
Capitellidae juv.	1761	15.14	1.43	SSD	UC
Ophiuridae juv.	1239	10.6	0.00	O	S
<i>Abra nitida</i>	1047	9.23	17.14	SD	S
<i>Scalibregma inflatum</i>	1000	5.95	21.43	SSD	B
<i>Nucula nitidosa</i>	810	5.5	7.14	SSD	S
<i>Spiophanes bombyx</i>	714	5.5	1.43	IF	UC/DC
He417-38/TS2 (March 2014)					
<i>Kurtiella bidentata</i>	3964	73.95	15.71	SF	S
<i>Nucula nitidosa</i>	429	19.88	11.43	SSD	S
<i>Nephtys</i> spp.	71	3.92	1.43	P	B
<i>Amphiura filiformis</i>	164	1.52	22.86	IF	B

Chapter 4: Diurnal variations of benthic oxygen and nitrate fluxes measured with an oxygen optode and the nitrate sensor SUNA V2

(in preparation)

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Abstract

In coastal areas, diurnal variability of light reaching the seafloor causes strong variations in benthic oxygen fluxes over time scales of hours. During daylight oxygen is produced by the photosynthetic activity of benthic algae. At night time oxygen is consumed by heterotrophs and the oxidation of reduced compounds. Diurnal variability in benthic oxygen concentrations might have a considerable impact on the benthic nitrogen cycle. Sediments were sampled in September within the Odense fjord (Denmark) and incubated over 12 hour light:dark cycles. Oxygen and nitrate were measured continuously with an optical nitrate sensor SUNA V.2 (Satlantic™) and an oxygen optode (Pyroscience™). The impact of benthic fauna on benthic oxygen and nitrate fluxes was studied by incubating one set of cores containing benthic macrofauna and one set of cores in which macrofauna was removed prior to the experiment.

In dark periods, oxygen consumption was closely coupled to the presence or absence of benthic macrofauna. In cores containing benthic macrofauna, oxygen consumption rates of $30 \text{ mmol m}^{-2} \text{ d}^{-1}$ were measured. In defaunated cores oxygen consumption rates were more than twice as high and in the range of $61 \text{ to } 76 \text{ mmol m}^{-2} \text{ d}^{-1}$. Approximately 2 to 2.9 hours after lights were turned on anoxic conditions ceased within the bottom water and were followed by a continuous production of oxygen, until saturating to supersaturating conditions were reached within the bottom water in the late afternoon.

Continuous monitoring of nitrate bottom water concentrations revealed that nitrate fluxes were affected by a combination of oxic-anoxic conditions and the availability of light. In general, nitrate effluxes were observed at night time when bottom waters were anoxic and during daytime when bottom waters were oxic. An influx of nitrate was measured at the onset of light as long as the bottom water was anoxic. These datasets underline the variability of the benthic oxygen and nitrate cycle over time scales of hours in coastal sediments.

Keywords: Diurnal cycles, benthic oxygen fluxes, benthic nitrate fluxes, benthic macrofauna, nitrate sensor

1. Introduction

In coastal, light-exposed marine sediments, benthic oxygen and nitrogen fluxes vary over diurnal time scales. The production and consumption of oxygen is regulated by a wide variety of autotrophic and heterotrophic microorganisms and metazoans. During daytime, benthic microphytes produce oxygen via photosynthesis which can lead to supersaturating oxygen concentrations in surface sediments and the overlying water column (Revsbech et al. 1980). At night time, anoxia might occur as a consequence of high respiratory demand of surface sediments (Revsbech et al. 1983). Although the oxygen and nitrogen cycles are intensively investigated, less is known about the variability of oxygen over time scales of hours and its link to the nitrogen cycle (Herbert 1999; Glud 2008).

The production and consumption of oxygen is highly dynamic over diurnal time scales. Benthic microphytes are the dominant primary producers in most unvegetated shallow water sediments (e.g. Thornton et al. 2002) and have an impact on benthic oxygen consumption rates. Benthic algae and excreted photosynthates provide a good food source in the photosynthetic zone of the sediment (Middelburg et al. 2000; Glud 2008). At night time accumulated labile organic matter induces excessive respiration rates. Furthermore anaerobic metabolites (e.g. metallic sulphides) are immobilised in surface sediments during night time. During the next day, a part of the photosynthetically produced oxygen is thereby needed to oxidize the reduced compounds (Fenchel and Glud 2000). Furthermore, benthic macrofauna has an important impact on oxygen fluxes in sediments which are inhabited by microphytobenthos. Labile organic matter, which accumulates within surface sediments, is grazed or transported into burrows by benthic macrofauna (Tang and Kristensen 2007). Benthic macrofauna thereby keeps a low but active biomass of microphytobenthos within surface sediments.

Besides the oxygen cycle, benthic microphytes have a considerable impact on the benthic nitrogen cycle. For example, the benthic production of oxygen can fuel nitrogen transformations such as nitrification (Risgaard-Petersen et al. 1994). Benthic primary producers further reduce the amount of nitrogen in pore waters via assimilatory uptake or the storage of nitrate in liquid vacuoles as intracellular nitrate $ICNO_3$ (Fossing et al. 1995; Lorenzen et al. 1998). Recently, benthic diatoms were identified which can utilize $ICNO_3$ in order to survive under anoxic dark periods via dissimilatory nitrate reduction to ammonium (Kamp et al. 2011; Stief et al. 2013). The steps of uptake, reduction and assimilation of nitrate require ATP, which is ultimately derived from photosynthesis and therefore potentially impacted by diurnal rhythms (Vincent 1992).

Diurnal variations in benthic oxygen and nitrate fluxes occur in temperate, light exposed coastal sediments and were addressed in several studies within the last decades (Risgaard-Petersen et al.

1994;; Risgaard-Petersen 2003; Wenzhöfer and Glud 2004; Tang and Kristensen 2007). State of the art oxygen sensors (e.g. oxygen micro sensors, planar optodes) revealed that oxygen fluxes are controlled by diurnal light:dark shifts and are considerably affected by benthic macrofauna (Tang and Kristensen 2007). However the role of nitrate is less clear, due to a lack of appropriate techniques, which could monitor nitrate continuously with a sufficient temporal resolution. Our objectives were to implement the nitrate sensor SUNA V2 (Satlantic™) and an oxygen optode (Pyroscience™) in closed microcosms and thereby monitor nitrate and oxygen concentrations continuously in incubation experiments. Based on this laboratory setup we studied the impact of macrofauna on benthic oxygen and nitrate fluxes over 12 hour light:dark shifts on a coastal sediment.

2. Material and Methods

2.1 Study site

Sediment samples were collected during a field campaign in September 2013 on the northern coast of the island of Fyn (Denmark) in the inner bay of the Odense Fjord (N55°29', E10°29'). The inner part of the Odense fjord has a surface area of 10.7 km² and a mean water depth of 0.8 m (Riisgård et al. 2008). The salinity of the water column varies from 5 to 17 with lowest salinities in winter (Fyns Amt 2004). Seasonal variations in the monthly mean water temperature are high ranging from 3 °C in winter to 19 °C in summer (Riisgård et al. 2008).

In the inner fjord, seasonal variations in water column dissolved inorganic nitrogen concentrations (DIN) are closely coupled to variations in pelagic primary production and freshwater input from land. In winter primary production is limited by the availability of light in the water column. Combined with a high freshwater input, highest annual NO₃ concentrations of up to 3500 µg l⁻¹ occur in the water column. In summer the water column is depleted in DIN and phytoplankton growth is limited by the availability of nitrogen (Riisgård et al. 2008; Kristensen et al. 2014).

Benthic diatoms are widely distributed within surface sediments of the fjord. In spring, microphytobenthic primary production (MPP) is stimulated by increasing availability of light at the sediment surface and enhanced nutrient concentrations both from the water column and from the sediment below. During spring benthic primary production may account for 75 % of the total primary production. In summer pelagic primary production reduces the light penetration to the seafloor and the dominant part of primary production shifts to the pelagic environment (Riisgård et al. 2008).

The sediments of the inner fjord consist of sand with a median grain size around 200 µm and low organic carbon contents of less than 3 % (Valdemarsen et al. 2014). In winter and spring the

sediments act as a net sink for nitrogen. Especially in spring the influx of nitrogen from the water column into the sediment can be high, due to high microphytobenthic primary production and high denitrification rates, coupled to high DIN concentrations in the water column. In summer, benthic mineralisation rates are high, which causes low oxygen availability and a net efflux of nutrients out of the sediments into the water column. During that time nitrogen occurs dominantly in the form of ammonia with a minor contribution of nitrate due to nitrification (Riisgård et al. 2008).

The environmental conditions of the inner part of the Odense fjord are highly variable including frequent and dramatic changes in salinity, temperature and oxygen conditions (Delefosse et al. 2012). Therefore relatively few species of benthic fauna are adapted to withstand these stressful conditions. The benthic fauna in the inner fjord is characterized by high abundances of opportunistic species like the oligochaete *Tubificoides benedii*, gastropods of the Hydrobiidae family, the crustacean *Corophium volutator*. The polychaete *N. diversicolor*, *Arenicola marina* and *Marenzelleria viridis* are less abundant but account of more than 75 % of the total biomass (Kristensen et al. 2014).

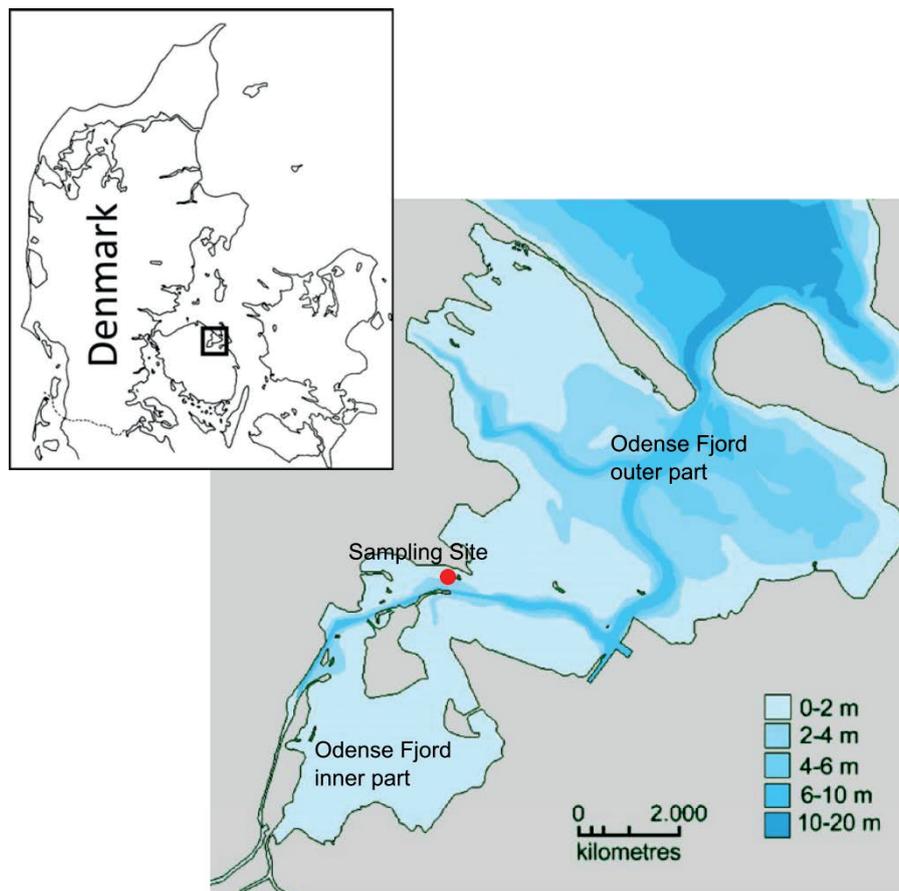


Figure 1: The Odense fjord and the sampling site at which sediments were obtained. The fjord is divided into an inner and outer part. The inner part is characterized by very shallow water depths which in general do not exceed 2 metres. The map was adapted from Valdemarsen et al. (2014).

2.2 Microcosm experiments

Sediment samples were taken by inserting Plexiglas core liners (diameter = 5.2 cm, length = 15 cm) into the sediment. Only cores with an intact, undisturbed sediment surface and an overlying water column of several centimetres were selected. The cores were subsequently sealed with rubber stoppers, placed in an insulated box and transferred to the laboratory.

In the laboratory the cores were separated into two groups: one group in which benthic macrofauna was maintained (faunated cores) and a second group in which benthic fauna was removed (defaunated cores). The first group of cores (faunated cores) were submerged in aerated bottom water (16 °C) from the sampling site and kept under constant conditions until incubations were carried out. The second group of cores (defaunated cores) were immediately frozen at -18 °C for 24 hours for the elimination of benthic macrofauna (Hancke et al. 2014). After a few days the frozen cores were placed in a box filled with aerated bottom water from the sampling site and thawed under a constant temperature of 16 °C. The cores were subsequently exposed to a 12:12 hour light:dark shift for a week by a halogen lamp (Philips SON-T 400W) (fig. 2, a). Thereby a clear stratification in between an upper oxic and a lower anoxic sediment layer developed when lights were switched on (fig. 2, b). The upper oxic zone was about 1 cm thick, indicated by a light, brownish colour of the sediment. The lower anoxic layer was indicated by dark colour of the sediment.

For incubation experiments both defaunated and faunated cores were adjusted to a constant water column height of 5.7 cm between the sediment surface and the upper part of the Plexiglas core liner. A teflon coated magnetic stirrer driven by an external rotating magnet mixed the bottom water in each core slightly without disturbing the sediments surface. Incubations were carried out under 12 hour light:dark shifts on separate sediment cores from both groups over 24 to 48 hours. Each respective core was sealed by a transparent acrylic lid. An air sealed continuous flow system was connected to the overlying bottom water of the core (fig. 2, a). An oxygen optode (Pyroscience™) and an optical nitrate sensor (Suna V2, Satlantic™) were connected to the flow system (fig. 2, c). By this mean, nitrate and oxygen were continuously monitored within a closed system without any interference due to sampling. The oxygen optode was calibrated by a 2-point calibration in anoxic and air saturated samples at a temperature of 16 °C before the experiment. The nitrate sensor was calibrated for seawater samples.

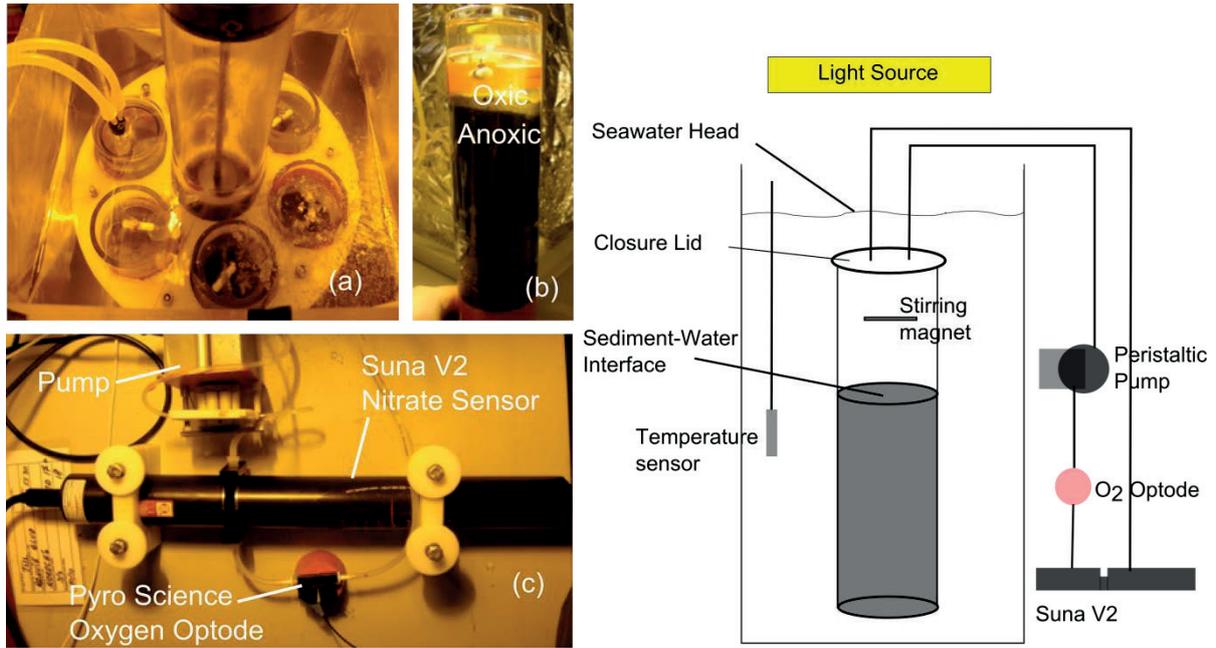


Figure 2: Experimental setup of microcosm studies. The cores were submerged in aerated water and exposed to 12 hour light:dark cycles (a). In each core a distinct boundary between oxic (bright) and anoxic (dark) conditions within the sediment were observed during light exposure (b). During incubation the cores were closed with a lid and connected to a continuous flow system in which nitrate and oxygen were continuously monitored (c).

2.3 Satlantic™ Sana V2 calibration and performance tests

The Sana V2 sensor (Satlantic™) measures the concentration of nitrate by the distinct ultraviolet adsorption spectra of its species (Johnson and Coletti 2002). According to the manufacturer the sensor has a detection range from 0.5 to 2000 $\mu\text{mol l}^{-1}$ and an accuracy of $\pm 2 \mu\text{mol l}^{-1}$. A deuterium lamp measures in a wavelength range of 190 to 370 nm with a path length of 1 cm. The sampling rate is 1 Hz. It has to be noted that the sensor is designed for *in situ* applications until water depths of 100 m. The precision and the accuracy of the sensor were tested in freshwater and seawater samples. Calibration runs were performed in freshwater and in a seawater matrix using potassium nitrate standards (KNO_3) ranging from 5 to 500 $\mu\text{mol l}^{-1}$.

The precision (pr) of the sensor was calculated according to formula (1):

$$pr = \frac{|\bar{x} - x_{ref}|}{\bar{x}} \quad (1)$$

with \bar{x} being the average measured nitrate concentration over a time interval of 20 seconds and x_{ref} being the referenced known nitrate concentration.

The accuracy (ac) of the sensor was calculated after formula (2):

$$ac = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (2)$$

with n being the number of measurements, \bar{x} being the average nitrate concentration over the 20 seconds measuring interval and x_i being the measured nitrate concentration of the n^{th} sample.

The sensor performed good in both freshwater and seawater samples with an r^2 of 0.9934 and 0.9993 respectively. A good accuracy was achieved for lower KNO_3 concentrations of about $25 \mu\text{mol l}^{-1}$. Within seawater (fig. 3, b) larger offsets between standards and measured nitrate concentrations were observed for higher KNO_3 concentrations. Within a concentration range of 25 to $100 \mu\text{mol l}^{-1}$ measured KNO_3 concentrations were about 10 % lower than the standard concentration. Within a concentration range of 200 to $500 \mu\text{mol l}^{-1}$ about 20 % lower concentrations were measured when compared to standard concentrations. In most unpolluted aquatic environments nitrate concentrations do not exceed $20 \mu\text{mol l}^{-1}$ (Canfield et al. 2005). Consequently, larger offsets in higher NO_3 concentrations are acceptable for our purposes.

Table 1: Standards (1), measured nitrate concentrations and the precision and the accuracy of each measurement in freshwater (2) and in seawater (3).

KNO_3 std ($\mu\text{mol l}^{-1}$) (1)	KNO_3 SUNA ($\mu\text{mol l}^{-1}$) (2.1)	Precision (2.2)	Accuracy (2.3)		KNO_3 SUNA ($\mu\text{mol l}^{-1}$) (3.1)	Precision (3.2)	Accuracy (3.3)
	<i>Freshwater</i>				<i>Seawater</i>		
5	5	0.50	0.00		5	0.47	0.07
10	12	0.49	0.17		11	0.35	0.11
25	26	0.48	0.05		23	0.86	0.10
50	52	0.49	0.04		45	1.85	0.11
100	-	-	-		88	3.07	0.14
200	203	0.15	0.01		160	5.73	0.25
300	292	1.16	0.03		235	3.67	0.28
500	432	2.90	0.16		405	19.08	0.24

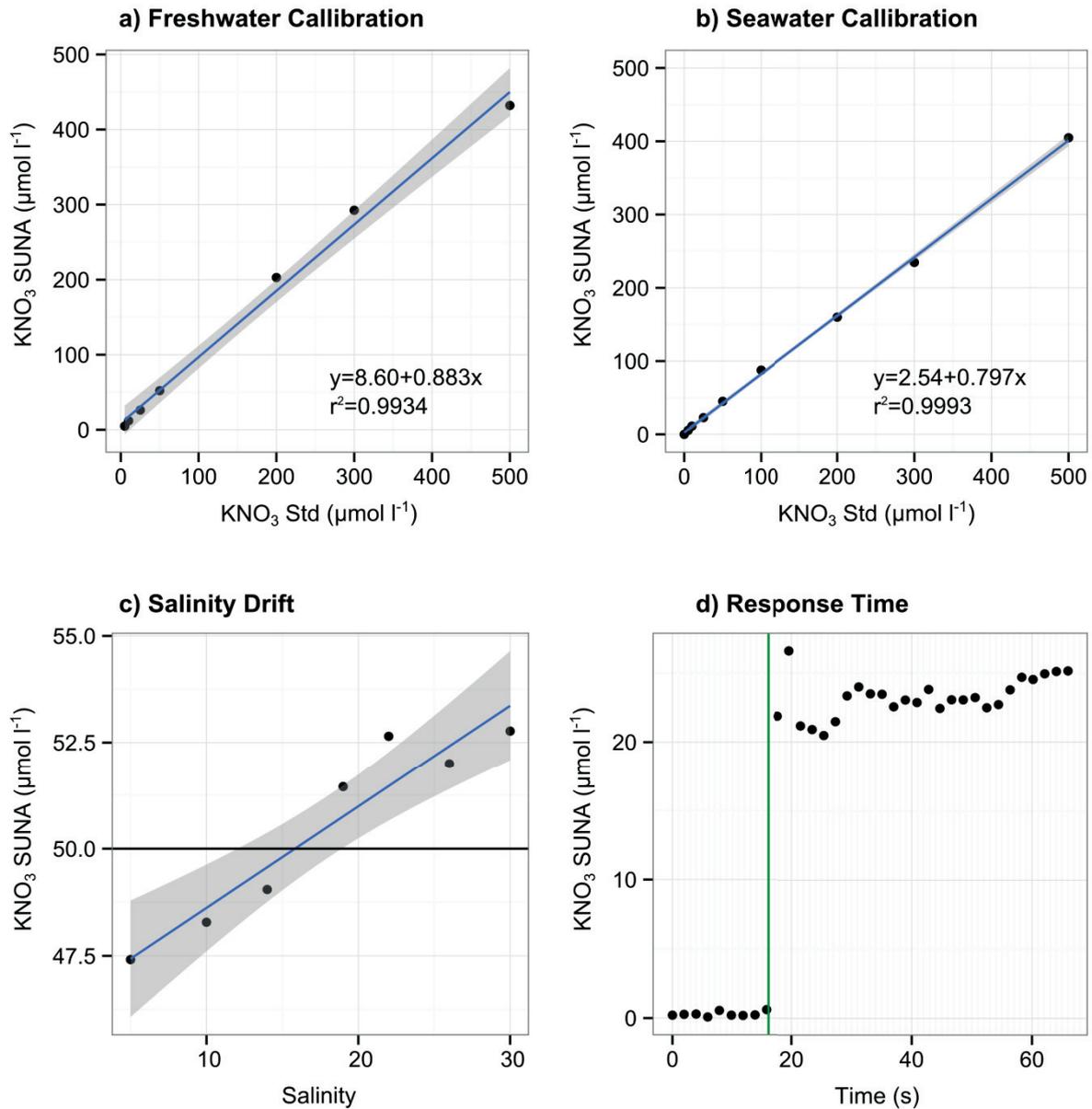


Figure 3: Nitrate Suna V2 sensor performance. Calibration of the nitrate sensor was carried out in freshwater (a) and seawater (b) standards. In order to check for possible salinity drift (c) KNO_3 standards ($50 \mu\text{mol l}^{-1}$) were tested in water samples with different salinities. The response time (d) was tested by injecting a KNO_3 spike (green line) into the measuring cell.

The influence of varying salinities on the measured nitrate concentrations was tested. Standards with different salinities ranging from 0 to 30 (fig. 3, c) and a constant KNO_3 concentration of $50 \mu\text{mol l}^{-1}$ (fig. 3, c black line) were prepared. The measured nitrate signal increased gradually with increasing salinities. Within a salinity range of about 0 to 15 measured nitrate concentrations were about $2.5 \mu\text{mol l}^{-1}$ lower than expected. In samples with highest salinities (20 to 30) measured KNO_3 concentrations were about $2.5 \mu\text{mol l}^{-1}$ higher than expected.

The response time (fig. 3, d) of the nitrate sensor was tested by placing the measuring cell in seawater containing no nitrate. A nitrate spike with a high KNO_3 concentration was injected into the measuring cell. The time difference in between the injection and the change in the nitrate signal was used to estimate the response time of the sensor. Tests were performed ten times under similar initial boundary conditions. Figure 3 (d) shows the measured nitrate concentrations with time during the experiment. The green line marks the time when the nitrate spike was injected into the measuring cell. Repetitive measurements showed that the sensor responded to changing nitrate concentrations within two seconds.

3. Results

3.1 Benthic oxygen and nitrate fluxes in faunated and defaunated cores

The production and consumption of oxygen in coastal surface sediments is regulated by various autotrophic and heterotrophic microorganisms and metazoans within the upper millimetres to centimetres of the sediment (Glud 2008). Under light conditions benthic algae produce oxygen via photosynthesis. Concurrently oxygen is consumed during light conditions by heterotrophs, the oxidation of reduced solutes and photorespiration (Glud 2008). Under dark conditions photosynthesis is obligatory inhibited and oxygen is consumed by heterotrophs and by the reoxidation of reduced inorganic solutes (Canfield et al. 1993).

In defaunated and faunated cores, oxygen fluxes followed the 12 hour dark:light cycles (fig. 4+5). Light periods are indicated by the white background and darkness by the blue background. Decreasing concentrations of oxygen with time reflect sediment consumption of oxygen (influx), while increasing concentrations with time reflect sediment production of oxygen (efflux). Anoxic conditions were defined as oxygen concentrations below 0.5 mg l^{-1} . The onset of anoxic conditions is marked in figure 4 and 5 by the red line and ceasing anoxic conditions are marked by the green line. The period of time, in which bottom waters were anoxic and lights were switched on, is marked by the orange background.

Cores in which macrofauna was removed prior to incubation (defaunated) are shown in figure 4. At the beginning of the incubation oxygen was supersaturated ($\sim 130\%$) in microcosm 1 and saturated ($\sim 100\%$) in microcosm 2. After lights were switched off, oxygen was consumed in both experiments until bottom waters reached anoxic levels (red line) after 2.3 to 2.9 hours (fig. 4). Oxygen fluxes were in the range of 60 to $76 \text{ mmol m}^{-2} \text{ d}^{-1}$. This is in a similar range found in undisturbed defaunated sediment cores from various locations in the Odense fjord (Valdemarsen et

al. 2014). As soon as light was switched on anoxia ceased in microcosm 1 and 2 within 2.9 and 2.7 hours, respectively (fig. 4, green line). Subsequently in both cores oxygen was produced within the bottom water until saturating to supersaturating concentrations were reached in the late afternoon.

Nitrate was measured in microcosm 1 within each hour for approximately 15 minutes and in microcosm 2 continuously (fig. 4). The nitrate signal showed some scatter which might be due to air bubbles or particles in the measuring cell. However, due to a high sampling frequency (0.5 Hz) large datasets were obtained (about 450 measurements within each 15 minute measuring interval). Box-whisker-plots over respective 15 minute measuring intervals revealed significant changes of median nitrate concentrations with time in microcosm 1 (fig. 4). In microcosm 1 and 2, linear regressions of nitrate concentrations were applied versus different periods of time: onset of darkness (blue line) to anoxic conditions (red line); anoxic conditions (red line) to onset of light (blue line); onset of light (blue line) to ceasing anoxic conditions (green line); oxic conditions (green line) until onset of darkness (blue line) or the end of the experiment.

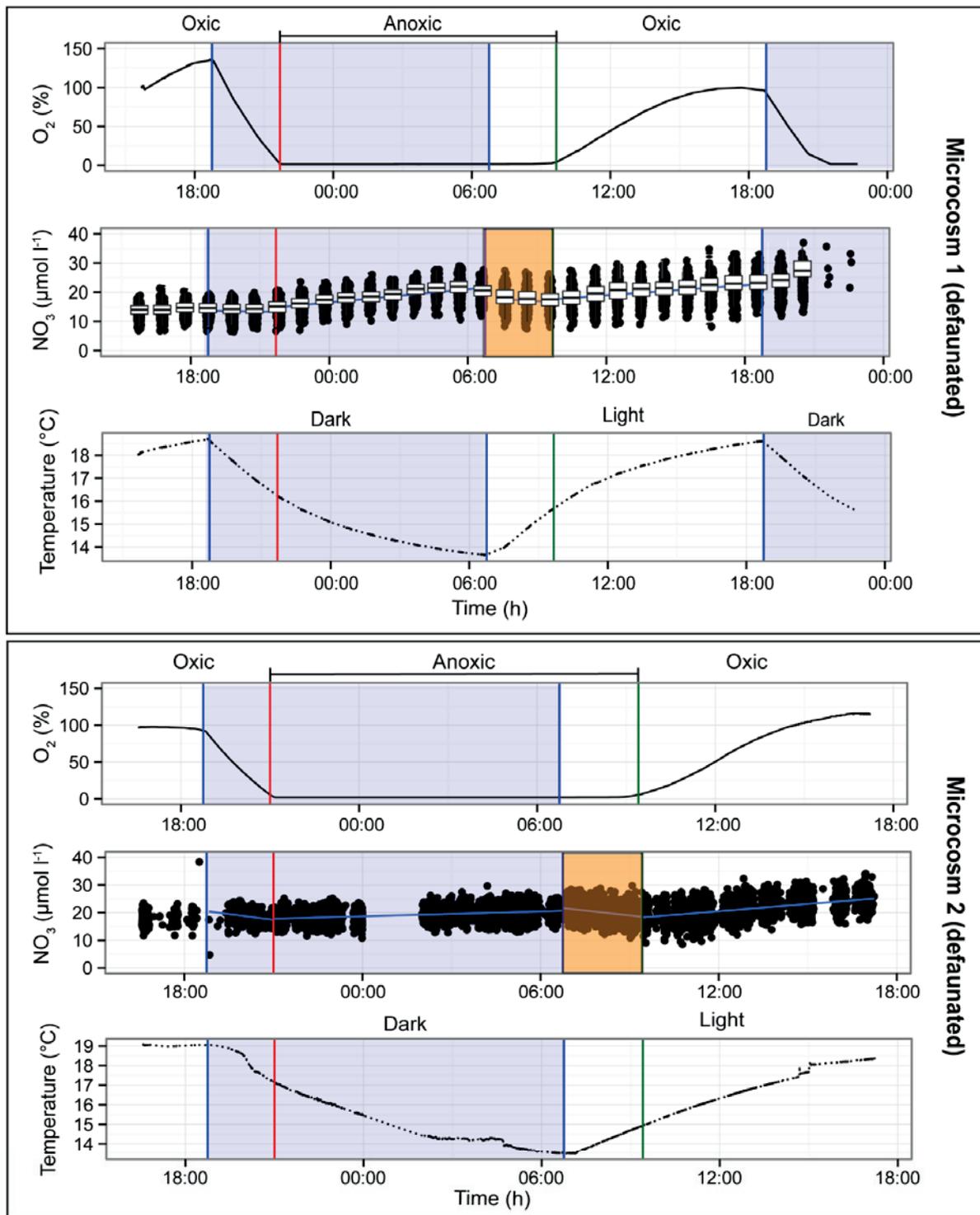


Figure 4: Time series of measured oxygen concentrations (%), measured nitrate concentrations ($\mu\text{mol l}^{-1}$) and the bottom water temperature ($^{\circ}\text{C}$) in microcosm 1 and 2. The sediment was defaunated prior to the incubation. Light:dark cycles are indicated by the blue (dark) and white (light) background. The onset of anoxic conditions in the bottom water is indicated by the red line. Ceasing anoxic conditions are marked by the green line. The orange background indicates the time interval at which anoxic conditions were observed while lights were switched on. In microcosm 1 box-whisker-plots for respective 15 minute measuring intervals of nitrate are shown.

Nitrate fluxes in defaunated cores were affected by a combination of light availability and oxic:anoxic conditions in the bottom water. In dark periods, a nitrate efflux (0.41 to $1.05 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed as soon as anoxic conditions were reached within the bottom water (fig. 4, red line). With the onset of light, the efflux of nitrate turned into an influx of 0.6 and $1.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ in microcosm 1 and 2, respectively (fig. 4, orange background). As soon as anoxic conditions ceased (fig. 4, green line at the end of the experiment), the nitrate influx turned back into an efflux.

In microcosm experiment 3 (fig. 5) benthic macrofauna inhabited the sediment. At the beginning of the experiment bottom waters were saturated in oxygen. Under dark conditions (fig. 5, blue background), oxygen was consumed ($31 \text{ mmol m}^{-2} \text{ d}^{-1}$) until anoxic conditions were reached after approximately 7 hours within the bottom water (fig. 5, red line). Anoxic levels were reached more than two times later when compared to the defaunated core. As a consequence, cores which were inhabited by benthic fauna were exposed to anoxia over shorter time intervals when compared to cores which were defaunated prior to the experiment. After the lights were switched on again bottom waters stayed anoxic for about 2 hours (fig. 5). As soon as anoxic conditions ceased (fig. 5, green line) oxygen concentrations increased within the bottom water. Within the faunated core a nitrate efflux was observed within the dark period. A slight nitrate influx of $0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ was observed as soon as lights were switched on (fig. 5, orange background).

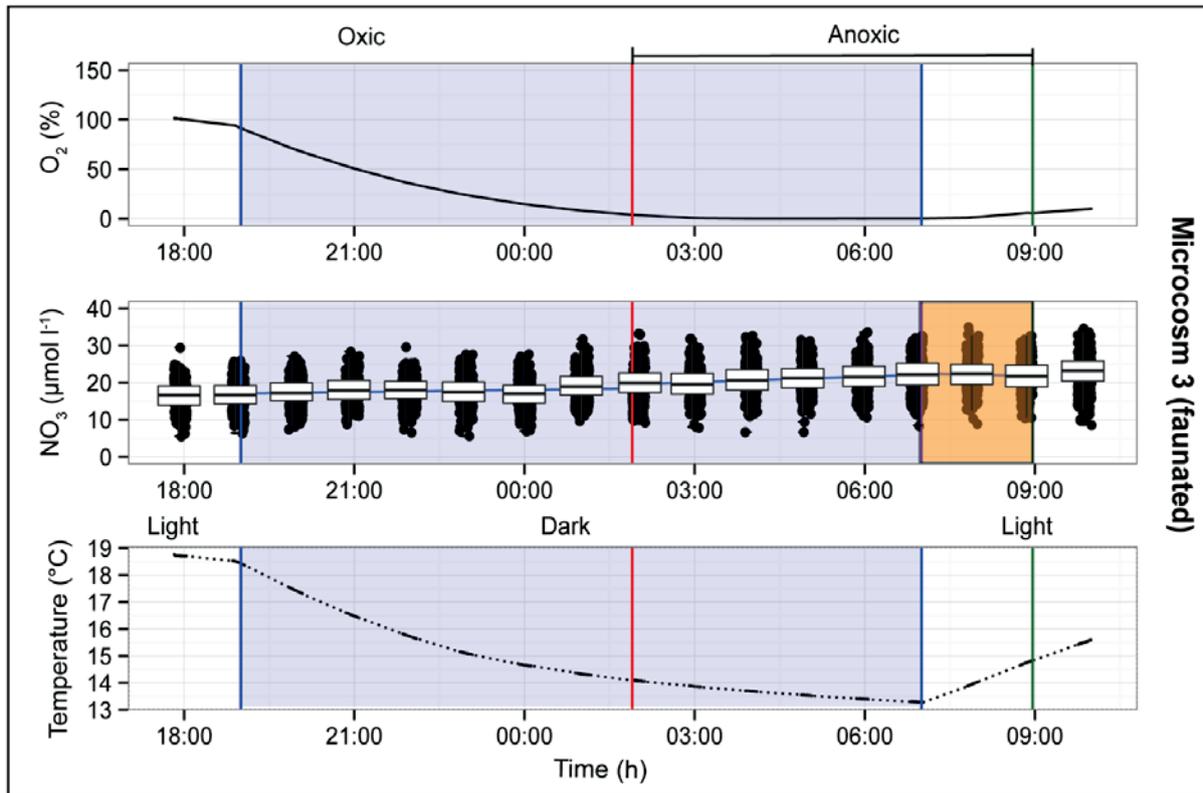


Figure 5: Time series of measured oxygen concentrations (%), measured nitrate concentrations ($\mu\text{mol l}^{-1}$) and the bottom water temperature ($^{\circ}\text{C}$) in microcosm 3. The sediment was inhabited by benthic fauna. Light:dark cycles are indicated by the blue (dark) and white (light) background. The onset of anoxic conditions in the bottom water is indicated by the red line. Ceasing anoxic conditions are marked by the green line. The orange background indicates the time interval at which anoxic conditions were observed while lights were switched on. Box-whisker-plots are shown for respective 15 minute measuring intervals of nitrate.

4. Discussion

4.1 The impact of benthic fauna on benthic oxygen production and consumption

During daylight the production of oxygen was observed in both faunated and defaunated cores. Furthermore an oxidized zone was observed within the upper centimetre of the sediment as indicated by a light brownish colour of the sediment (fig. 2, B). The production of oxygen during illumination is most likely caused by benthic algae in surface sediments. Within the sediments of the Odense fjord benthic diatoms are known to occur widespread (Riisgård et al. 2008). Diatoms were observed on the sediment surface, indicated by a brownish layer, during sampling in the field and in the laboratory. We expect that the production of oxygen was most likely dominated by benthic diatoms. Some macrophytes including seagrass, *Ruppia maritima* and *Ulva lactuca* are further known to occur in the fjord (Riisgård et al. 2008), but were not observed during sampling or in the laboratory. At the end of the light periods the oxygen production declined (fig. 4) which might be caused by nutrient limitation for the growth of diatoms or higher microbial mineralisation fuelled by

labile photosynthates which accumulate in the sediment (Winder et al. 1999; Orvain et al. 2003; Stal 2003).

High oxygen consumption rates were observed during night time (fig. 4) in cores which were not inhabited by benthic macrofauna. The consumption might be caused by heterotrophic activity of microbes and/or the oxidation of reduced solutes (Glud 2008). High oxygen consumption rates are possibly fuelled by the development of microalgal mats and/or accumulation of labile organic matter within surface sediments (Tang and Kristensen 2007). For example, during daytime oxygen concentrations sometimes reach supersaturating concentrations in dense microphytic communities. Photorespiration may induce the leakage of labile photosynthates which might serve as an important carbon source for heterotrophs (Glud 2008). At night time the accumulated organic carbon pool can induce enhanced heterotrophic activity, which gradually declines as the labile organic carbon pool declines (Fenchel and Glud 2000; Tang and Kristensen 2007).

In sediments which are inhabited by benthic microphytes, benthic macrofauna has an important function for the regulation of the amount of labile amount of organic matter in the sediment (Tang and Kristensen 2007). Grazing by macrofauna can reduce the microphytobenthic biomass within surface sediments (Miller et al. 1996). Furthermore labile organic material (e.g. photosynthates) is grazed or transported into burrows by benthic macrofauna. In this context the large bodied polychaetes *N. diversicolor*, *A. marina* and *M. viridis* were identified as dominant bioturbators in the Odense fjord, having a substantial impact on sediment reworking and burrow ventilation (Kristensen et al. 2014).

The lag in the oxygen production after the onset of light might be due to a lag in primary production cellular machinery (Peters 1996). Furthermore photosynthetically produced oxygen may be used for the oxidation of reduced species (e.g. ferrous iron, sulphides, Fe^{2+} , Mn^{2+}), which accumulated within surface sediments and the overlying water column during darkness (Epping et al. 1998; Fenchel and Glud 2000).

4.2 The response of benthic nitrate fluxes to light and oxic:anoxic conditions

The aim of this study was to implement the nitrate sensor SUNA V2 into microcosm experiments in order to study the variability of benthic nitrate fluxes over diurnal cycles. We observed distinct changes in nitrate fluxes over time scales of hours which seemed to be dependent on a combination of light availability and oxygen concentrations. It has to be noted that discussing the nitrate fluxes remains very hypothetical, as other nitrogen species (e.g. NH_4 , NO_2) were not measured within this study.

During most of the time a nitrate efflux was observed in both faunated and defaunated cores (fig. 4+5). Sediments were sampled within the Odense fjord in late summer, a season at which benthic mineralization rates are high, the oxygen penetration into the sediment is low and a net efflux of nutrients can be expected (Riisgård et al. 2008). We suppose that a net efflux of nitrate over the diurnal cycle was most likely attributed to the heterotrophic state of the sediment. During exceptional periods of time the sediment efflux of nitrate turned into an influx. A sediment influx of nitrate could either be due to an uptake by benthic organisms or due to dissimilatory microbial processes in which nitrate is used as an oxidant (Thamdrup 2012).

After the dark period a nitrate influx was observed initially after the lights were turned on. The influx prevailed as long as the bottom water was anoxic within the microcosm (fig. 4+5, orange background). This is remarkable and has so far not been observed in other studies. One explanation might be that nitrate was used for anaerobic oxidation of reduced inorganic compounds which accumulated in the dark period (Canfield et al. 2005). Sulphur bacteria (e.g. *Beggiatoa*) oxidize H_2S with NO_3 as long as enough H_2S and NO_3 is available (Sayama et al. 2005). They might be active during the onset of light as long as H_2S is available within the surface sediment.

The influx of nitrate might as well be explained by the uptake of nitrate by benthic fauna or bacteria for assimilation. Diurnal variations of phytoplankton nutrient uptake are well known (e.g. Cochlan et al. 1991), at which highest NO_3 assimilation rates occur during daylight. The uptake and assimilation of NO_3 requires ATP which is derived from photosynthesis (Vincent 1992). Diatoms are known to preferentially assimilate nitrate while being photosynthetically active (Dortch et al. 1984; Lomas and Glibert 2000; Needoba and Harrison 2004) and might therefore force nitrate influx into the sediment.

Besides assimilation the intracellular uptake and storage of nitrate might have forced an influx of nitrate as well. Some Prokaryotes and Eukarya store nitrate intracellular in order to survive under anoxic dark periods (Fossing et al. 1995; Kamp et al. 2011). These include benthic algae such as diatoms (Kamp et al. 2011) or sulphur bacteria (Fossing et al. 1995; McHatton et al. 1996; Schulz et al. 1999). Within environments which are affected by sharp diurnal oxic:anoxic shifts it is imaginable that intracellular storage of nitrate is an important mechanism to survive anoxic conditions.

5. Conclusion

On a global scale, shallow water coastal sediments in which diurnal light:dark shifts might influence biogeochemical cycles of surface sediments are widespread. Implementing the nitrate sensor SUNA V2 (Satlantic™) and an oxygen optode (Pyroscience™) into closed microcosm lab experiments allowed us to study benthic oxygen and nitrate fluxes with a temporal resolution of seconds to hours.

Sediment cores were collected in the Odense fjord (Denmark) and incubated for 24 to 48 hours under 12 hour light:dark cycles. Benthic oxygen fluxes followed the diurnal light:dark shifts and were characterized by production during daylight and consumption at night time. Comparing cores in which benthic macrofauna was removed prior to the experiment and cores in which benthic macrofauna was present revealed distinct different oxygen consumption rates in darkness. In defaunated cores oxygen consumption was almost twice as high when compared to faunated cores. Similar consumption rates were observed in various sites in the Odense fjord by Valdemarsen et al. (2014). Excessive respiration on labile organic matter which accumulated in defaunated cores might have forced high oxygen consumption rates (Tang and Kristensen 2007).

Monitoring nitrate with a high temporal resolution revealed that benthic nitrate fluxes are complex and highly dynamic over time scales of hours. On a net heterotrophic sediment metabolism the onset of light triggered a sediment nitrate influx under anoxic conditions. These datasets underline the importance, to study the benthic oxygen and nitrate cycles in coastal marine sediments with a sufficient temporal resolution.

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Conclusions and Outlook

In this thesis the seasonal and diurnal variations of oxygen and nutrient fluxes were investigated. In chapter 2, *in situ* measurements with the benthic lander NuSObs revealed that benthic oxygen and nitrogen fluxes vary considerably over seasonal and spatial scales. Seasonal variations of benthic oxygen fluxes seem to be related to variations in the water column temperature, benthic macrofauna and probably by the timing of the settling of primary produced organic matter at the seafloor. Bromide tracer studies and calculations of respiration rates of benthic macrofauna suggested that in winter faunal induced transport processes are low. Spatial variations in benthic mineralisation rates are related to different feeding types and biomass of benthic macrofauna. Especially *Ensis directus* (this study), *Lanice conchilega* (Forster and Graf 1995) or *Corbula gibba* (Moodley et al. 1998) have an pronounced impact on benthic carbon fluxes. It would be advantageous to determine diffusive oxygen uptake (DOU) in future studies, as differences in between TOU and DOU can be used to calculate the faunal mediated mineralisation rate and the fauna respiration (Glud 2008).

In many coastal areas light penetrates up to 40 m into the water column, hence reaching the seabed. Therefore, it is possible that benthic production of oxygen by benthic microphytes has a considerable effect on benthic oxygen and nutrient fluxes. Diurnal variations of benthic oxygen and nitrate fluxes were investigated in laboratory experiments in chapter 4. Macrofauna reduced oxygen consumption rates of sediments possibly by grazing on labile organic matter. Benthic nitrate fluxes were highly dynamic over time scales of hours, as it was observed by continuous monitoring of NO_3 with the nitrate sensor SUNA V2. In chapter 2 no significant nitrate fluxes could be measured by conventional sampling techniques in the southern North Sea. In this case nitrate fluxes were probably not observed due to a low temporal resolution of nitrate measurements. These restrictions might be solved by applying the nitrate sensor to *in situ* benthic chamber incubations in the southern North Sea.

In chapter 3, *in situ* flux measurements with the benthic lander NuSObs, *ex situ* flux measurements, as well as sediment and pore water studies indicate that the silica cycle of the southern North Sea is highly dynamic over seasonal cycles. *In situ* flux measurements show strong seasonal variations with high silicic acid effluxes in summer (June and August) and autumn (November) (2.0 to $8.3 \text{ mmol m}^{-2} \text{ d}^{-1}$) and low effluxes in winter (March) (0.3 to $1.3 \text{ mmol m}^{-2} \text{ d}^{-1}$). Seasonal variability in flux rates occurred in conjunction with variations in the bottom water temperature, indicating that abiotic processes (e.g. diffusion, solubility, reaction rate) combined with the activity of benthic macrofauna are important factors regulating the benthic silica cycle over seasonal time scales. High benthic effluxes of silicic acid in June and August might follow the deposition of spring diatom blooms in the second half of April (Radach et al. 1990).

Mass budget calculations indicate a bSi flux of about 1.7 to 2.2 $\text{mol Si m}^{-2} \text{a}^{-1}$ from the water column to the sediment. These flux rates are about ten times higher when compared to other regions such as the North Atlantic, North Pacific or the Indian Ocean (Tréguer and De La Rocha 2013). Only major accumulation areas of biogenic silica such as the Opal belt of the Southern Ocean show similar rain rates. However biogenic silica contents of surface sediments are rather low (0.2 to 3.7 wt%) and similar to other coastal areas such as the amazon shelf (~0.2 to 0.4 wt%, DeMaster et al. 1983) or the Monterey Bay (<1 wt%, Berelson et al. 2003). The low bSi contents, in conjunction with high effluxes of silicic acid, indicate that the southern North Sea is characterized by a close benthic-pelagic coupling, due to settling of highly reactive biogenic material and a high reflux of silicic acid. Estimated carbon rain rates from the water column to the seafloor were in the range of 5 to 11.8 $\text{mol C m}^{-2} \text{a}^{-1}$. Assuming that approximately 22 $\text{mol C m}^{-2} \text{a}^{-1}$ are produced by primary production within the German Bight (Howarth et al. 1993), about 20 to 50 % of that organic carbon would settle at the sediment water interface. These estimates are comparable with other coastal regions (e.g. Wollast 1998).

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