The impact of sedimentary alkalinity release on the water column CO$_2$ system in the North Sea

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Abstract. Recently, it has been proposed that alkalinity release from sediments can play an important role in the carbonate dynamics on continental shelves, lowering the $pCO_2$ of seawater and hence increasing the CO$_2$ uptake from the atmosphere. To test this hypothesis, sedimentary alkalinity generation was quantified within permeable and muddy sediments across the North Sea during two cruises in September 2011 (basin-wide) and June 2012 (Dutch coastal zone). Benthic fluxes of alkalinity ($A_T$) and dissolved inorganic carbon (DIC) were determined using shipboard closed sediment incubations. These results show that sediments can be an important source for alkalinity, particularly in the shallow southern North Sea, where high $A_T$ and DIC fluxes were recorded in near shore sediments of the Belgian, Dutch and German coastal zone. In contrast, fluxes of $A_T$ and DIC are substantially lower in the deeper, seasonally stratified, northern part of the North Sea. Overall, our results show that sedimentary alkalinity generation should be considered as an important factor in the CO$_2$ dynamics of shallow coastal systems.

1 Introduction

Coastal seas play a crucial role in the global carbon cycle by connecting the terrestrial, oceanic and atmospheric reservoirs \cite{Regnier2013}. Although continental shelves cover only 7% of the total global ocean surface, they are estimated to account for up to 30% of the oceanic primary production \cite{Gattuso1998} and between 10 and 25% of the current day oceanic CO$_2$ uptake \cite{Regnier2013, Bauer2013}. In general, most open shelves in the temperate and high-latitude regions seem undersaturated with respect to atmospheric CO$_2$, while the low-latitude shelves generally tend to be supersaturated \cite{Cai2006, Chen2009}. However, this rule is far from absolute. Although temperate coastal areas are generally acting as a CO$_2$ sink, considerable variability has been observed in the CO$_2$ uptake within and between systems, which may be explained by a dominance of different drivers of CO$_2$ uptake. High nutrient inputs from land fuel intense primary production and hence stimulate atmospheric CO$_2$ uptake, while respiration of
organic matter exported from terrestrial ecosystems stimulates the release of $CO_2$ in coastal areas (Bozec et al., 2006; Jönsson et al., 2011; Schiettecatte et al., 2007). In addition to these biological sinks and sources, the effect of temperature on the $CO_2$ solubility controls the magnitude and direction of the $CO_2$ exchange between coastal waters and the atmosphere (Kitidis et al., 2012; Borges and Frankignoulle, 2003). Therefore the question remains which particular drivers are governing the $CO_2$ dynamics in a given coastal system (Borges and Frankignoulle, 2003).

In addition to water column processes, sediments have also been suggested to play a role, as the shallowness of coastal seas permits a close interaction between the sediment, the water body and the atmosphere. Coastal water bodies are characterized by either a permanently or seasonally mixed water column, which hence establishes a direct link between the sediment and the atmosphere, acting on a time scale of days to months. In contrast, in the open ocean, the sediment and the atmosphere can only interact over much longer time scales ($\approx 1000$ yr of global oceanic circulation). However, the extent to which sediment geochemistry plays a role in the $CO_2$ uptake of coastal system remains largely unresolved.

It has been proposed that alkalinity generation caused by anaerobic organic matter degradation in shallow coastal sediments can increase the $CO_2$ buffer capacity of coastal waters and therefore increase atmospheric $CO_2$ uptake. When coining this hypothesis, Thomas et al. (2009) estimated that alkalinity generation in Wadden Sea sediments could be responsible for 20-25% of the total $CO_2$ uptake of the entire North Sea. However, Moore et al. (2011) estimated a much smaller $A_T$ flux between the Wadden Sea and the North Sea based on activity measurements of radium isotopes in surface water. While the total strength of the $A_T$ flux between the Wadden Sea and the North Sea remains widely unknown, the Wadden Sea has been identified as a crucial source of $A_T$ for the North Sea (Brasse et al., 1999; Thomas et al., 2009; Provoost et al., 2010; Moore et al., 2011). In the East China Sea it was already suggested by Chen and Wang (1999) that alkalinity generation due to anaerobic degradation processes in sediments adds considerably to the total alkalinity budget in this area.

Furthermore, Chen (2002) proposed that shelf-generated alkalinity release from benthic anaerobic processes could be almost as important as alkalinity generated by dissolution of carbonates in the open ocean. Finally, based on modeled nitrogen and carbon budgets for the northwestern North Atlantic continental shelf, Fennel (2010) suggested that shelf sediments must be an important source of alkalinity. However, Hu and Cai (2011a) obtained a much smaller alkalinity flux from global coastal sediments based on the upscaling of local denitrification and sulfate reduction rates. They concluded that sedimentary alkalinity fluxes are too low to significantly affect the alkalinity budget of the global ocean, but also stated that sedimentary anaerobic processes could be important on regional scales as an alkalinity release mechanism. From these results, it is clear that currently, there is uncertainty as to what extent coastal sediments are an important source of alkalinity to coastal oceans.

In this study, we aim to quantify sedimentary alkalinity generation within various sediment-types in the North Sea. During two cruises samples were collected in September 2011 (basin-wide) and
June 2012 (Dutch coastal zone). Benthic fluxes of alkalinity, dissolved inorganic carbon and oxygen were determined using closed sediment incubations and microsensor profiling. Subsequently, we analyzed the sources of the observed sedimentary alkalinity release, and after implementing an alkalinity budget for both water column and sediment, we constrained the net CO$_2$ uptake from the atmosphere associated with the sedimentary alkalinity release.

2 Materials and Methods

2.1 North Sea System

In this paper we divide the North Sea into three different hydrogeographical zones: the southern North Sea (SNS), the northern North Sea (NNS) and the Skagerrak and the Norwegian Trench (SKNT). The SNS (surface area: 329.230 km$^2$) encompasses the Southern Bight (between Belgium/Netherlands and the UK), the shallow Wadden Sea (running along the Dutch and German coast up to Esbjerg in Denmark), the German Bight, and the central part of the North Sea (Figure 1). The major difference between the SNS and the NNS is the stratification regime. Whereas the shallow SNS has a fully mixed water column throughout the year, the NNS is thermally stratified in summer, but fully mixed during winter, due to strong wind forcing and surface cooling (Elliott et al., 1991). As the operational border between the SNS and NNS, we use the 100 m depth bathymetric isoline. The third hydrogeographical zone constitutes the Skagerrak and the Norwegian Trench (SKNT), which forms one of the major sediment depositional areas of the North Sea (de Haas and van Weering, 1997). The Skagerrak is part of the transition area that connects the North Sea with the Baltic Sea. It is a rather small strait (200 by 100 km) between the southeast coast of Norway, the southwest coast of Sweden, and the Jutland peninsula of Denmark. The average depth of the Skagerrak is about 210 m. The Skagerrak is strongly stratified in summer, but also features a weak stratification in winter driven by Baltic freshwater inputs (Gustafsson and Stigebrandt, 1996; Rodhe, 1987). The Skagerrak is connected to the Norwegian Sea through the Norwegian trench with a sill depth of 270 m. The Norwegian Trench itself is a deep sedimentary basin (250 - 700 m) that reaches from the Oslofjord in the southeast to the Stad peninsula in the northwest up (Rodhe, 1996). Like the Skagerrak, the Norwegian Trench is characterized by haline stratified water masses (Reid and Edwards, 2001).

The water transport in the NNS is dominated by the large open boundary with the North Atlantic in the north. Water entering through the Shetland Channel and the Faire Island Channel turns eastwards and leaves the North Sea via the Norwegian Trench in the east. The residence time of the water is about one year. Generally, water entering the NNS does not influence the SNS, as just 5% of the North Atlantic water entering the northern boundary reaches the SNS (Lenhart and Pohlmann, 1997). The water transport in the SNS is mainly determined by inflow of Atlantic Ocean through the English Channel, which mixes with low salinity water coming from rivers and moves along the eastern coastlines towards the north-east. Baltic Sea water entering through the Kattegat and coastal
run-off are important in maintaining the Norwegian Coastal Current that initiates in the Skagerrak. This northwards directed current is the only net outflow of the North Sea and thus balances all incoming water inputs as described above. Additionally, the shallow SNS is influenced by strong tidally induced currents and mixing (Dauwe 1999). The tides in the SNS are diurnal, whereas maximum surface currents at spring tide occur on the western and southern parts of the SNS. More the the north and into the German Bight, the tidal current velocities decrease (Van der Molen 2002).

The seafloor of the North Sea predominantly consists of permeable sediments. Medium and fine sand is the main sediment type and occupies the largest part of the North Sea basin. Coarse sand is found at confined locations throughout the entire North Sea basin with larger areas of coarse grained sediments present along the English coast and in front of the German and Danish coasts. Mud and sandy mud are mainly found in the deep trenches along the Norwegian coast, off the coast of Scotland, in particular locations along the Belgian coast, in smaller areas north and east of the German Bight and near Helgoland in the German Bight (Lüders 1955; Schlüter and Jerosch 2009; Hebbeln et al. 2003; Braeckman et al. 2014).

2.2 Sediment Sampling

During a cruise onboard RV Pelagia in September 2011 we sampled a total of 19 stations across the whole North Sea basin (Table 1). On a second cruise in June 2012, we sampled 7 stations along a transect perpendicular to the Dutch coast from the Wadden island of Terschelling up to the Oyster Grounds in the central North Sea (1b - 7b in figure 1). Sediment cores were collected at each site using a Reineck box corer. Polymethyl methacrylate (PMMA) core barrels (19 cm inner diameter) were subsequently inserted into the sediment of the box core to a depth of 10 to 15 cm enclosing 15 to 20 cm of overlying water. The cores were excavated from the box core, closed off with a lid at the bottom and immediately transferred into a water-filled reservoir in a thermo-controlled container that was kept at in-situ bottom water temperature. These sediment cores were subsequently used for closed core flux incubations as described below.

During the September 2011 cruise, small sediment cores were retrieved for solid phase analysis and microsensor profiling and these were taken from the same box core as the flux cores. For solid phase analysis, acrylic core barrels (5 cm i.d.) were inserted into the sediment of the box core. The upper 10 cm of each core was sliced in 1 cm intervals and sediment samples were analyzed for porosity and grain size distribution. Porosity was determined by weight loss after freeze-drying, accounting for salt precipitation in the saline pore water. Grain size distribution was determined using a Malvern Mastersizer 2000 particle analyzer.

For O$_2$ and pH microsensor profiling, acrylic core liners (3 cm i.d.) were inserted into the sediment of the box core, and afterwards, the sediment was brought level to the rim of the core liner. Cores were subsequently placed in an aquarium containing bottom water at in-situ temperature, which was constantly bubbled with ambient air, to ensure constant water flow over the sediment. Bottom water
to top up sediment cores for flux measurements was retrieved by casts with 25 L Niskin bottles (Ocean Test Equipment/Fort Lauderdale (USA)) retrieving water at approximately 1 meter above the sediment surface. A conductivity, temperature, depth (CTD) was mounted on a standard rosette frame together with 24 Niskin bottles. The CTD was equipped with a SBE3+ thermometer, a SBE4 conductivity meter and a SBE43 dissolved oxygen sensor (Seabird, USA).

### 2.3 Solute flux measurements

Flux chamber incubations are potentially susceptible to various methodological artifacts resulting from sediment enclosure, which relate to the sensitivity of benthic fluxes to changes in ambient hydodynamics and altered benthic faunal activity \cite{Santschi1991, Tengberg2005, Lehrter2011}. In permeable sediments, fluxes are particularly susceptible to the imposed stirring regime and the associated local pressure gradients that are generated in the flux chamber, which drive the advective pore water exchange between sediment and overlying water \cite{Huettel1992, Janssen2005}. The flux chamber type employed here was based on the design as in Huettel and Gust \cite{1992}, which was specifically developed for flux studies in permeable sediments. The sediment cores retrieved were closed off with a PMMA top lid that was equipped with a large central stirring disc (diameter: 14 cm). The rotation of the disc mixes the overlying water and establishes a specific radial pressure gradient, which drives pore water exchange in the chamber. A major challenge for flux chamber studies in permeable sediments is the selection of the appropriate stirring regime. Without knowledge of the local in-situ hydrodynamics, it is impossible to predict a priori which stirring regime is appropriate for a given site. Here we used two different stirring rates at each station (40 and 80 rpm), to mimic a range of interfacial pressure gradients and solute exchange conditions \cite{Huettel1992, Janssen2005, Rao2012}. By taking this approach, we are able to discern how sensitive the fluxes at each station are to advective exchange, and thus, we get an idea of the uncertainty on our flux estimates for the permeable sites that we visited.

Prior to the start of the flux measurements, the overlying water in each core was replaced with ambient bottom water to ensure that the chemical composition of the overlying water closely resembled in-situ conditions. Each set of flux measurements began by securing gas-tight lids equipped with O-ring seals on each core. Core lids contained two sampling ports on opposite sides for subsampling during the incubation and these ports were carefully purged with bottom water prior to the start of each incubation to remove any air bubbles trapped. Fiber-optical oxygen sensors (FireSting OXF1100) were inserted into a third opening in the top lid. The chambers were closely inspected to ensure that no gas bubbles remained inside the chamber. Two or three replicate chamber incubations were made per station.

The temporal evolution of the oxygen concentration in the overlying water of the flux chambers was continuously monitored using oxygen optodes at a sample interval of 1 minute. Optodes were pre-calibrated on the same day using a two-point calibration with ambient seawater at 0% (saturated
with sodium sulphite) and 100% O$_2$ saturation (bubbled with air). Optode results were verified with measurements of the O$_2$ concentration by Winkler titration in discrete water samples before and after incubation (Grasshoff et al., 2009).

A water subsample (∼ 50 mL) was withdrawn from the chambers at 4-6 h intervals for solute analysis as described below. When a water sample was extracted via one sampling port, an equal amount of ambient bottom water entered through the replacement tube connected to the other sampling port. Samples were collected in plastic syringes for alkalinity ($A_T$) and in glass syringes for dissolved inorganic carbon (DIC) analysis. Water samples for $A_T$ (∼ 10 mL) were filtered (0.45 µm Millex-HA syringe filter) and stored in the dark at 4°C. DIC water samples (∼ 12 mL) were not filtered, but poisoned with 10 µL HgCl$_2$ and stored submerged at 4°C in a fridge.

The Total Oxygen Uptake (TOU) rate and the flux of DIC and $A_T$ were determined from a linear regression of overlying water concentrations versus incubation time (Equation 1).

$$J = \frac{V_{ow}}{A} \frac{dC_{ow}}{dt} \quad (1)$$

At the end of the incubation, the top lid was removed, and the height of the overlying water ($H = V_{ow}/A$) was measured at four points along the side of the core using a ruler and the mean height was calculated. Glud (2008) suggested that an oxygen decrease by more than 10-15% from the initial conditions can already stimulate processes that cause a non-linear decrease in oxygen concentrations, which also might affect other solute fluxes across the sediment-water interface. Here we found that the linear regressions used to calculate the oxygen uptake were insensitive to an oxygen decrease of 30% or more (for examples see figure 3).

2.4 Analytical Methods

$A_T$ was determined via an open-cell titration procedure, using a Metrohm Titrand 888 system with a combined Metrohm glass electrode (Unitrode) following the procedure SOP3a as described in Dickson et al. (2007). Samples (10 ml) were placed in a temperature regulated open cell (25°C) and titrated with a solution of hydrochloric acid (0.1 N) in a two-stage process. First the sample (10 mL) was acidified to a pH close to 3.5 and then titrated in small steps down to a pH of 3.0. Subsequently, $A_T$ was calculated using a non-linear regression approach based on SOP3a from Dickson et al. (2007). Two replicate measurements were carried out for each sample analyzed. Titrations (n=10) of Certified Reference Materials (CRM Batch 116 provided by A.G. Dickson) were on average within 4 µmol kg$^{-1}$ of the nominal value with a precision of 5 µmol kg$^{-1}$.

DIC was determined using an AS-C3 DIC analyzer (Apollo SciTEch, U.S.A.), in which the sample (0.8 ml) was acidified and the released CO$_2$ was detected using a solid state infra-red CO$_2$ detector (LI-7000, LI-COR Biosciences, U.S.A.). Two replicate measurements were carried out for each sam-
ple analyzed. Quality assurance of the DIC analysis was also based on CRM (Batch 116 - accuracy & precision: 3 µmol kg\(^{-1}\)).

2.5 O\(_2\) and pH microprofiling

Microsensor profiling was performed using commercial Clark-type O\(_2\) (accuracy: 0.3 µmol and potentiometric pH (accuracy: 0.1) microsensors operated with a motorized micromanipulator (Unisense A.S., Denmark). To minimize the error by ship movement, the microprofiling setup was placed in the center, the most stable spot, of the ship. Under strong wind conditions, microprofiling was not performed in order to prevent sensor damage. Vertical depth profiles of O\(_2\) were recorded using an electrode with a tip size of 100 µm at 250 µm steps, beginning at 2 mm above the sediment-water interface until either anoxia or 20 mm depth. The O\(_2\) microsensors were calibrated with a 2-point calibration made in air-saturated seawater (100% saturation) and at depth in anoxic sediment (0% saturation). Depth profiles of pH were measured using microsensors with a tip size of 200 µm in 1 mm steps, beginning 4 mm above the sediment surface until 35 mm depth. Measurements were always started within 1 hour after sampling. The pH microsensors were calibrated using NBS buffers (pH 4 and 7) and TRIS buffer [DelValls and Dickson 1998], and the pH is reported on the total scale.

The diffusive oxygen uptake (DOU) of the sediment was calculated from the O\(_2\) depth profiles as

\[
DOU = -D_{O_2} \frac{d[O_2]}{dz}
\]

where \(z\) is the depth and \([O_2]\) denotes O\(_2\) concentration. The slope \(d[O_2]/dz\) was determined from the gradient in the diffusive boundary layer [Glud 2008], and while profiling, the overlying water was bubbled with air to ensure a water flow over the sediment surface. The molecular diffusion coefficient of O\(_2\) in seawater (\(D_{O_2}\)) was calculated as a function of the bottom water salinity and temperature using the CRAN:marelac extension package in the open-source programming language R [Soetaert et al. 2010].

2.6 Statistical Analyses

Results are reported as the mean ± 1 standard deviation (SD) of \(n\) replicate measurements. Non-parametric statistics were used in the interpretation of results, including the Mann-Whitney U-test (\(p\)) for comparison of the mean of two independent groups of measurements, and the Spearman’s rank correlation coefficient (\(\rho\)) as a measure of the statistical dependence between two variables. Statistical analyses were conducted in R using the CRAN:stats package.
3 Results

3.1 Bottom water characteristics

Bottom water salinity, temperature and oxygen concentration as obtained by CTD profiling are listed in Table 1 and characteristic temperature depth profiles are displayed in Fig. 2. Bottom water salinity and temperature of stations from the basin wide North Sea cruise ranged from 35.39 PSU (NNS) to 29.35 PSU (SNS) and 17.41 °C (SNS) to 6.02 °C (NNS). The bottom water in the NNS and SKNT was generally colder and more saline than bottom water in the SNS (Mann-Whitney; Temperature: \( p = 0.001 \); Salinity: \( p < 0.001 \)). A thermocline was formed between 20 - 50 m water depth in all stations of the NNS and SKNT, but just in two stations of the SNS (Figure 2 & Table 1). The bottom water oxygen concentrations did however not exhibit significant differences between the SNS and other parts of the North Sea (Mann-Whitney; \( p > 0.5 \)).

3.2 Sediment properties

The median grain size for all stations visited during the basin wide North Sea campaign in 2011 ranged from 28 to 499 µm (mean median grain size: 215 µm). In the SNS the median grain size ranged from 138-499 µm (mean median grain size: 249 µm), and according to the Wentworth scale, the SNS sediments can be classified as fine to medium sand (Table 1). Sediments in the NNS (median grain size range 119-314 µm; : mean 227 µm) were not significantly different from the SNS (Mann-Whitney; \( p = 0.8 \)), hence also classifying as fine to medium sand. In contrast, sediments from the Skagerrak and Norwegian Trench (SKNT) were considerably finer (Mann-Whitney; \( p < 0.01 \)), with the median grain size ranging from 21-62 µm. Thus, sediments of SKNT classified as fine to coarse silt on the Wentworth scale (Table 1).

Porosity for all stations in the North Sea basin varied from 0.32 to 0.74 . Between sediments of the SNS (mean: 0.34) and NNS (mean: 0.37) no significant differences in porosity were found (Mann-Whitney; \( p = 0.31 \)). However, sediments of the SKNT displayed a significantly higher porosity (mean: 0.67) than sediments from the SNS or NNS (Mann-Whitney; \( p < 0.05 \)).

3.3 Benthic flux chamber incubations

The concentration changes over time of \( O_2 \), DIC and \( A_T \) in the overlying water from flux chamber incubations at representative stations from each of the three zones (SNS, NNS, SKNT) is presented in Figure 3. Stations were chosen to represent average benthic fluxes for the respective region of the North Sea, thus not considering stations which are likely to under-, or overestimate benthic fluxes (e.g. station 20). The oxygen data display a linear decrease, while the DIC and \( A_T \) data display an increasing trend, albeit with greater variability due to the limited number of subsamples (4 or 5). Fluxes were only considered if their calculation is based on a linear regression of at least 4 points combined with an \( r^2 \) value greater than 0.8. Furthermore, fluxes were set to zero in case the slope of
the linear regression was not significantly different from zero.

During the basin-wide campaign in September 2011, TOU rates ranged from 3.1 to 28.7 mmol m\(^{-2}\) d\(^{-1}\) for the SNS, 0.7 to 6.2 mmol m\(^{-2}\) d\(^{-1}\) for the NNS and 2.9 to 5.7 mmol m\(^{-2}\) d\(^{-1}\) for the SKNT. During the Dutch transect cruise in June 2012, TOU rates ranged from 6.5 to 25.1 mmol m\(^{-2}\) d\(^{-1}\) (Table 2). Thereby, the highest oxygen uptake rates were measured in the SNS, followed by the SKNT, while the lowest TOU rates were measured in the NNS (mean value SNS: 10.0 mmol m\(^{-2}\) d\(^{-1}\) in 2011 and 13.5 mmol m\(^{-2}\) d\(^{-1}\) in 2012; SKNT: 3.9 mmol m\(^{-2}\) d\(^{-1}\); NNS: 3.4 mmol m\(^{-2}\) d\(^{-1}\)). In general, TOU rates in the SNS are significantly higher than TOU rates of the NNS and the SKNT (Mann-Whitney; NNS: \(p < 10^{-5}\); SKNT: \(p < 0.001\)). Between TOU rates from the NNS and TOU rates from the SKNT no statistical difference could be identified (Mann-Whitney; \(p = 0.6\)). Furthermore, TOU rates measured in the SNS in June 2012 are not significantly different from TOU rates measured in September 2011 (Mann-Whitney; \(p > 0.05\)).

Within the permeable sediments of the SNS and NNS, flux chamber incubations were performed at two different stirring speeds (40 RPM and 80 RPM). In general, the TOU rates were about 80% higher at the higher stirring speed (Figure 4a), indicating an advective dominated transport within the sediments (TOU rates at 40 and 80 RPM; Spearman’s; \(p < 0.01\)). On the other hand, a correlation between median grain size of the sediments and TOU rates could not be confirmed.

In general, \(A_T\) and DIC concentrations increased linearly with time in the overlying water of the flux incubations for most stations. \(A_T\) fluxes for both campaigns ranged from 0 to 21.4, 0 to 3.0 and 1.4 to 9.9 mmol m\(^{-2}\) d\(^{-1}\) for the SNS, NNS and SKNT respectively. The highest \(A_T\) fluxes were observed in the SNS (mean: 6.5 mmol m\(^{-2}\) d\(^{-1}\) in 2011 and 5.7 mmol m\(^{-2}\) d\(^{-1}\) in 2012) and in the SKNT (4.3 mmol m\(^{-2}\) d\(^{-1}\)). The lowest mean \(A_T\) flux was calculated for the NNS (1.8 mmol m\(^{-2}\) d\(^{-1}\)). Only the \(A_T\) fluxes of the SNS are significantly higher than \(A_T\) fluxes of the NNS (Mann-Whitney; SNS: \(p < 0.001\); SKNT: \(p = 0.2\)). \(A_T\) fluxes measured during the basin wide cruise in 2011 are similar to those measured along the Dutch transect in 2012 (Mann-Whitney; \(p = 0.3\)).

DIC fluxes varied between 1.5 - 29.1, 0 - 6.2 and 4.2 - 7.2 mmol m\(^{-2}\) d\(^{-1}\) for the SNS, NNS and SKNT respectively. The trends in DIC flux were similar as those obtained for the TOU rates and \(A_T\) fluxes. The highest DIC fluxes were measured in the SNS, followed by the SKNT and the NNS (mean: SNS: 11.5 mmol m\(^{-2}\) d\(^{-1}\) in 2011 and 12.3 mmol m\(^{-2}\) d\(^{-1}\) in 2012; SKNT: 6.1 mmol m\(^{-2}\) d\(^{-1}\); NNS: 0.9 mmol m\(^{-2}\) d\(^{-1}\)). DIC fluxes were significantly higher in the SNS than in the NNS, but showed no differences to the DIC fluxes measured in the SKNT (Mann-Whitney; NNS: \(p < 0.01\); SKNT: \(p = 0.3\)), while also no significant difference was found between DIC fluxes of the SKNT and the NNS (Mann-Whitney; \(p = 0.08\)). As found for TOU rates and \(A_T\) fluxes, the DIC fluxes in the SNS were similar between both campaigns (Mann-Whitney; \(p = 0.7\)).

This allows us to examine all solute fluxes recorded in the SNS as one single group in the discussion section.
3.4 O\textsubscript{2} and pH microprofiling

Representative examples of O\textsubscript{2} and pH depth profiles in stations from all three zones of the North Sea are presented in figure 5. In some stations pore water profiles could not be measured due to the coarse grain size and the presence of carbonate shell fragments, which induces a high risk of damaging the microsensors. In general, pore water O\textsubscript{2} declines as a result of O\textsubscript{2} consumption associated with organic matter degradation. From the O\textsubscript{2} depth profiles the DOU rates of the sediments were calculated as detailed in section 2.5. In the SNS, DOU rates ranged from 0.20 to 6.95 mmol m\textsuperscript{-2} d\textsuperscript{-1}, while in the NNS and SKNT, a range of 1.47 to 4.33 mmol m\textsuperscript{-2} d\textsuperscript{-1} and 0.83 to 2.49 mmol m\textsuperscript{-2} d\textsuperscript{-1} were found (Table 3). The lowest mean DOU rate was measured in the SKNT, followed by the DOU rates of the NNS and SNS (SKNT: 1.77 mmol m\textsuperscript{-2} d\textsuperscript{-1}, NNS: 2.20 mmol m\textsuperscript{-2} d\textsuperscript{-1}; SNS: 2.39 mmol m\textsuperscript{-2} d\textsuperscript{-1}).

The oxygen penetration depth (OPD) is defined as the thickness of the oxic zone in marine sediments (Cai and Sayles, 1996), and was operationally defined as the depth below which the O\textsubscript{2} concentration drops below 1 \textmu mol kg\textsuperscript{-1}. In some permeable sediments, the oxygen did not fully deplete over the measured depth profiles (first 2 cm), and so the OPD could not be determined. In the remaining cores, the OPD was as shallow as 8.4 ± 6.7 mm for the SNS, 18.1 ± 1.4 mm for the SKNT and 7.8 ± 2.8 mm for the NNS.

Table 3 compares the TOU with the corresponding DOU for the basin-wide campaign in September 2011. The TOU/DOU ratio ranged from 50.1 (SNS) to 1.1 (NNS), and DOU rates were significantly lower than TOU rates (Spearman’s; \( p < 0.01 \)), indicating that physical or biological driven advective transport strongly enhanced the sedimentary oxygen uptake.

Depth pH profiles of representative cores are presented in Figure 5. Depth profiles generally show a decline of pH in all profiled cores, which can be attributed to the release of CO\textsubscript{2} resulting from organic matter degradation. Furthermore, the cores from the NNS and SKNT were typically characterized by a sub-surface minimum in pH, while the depths of these pH minima matched the corresponding OPD. Hence, we interpret these sub-surface pH minima as resulting from the aerobic oxidation of reduced substances transported upwards from deeper sediment layers. Generally, the pH increased again at depth in the cores, most likely due to \( A_T \) generation associated with the anoxic degradation of organic matter (see discussion below).

4 Discussion

4.1 Benthic mineralization in the North Sea

Several studies have previously addressed benthic oxygen consumption in the North Sea, although most studies are restricted to the southern North Sea (Table 4). All TOU rates presented in the following section are not subdivided between both stirring speeds, but discussed together. The TOU
rates found in the present study for the North Sea (range 3.1 - 28.7 mmol O$_2$ m$^{-2}$ d$^{-1}$) fall within the range of previously published TOU rates (range 0 - 57.1 mmol O$_2$ m$^{-2}$ d$^{-1}$), which is however large. Due to temporal variability (seasonality), spatial variability (e.g. substrates ranging from cohesive mud to highly permeable sand), but also differences in methodology (see discussion below on the impact of stirring rate), it remains difficult to intercompare the oxygen consumption rates that have been obtained in different studies. So despite this growing database of TOU rates, a more accurate assessment of the spatial and temporal variation of the oxygen consumption in the North Sea remains an outstanding challenge.

In our basin wide campaign in 2011, we obtained the highest mean TOU rate in the SNS (10.0 mmol m$^{-2}$ d$^{-1}$), followed by the SKNT (3.9 mmol m$^{-2}$ d$^{-1}$), while the lowest TOU rates were measured in the NNS (3.4 mmol m$^{-2}$ d$^{-1}$). One important environmental factor in controlling the TOU rates is the amount of primary production in these different regions. Part of this organic matter produced during photosynthesis is respired in the water column, while the remaining part sinks down to the sediments and undergoes respiration there. As oxygen serves as the ultimate electron acceptor for almost all respired organic carbon \cite{Thamdrup2000}, high primary production rates tend to relate to high TOU rates in the sediments. Note, that besides primary production rates, also the water depth and thereby the amount of organic carbon which reaches the sediments is of great importance. Because of the shallow water depth, the fraction of organic carbon which reaches the sediments in the southern North Sea is considerably higher than in the northern North Sea, hence further increasing the TOU rates in this region \cite{Kuhn2010}. Based on measured surface chlorophyll concentration in the southern North Sea, \cite{Joint1993} estimated primary production rates for a period from August 1988 to October 1989, and found clear regional differences in primary production in the SNS ranging from 18 mmol C m$^{-2}$ d$^{-1}$ along the British Coast to 59 mmol m$^{-2}$ d$^{-1}$ in the German Bight. A model study by \cite{Moll1998} covering the whole North Sea confirmed the large regional variation in depth-integrated annual primary production rates ranging from 21 mmol C m$^{-2}$ d$^{-1}$ in the NNS to 79 mmol C m$^{-2}$ d$^{-1}$ in the German Bight of the SNS. TOU rates observed are congruent with these previous observational and modeling studies, with high values in the southern North Sea, and in particular in the German Bight, to lower values in the northern North Sea.

A second important environmental factor controlling the North-South gradient in TOU rates is the bottom temperature exhibiting a north – south gradient in summer, with higher temperatures in the south. In a recent seasonal flux study of shallow coastal sediments from the North Sea, a positive correlation was found between benthic solute fluxes and water temperature \cite{Rao2014}. These authors proposed that higher bottom water temperatures in summer are a main driver for higher benthic fluxes as increased temperatures enhance the metabolic activity in the sediment. In September 2011, the thermocline was formed between 20 and 50 m (Figure 2 & Chapter 3.1), and the whole NNS and SKNT were stratified, while in contrast, the SNS was fully mixed (apart from the stations
38 & 45 on the border with the NNS). As a result, the bottom water in the NNS and SKNT was substantially cooler than bottom water in the SNS ($\approx 11^\circ C$ difference between SNS and NNS/SKNT - Table 1). Adopting a temperature Q10 coefficient of $\approx 2$ for benthic respiration (Denman and Pena 2002; Schrum et al. 2006), one would expect a nearly doubling of the TOU between the NNS and SNS due to bottom water temperature, all other environmental factors being the same. Accordingly, lower bottom water temperatures in the NNS and SKNT could indeed partially explain the lower TOU values recorded compared to the SNS (Table 3). Although station 38 and 45 are both within the SNS, their TOU values are closer to values typical for the NNS, as both stations exhibit lower bottom water temperature compared to other stations of the SNS.

To further identify the drivers of the observed spatial variability across the North Sea, we examined the correlation of TOU rates with water depth, porosity and grain size (Figure 6). We found significant correlations between TOU values and water depth (Spearman’s; $p < 0.01$), suggesting that increased water depth reduced the benthic pelagic coupling in the NNS and SKNT. As more organic matter is remineralized upon the longer transit through the water column, less detritus reaches the seafloor, and this hence decreases the contribution of benthic mineralization in the overall respiration. Finally, we also found both a negative correlation between TOU and porosity (Spearman’s; $p < 0.02$) and a significant negative correlation between TOU and median grain size (Spearman’s; $p < 0.01$). This opposes the classical picture of sedimentary diagenesis, where high oxygen consumption rates and intense biogeochemical cycling are typically linked to fine-grained organic rich sediments. Instead, we found the highest TOU values in the permeable sediments of mostly the SNS (low porosity, high median grain size), which supports the more recent ideas of permeable sediments as active bio-catalytic filters (Huettel and Rusch 2000), which actively trap suspended detritus by means of advective currents through the upper sediment layers and rapidly mineralize this trapped organic matter. As a result, these permeable sediments display low standing stocks of organic matter, but high TOU values.

The importance of wind and tidal induced advective transport for the benthic oxygen dynamics is emphasized by the deep oxygenation of the surface sediment at permeable sites (Figure 5a). This is reconstructed by the strong impact of benthic chamber stirring speed on the TOU (Figure 4), and by the strong difference between TOU values as measured by benthic incubations and the corresponding DOU values as obtained by microprofiling (Table 3). We found that DOU values were always smaller than TOU values for all stations throughout the North Sea. In general, the total oxygen uptake can be decomposed as $\text{TOU} = \text{DOU} + \text{BMU} + \text{AMU}$ (Glud 2008), where BMU represents benthos mediated $O_2$ uptake resulting from burrow irrigation and the respiration of infauna, and AMU represents the enhancement of the sedimentary $O_2$ uptake by purely physical transport processes, such as pore water advection induced by currents over bottom topography (Huettel and Rusch 2000; Meysman et al. 2007) and oscillatory pore water mixing induced by waves (Shum 1992).

A second signature of physical and or biological pore water irrigation is the deep oxygenation of
the surface sediment. As already noted above, in some highly permeable sites, the surface sediment remained completely oxygenated over the whole surface layer that was examined by \( O_2 \) microsensor profiling (first 20 mm), and so no oxygen penetration depth (OPD) could be determined. For those stations that did allow to determine the OPD (i.e., the pore water \( O_2 \) signal decreased to zero), we employed the analytical model of Cai and Sayles (1996), which provides an inverse relation between OPD and DOU (Figure 7 (a)) (Equation 3).

\[
L = 2\phi D_s \frac{[O_2]_{bw}}{F_{O_2}^0},
\]

(3)

In this expression, \( L \) is the theoretical OPD of the sediment, \( \phi \) is the porosity, and \( D_s \) is the effective diffusivity of \( O_2 \) in the pore water (i.e., corrected for tortuosity) \([O_2]_{bw}\) is the bottom water concentration of \( O_2 \) and \( F_{O_2}^0 \) is the benthic diffusive oxygen flux. This relationship is based on the balance between diffusive oxygen fluxes and oxygen consumption rates under steady state conditions and negligible advection. The above relation was used to estimate the theoretical OPD from the measured DOU as shown in Figure 7 (b). The actually measured OPD is systematically larger than the predicted OPD for all stations (with the SKNT stations 52 and 65 being the exception from this rule). As the equation [3] holds for sediments that only experience diffusive transport, the discrepancy suggests that non-diffusive transport (i.e. bio-irrigation or physical advection) increases the oxygen availability and penetration in the sediment (Archer and Devol, 1992).

### 4.2 Benthic DIC release in the North Sea

The benthic DIC release in the North Sea follows the same spatial pattern as the benthic oxygen uptake: the highest DIC effluxes were recorded in the SNS (mean: 11.5 mmol m\(^{-2}\) d\(^{-1}\) in 2011 and 12.3 mmol m\(^{-2}\) d\(^{-1}\) in 2012), followed by the SKNT (mean: 6.1 mmol m\(^{-2}\) d\(^{-1}\)) and the NNS (mean: 0.9 mmol m\(^{-2}\) d\(^{-1}\); Table 2). However, while TOU values were comparable in NNS and SKNT, the DIC flux in the SKNT was significantly higher than in the NNS. As for the TOU, we found a significant positive correlation between the DIC efflux and water depth (Spearman’s; \( p = 0.02 \)) and a weak negative correlation between the DIC efflux and median grain size (Spearman’s; \( p = 0.07 \)) and a significant negative correlation between the DIC efflux and median grain size (Spearman’s; \( p < 0.01 \); Fig.6). Overall, this suggests that the same environmental factors (pelagic primary production, temperature, water depth, sediment permeability) that are driving the TOU are also controlling the spatial pattern of the sedimentary DIC release in the North Sea.

Overall, we found DIC fluxes to be strongly positively correlated with TOU rates (Figure 8 a; Spearman’s; \( p < 0.0001 \)). The ratio between the DIC efflux and the TOU at a given site represents the respiratory quotient (RQ), and we found that the mean RQ value for the SNS (0.95), NNS (0.94) and SKNT (1.00) to be all similar. No significant differences were detected between the three zones (Mann-Whitney; \( p > 0.05 \)). In general, the RQ can be used as an indicator for the degree of reoxida-
tion of reduced compounds associated with anaerobic remineralization (Therkildsen and Lomstein, 1993). Assuming that (1) no carbonate dissolution occurs in the sediment, (2) that the stoichiometry of organic matter follows the Redfield ratio \( C : N : P = 106 : 16 : 1 \) (Redfield, 1958), and (3) that organic matter is oxidized using oxygen as the sole electron acceptor, one would obtain a RQ of 0.77 (solid line in figure 8a; Paulmier et al. (2009)). Note, that a RQ close to Redfield ratio serves as a baseline rather than an expected result in this study. In principle, the RQ value is expected to increase with increasing importance of suboxic and anoxic respiration pathways, and subsequent accumulation of reduced compounds such as pyrite, as respiration along these pathways is releasing DIC without consuming oxygen. Alternatively, dissolution of carbonates may also lead to an increased RQ due to the release of two moles DIC per one mole \( \text{CaCO}_3 \) dissolved. Equally, the RQ value is expected to decrease when a stock of reduced compounds is being re-oxidized, i.e., the annihilation of a previously accumulated oxygen debt.

### 4.3 Benthic alkalinity release in the North Sea

Our results show that North Sea sediments can be a substantial source of \( A_T \) with sediment effluxes ranging from 0 to 28.7 mmol m\(^{-2}\) d\(^{-1}\) (Figure 8b). The \( A_T \) fluxes reported here were obtained by monitoring the temporal evolution of \( A_T \) in the overlying water of enclosed sediment incubations. In the same sediment incubations, Burt et al. (2014) measured the efflux of the short-lived Radium isotopes \( ^{224} \text{Ra} \) and \( ^{223} \text{Ra} \) and subsequently estimated \( A_T \) fluxes. To this end, these authors used the Ra-isotope data to estimate the overall water exchange rate between the pore water and the overlying water column. This water exchange rate was then multiplied by the excess concentration of \( A_T \) in pore water, which was estimated from pore water analysis. This indirect estimate procedure resulted in benthic \( A_T \) fluxes between 4.7 and 22.1 mmol m\(^{-2}\) d\(^{-1}\), and is in good agreement with the \( A_T \) flux values obtained here (Figure 10). The disagreement (e.g. at station 38) between observed and calculated \( A_T \) flux may result from applying the same \( A_T \) pore-water concentration for all stations in calculating the \( A_T \) fluxes based on Radium-isotope data. This assumption might be wrong and could lead to an over-estimation of the \( A_T \) flux in station 38. For a more detailed discussion on the correlation between both methods see Burt et al. (2014).

The benthic \( A_T \) release in the North Sea follows the same spatial pattern as the benthic oxygen uptake and the DIC efflux, suggesting that organic matter mineralization is the primary driver for the \( A_T \) release from sediments. We observed the highest \( A_T \) release in the SNS (mean: 6.5 mmol m\(^{-2}\) d\(^{-1}\) in 2011 and 5.7 mmol m\(^{-2}\) d\(^{-1}\) in 2012), closely followed by the SKNT (mean: 4.3 mmol m\(^{-2}\) d\(^{-1}\) ). The lowest \( A_T \) fluxes were obtained in the NNS (mean: 2.8 mmol m\(^{-2}\) d\(^{-1}\) ). As for the TOU and DIC efflux, we found a weak positive correlation between \( A_T \) efflux and water depth (Spearman’s: \( p = 0.06 \)), though no significant correlation between \( A_T \) efflux and porosity (Spearman’s: \( p = 0.4 \)) and a significant negative correlation between the \( A_T \) efflux and median grain size (Spearman’s: \( p < 0.01 \)). The lack of negative correlation with porosity is mainly due to SKNT
stations, which showed a high $A_T$ efflux at high porosity. Furthermore, the increase of $A_T$ fluxes with increasing TOU rates (Figure 8) is an indication for metabolic driven dissolution of CaCO$_3$, as it is fueled by CO$_2$ released during organic matter mineralization and by the oxidation of reduced compounds produced during anaerobic respiration. Metabolic dissolution would induce a $A_T$/DIC flux ratio of 1, which is indeed confirmed in some stations, though not for all (Figure 11). A positive correlation is obtained between $A_T$ and DIC fluxes (Spearman’s; $p = 0.02$), but there are marked differences in the $A_T$/DIC flux ratio between different stations, which suggests that a different type of biogeochemistry is acting at different locations. Below we will discuss in more detail how different biogeochemical processes in the sediment are releasing $A_T$ and DIC in distinct ratios.

To our knowledge, the $A_T$ fluxes presented here are the first field observations of such fluxes in the North Sea area. Thomas et al. (2009) estimated sedimentary $A_T$ fluxes in the southeastern bight of the North Sea and the Wadden Sea during summer and autumn based on water column data. In this approach, the sedimentary $A_T$ release appeared as the unknown closure term in an $A_T$ budget based on water column data, which provided $A_T$ flux estimates of about 8.0 mmol m$^{-2}$ d$^{-1}$. These values are similar to the benthic $A_T$ fluxes reported here for the SNS. $A_T$ release from sediments has also been the subject to a number of studies on other coastal systems than the North Sea. Based on basin-wide budget calculations, Gustafsson et al. (2014) estimated that sediments of the Baltic Sea generate $A_T$ with a mean rate of 2.4 mmol m$^{-2}$ d$^{-1}$, which is in the same order as the $A_T$ input by rivers in that basin. As main sources for $A_T$ these authors propose denitrification together with sulfate reduction and/or silicate weathering. Chen and Wang (1999) estimated that sediments in the East China sea generate between 2.9 and 4.9 mmol m$^{-2}$ d$^{-1}$ $A_T$. Over 80% of this $A_T$ flux was thereby attributed to iron and sulfate reduction, with no contribution from carbonate dissolution.

Krumins et al. (2013) used a one-dimensional reactive transport model to estimate $A_T$ fluxes from coastal sediments. For that study, the authors divided the global shelf into four different environments, each with distinctive particular organic and inorganic carbon fluxes. Ultimately, they identified non-carbonate shelves (e.g. the North Sea) as an $A_T$ source of 2.7 mmol m$^{-2}$ d$^{-1}$.

On a global scale, Krumins et al. (2013) estimated an $A_T$ flux for the coastal ocean of 29 Tmol yr$^{-1}$. Whereas this estimate agrees well with an independent estimation by Chen (2002) (16-31 Tmol yr$^{-1}$), Hu and Cai (2011a) obtained a much smaller flux of 4-6 Tmol yr$^{-1}$. Note, that all these three studies are based on different assumptions on the underlying processes that are generating $A_T$. Whereas the $A_T$ flux estimated by Chen (2002) is mainly generated by sulfate reduction with zero contribution of carbonate dissolution, Krumins et al. (2013) acknowledged carbonate dissolution as a benthic $A_T$ source. Hu and Cai (2011a) is based on anaerobic $A_T$ generation alone, hence possible contributions by carbonate dissolution are not taken into account. Furthermore, these latter authors treat the coastal sediment-water column system as a single system, while the other two papers only consider the sediment.
To put these different assumptions into perspective, and verify their consequences, we now develop an alkalinity budget for the SNS, in which we first provide a sediment budget, and subsequently, we extend this argument to arrive at a combined sediment and water column alkalinity budget. We restrict this discussion to the SNS, as we have shown in section 3.3 that $A_T$ fluxes in the SNS significantly exceed those of the other two zones. High primary production, riverine input of terrestrial organic matter, and the shallow water depth favor a high benthic respiration rate in the SNS. Furthermore, in the context of atmospheric $CO_2$ uptake, a direct link between alkalinity release from the sediments and the atmosphere is needed, which requires a non-stratified water column as encountered in most parts of the SNS.

4.4 Sources of alkalinity in sediments of the SNS

The high benthic $A_T$ effluxes observed in the SNS invoke the question which processes are generating $A_T$ in the sediment. In the following we will discuss how different biogeochemical pathways contribute to the overall $A_T$ release from sediments, and in this way, we will try to assemble a closed $A_T$ budget for the SNS sea floor. To this end, we developed a simplified biogeochemical model of the SNS sediment, which accounts for carbonate dissolution (CD), aerobic respiration (AR), nitrification (NI), denitrification (DNF), iron reduction (IR), sulfate reduction (SR), free sulfide oxidation (SO), and pyrite formation (PF) as biogeochemical pathways. The input parameters, diagenetic relations, and output variables are summarized in Table 5. The $A_T/DIC$ flux ratio for each of these reactions is indicated as a straight line in Figure 11. In the next paragraphs, we discuss how the rates of the individual reactions can be constrained based on our flux measurements and literature data. In theory, the dissolution of one mole of $CaCO_3$ releases two moles of $A_T$, assuming no other processes are acting.

$$CaCO_3 \rightarrow CO_3^{2-} + Ca^{2+}$$

The undersaturation of the pore water with respect to the phases of calcium carbonate present (e.g. high Mg calcite, aragonite or calcite) determines the rate at which carbonate will dissolve. In general the undersaturation of the pore water can have two causes (Boudreau et al., 2010): (1) undersaturation of the overlying water and (2) additional undersaturation of the pore water due to metabolic respiration. In the North Sea, the overlying water is always oversaturated with respect to all common carbonate phases (Frankignoulle et al., 1998; Kühn et al., 2010), and so, dissolution of $CaCO_3$ in the sediment must be exclusively metabolically driven. Both the $CO_2$ production during organic matter mineralization as well as the oxidation of reduced compounds produced during anaerobic respiration processes can make the pore water undersaturated with respect to carbonates, and therefore, fuel metabolic driven dissolution (Jahnke et al., 1994). The increase of the $A_T$ fluxes with increasing TOU rates (Figure 8 b) forms indeed an indication for metabolic driven dissolution.
of \( \text{CaCO}_3 \) (Jahnke and Jahnke, 2004).

From the flux dataset available here, it is not possible to constrain the actual \( \text{CaCO}_3 \) dissolution rate in each station. However, it is still possible to provide an upper limit for the \( \text{CaCO}_3 \) dissolution rate on a larger geographic scale. Gazeau et al. (pers. comm.) recently estimated carbonate production in the southern North Sea to be \( 2.7 \, \text{mmol C m}^{-2} \, \text{d}^{-1} \). Net carbon burial does not occur in the North Sea, except for small amounts in the Skagerrak and the Norwegian Channel (de Haas et al., 2002; Thomas et al., 2005; Bozec et al., 2006). Therefore, we consider carbonate production and dissolution to be in steady state. Accordingly, carbonate dissolution in sediments can release up to \( 5.4 \, \text{mmol m}^{-2} \, \text{d}^{-1} \) of \( A_T \).

In addition to carbonate dissolution, \( A_T \) generation can be linked to various organic matter degradation pathways and secondary re-oxidation reactions. In the presence of oxygen, aerobic respiration is used to break down organic matter:

\[
OM + 15H^+ + 106O_2 \rightarrow 106CO_2 + 16NH_4^+ + H_2PO_4^- + 148H_2O
\]  

(5)

where we assume organic matter (OM) to be of Redfield elemental composition and follows the classical expression for the composition of organic matter \( ((CH_2O)_{106}(NH_3)_{16}(H_3PO_4)) \) after Richards (1965); Paulmier et al. (2009) (Redfield, 1958). This reaction essentially generates \( A_T \) by the consumption of protons linked to ammonium release, and to a lesser extent, it consumes \( A_T \) by the release of phosphate. Thamdrup and Canfield (2000) have estimated that aerobic respiration accounts for between 5-25% of the total benthic mineralization in shelf and coastal sediments. If we adopt a value of the benthic mineralization rate \( R_{min} = 10.0 \, \text{mmol C m}^{-2} \, \text{d}^{-1} \), which is the mean TOU value recorded for the SNS in September 2011 (Table 2; see also discussion below), we can estimate the aerobic respiration rate to range between 0.50 and 2.50 mmol C m\(^{-2}\) d\(^{-1}\) for the SNS (mean: 1.50 mmol C m\(^{-2}\) d\(^{-1}\)). Accounting for stoichiometry (\( A_T/O_2 \) ratio = 15/106), the corresponding \( A_T \) release ranges from 0.07 to 0.35 mmol m\(^{-2}\) d\(^{-1}\), with a mean of 0.21 mmol m\(^{-2}\) d\(^{-1}\). A theoretical doubling of \( R_{min} \) would lead to a \( \approx 7\% \) increase in the benthic \( A_T \) flux, and to a \( \approx 115\% \) net \( A_T \) increase in the water column (Figure 9). That is, if \( R_{min} \) is the only parameter changed and thus the relative importance between different diagenetic processes remain the same.

Nitrification of ammonium released during mineralization consumes \( A_T \) and can be represented by the reaction equation:

\[
NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+
\]  

(6)

Per mole of ammonium that is released during mineralization, exactly 2 mole of \( A_T \) is consumed. If we use the TOU as a proxy for \( R_{min} \), the rate of ammonification (i.e. \( 16/106 \, R_{min} \)) becomes 1.51 mmol N m\(^{-2}\) d\(^{-1}\) for the SNS. If all the ammonium is re-oxidized, and hence no ammonium escapes
the sediment, the nitrification rate should match the ammonification rate, and so the associated \( A_T \) consumption becomes 3.02 mmol m\(^{-2}\) d\(^{-1}\). Also note that complete aerobic respiration (i.e. the combination of aerobic respiration \( ^3 \) with nitrification \( ^4 \)) consumes 17 mole \( A_T \) per 106 mole of DIC released.

Denitrification is a second mineralization pathway via which organic matter degradation proceeds in the sediment, and can be represented as:

\[
OM + 84.8NO_3^- + 99.8H^+ \rightarrow 106CO_2 + 42.4N_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \quad (7)
\]

Per carbon atom in organic matter denitrified, the \( A_T \) increases by \( 0.94 = 99.8/106 \) mole. To discuss the impact of denitrification on sedimentary \( A_T \) release, we need to consider the origin of the nitrate that is used for denitrification. A portion of the nitrate is internally generated in the sediment through coupled nitrification/denitrification, while another part of the nitrate is derived externally (i.e., from the overlying water column). It has been estimated that these coupled nitrification/denitrification reactions account for 80% of the total denitrification rates in coastal environments (Middelburg et al. [1996], Seitzinger et al. [2006]), which thus implies that the total denitrification rate should scale as \( 1/0.8 \) times the nitrification rate (1.51 mmol N m\(^{-2}\) d\(^{-1}\)). This way, we obtain a denitrification rate of 1.89 mmol N m\(^{-2}\) d\(^{-1}\) or 2.36 mmol C m\(^{-2}\) d\(^{-1}\), with an associated \( A_T \) release of 2.22 mmol m\(^{-2}\) d\(^{-1}\). In the North Sea, a tight coupling of nitrification and denitrification has indeed been reported by Lohse et al. [1993] and Pätsch and Kühn [2008], and observed benthic denitrification rates in the SNS range from 1.6 to 4.6 mmol C m\(^{-2}\) d\(^{-1}\) (Lohse et al. [1996], Hydes et al. [1999]), a range that centrally embraces our estimate here. Note that the coupling of ammonification, nitrification and subsequently denitrification does not lead to net production of \( A_T \).

Only if nitrate is derived from the overlying water column, one obtains a net production of \( A_T \) in the pore water (Hu and Cai [2011a]). Once nitrate and oxygen are fully consumed, dissimilatory iron reduction and sulfate reduction are the prevailing respiration pathways (in the SNS we assume manganese oxides to be a minor electron acceptor, and so we ignore this pathway).

\[
OM + 53SO_4^{2-} + 121H^+ \rightarrow 53H_2S + 106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \quad (8)
\]

\[
OM + 424FeOOH + 863H^+ \rightarrow 424Fe^{2+} + 106CO_2 + 16NH_4^+ + H_2PO_4^- + 742H_2O \quad (9)
\]

Both reactions are consuming protons, and hence producing \( A_T \). Per carbon atom in organic matter oxidized, sulfate- and iron reduction are releasing 1.14 and 8.14 moles of \( A_T \) respectively. However, to assess the net \( A_T \) generation in the sediment, we need to take the fate of the reduced
species into account. The free sulphide that is generated by sulfate reduction can follow two major pathways. Some of the free sulphide (fraction $p$) will react with the reduced iron liberated by iron reduction to form pyrite. Due to its thermodynamic stability, pyrite is considered to be the primary sink for both iron and sulfur on the time scales of early diagenesis (Hu and Cai, 2011a). Dissolved iron fluxes between the sediment and the overlying water column are considered to be low throughout the southern North Sea and thus ignored for the following discussion (Slomp et al. 1997). The overall process of pyrite formation can be represented by the reaction equation:

$$\frac{1}{2} Fe^{2+} + \frac{1}{4} O_2 + H_2S \rightarrow \frac{1}{2} FeS_2 + H^+ + \frac{1}{2} H_2O$$ (10)

First, reduced iron reacts with $HS^-$ to form $FeS$ and in a second step the produced $FeS$ reacts with $H_2S$ to form pyrite ($FeS_2$) (Hu and Cai 2011b). The remaining part of the free sulphide generated by sulfate reduction (fraction $1 - p$) is transported upwards towards the oxic zone and re-oxidized with oxygen:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$ (11)

Both pyrite formation and free sulfide reoxidation consume alkalinity. However, when combined with the alkalinity impact of sulfate reduction, pyrite formation results in a net generation of alkalinity, while the alkalinity consumed in free sulfide reoxidation exactly compensates the alkalinity generated during sulfate reduction. Thamdrup et al. (1994) calculated for sediments of the Aarhus Bay that the burial of reduced sulfur accounts for only 20% of the total sulfate reduction rate, and similar values are reported in other studies (Jørgensen, 1977; Berner and Westrich, 1985; Jørgensen et al., 1990). The sediments of SNS are generally coarser and more permeable than those of Aarhus Bay, which leads to more advection and reoxygenation, which favors sulfide reoxidation as opposed to pyrite formation. Therefore, here we adopt a reduced degree of pyrite formation ($p = 0.1$; Table 5).

Adopting steady state, our simplified diagenetic model provides a set of linear relations (Table 5), which generate a particular division of the total organic matter mineralization into aerobic respiration (15%), denitrification (24%), iron reduction (0.4%) and sulfate reduction (61%). These estimates are comparable to the model analysis of Krumins et al. (2013), who estimated that sulfate reduction is the main respiratory pathway on continental shelves, accounting for 77-85% of the organic matter mineralization, followed by aerobic respiration (16%), denitrification (2-4%) and iron-reduction (0.3-0.7%). Similarly, Nedwell et al. (1993) estimated that sulfate reduction accounted for 10-53% of the total organic matter mineralization in the SNS, while a coupled benthic-pelagic model for the North Sea suggests that up to 30% of the organic matter is mineralized using sulfate as the electron acceptor (Luff and Moll 2004). The TOU rate predicted by the model (10.1 mmol O$_2$ m$^{-2}$ d$^{-1}$)
agrees well with the mean TOU observed in the SNS in September 2011 (10.0 mmol O\textsubscript{2} m\textsuperscript{-2} d\textsuperscript{-1}), but the predicted respiratory coefficient \((RQ = 1.26)\) is higher than the observed one \((RQ = 0.95)\). This higher simulated RQ could be due to an overestimate of carbonate dissolution rate. However, such a reduction of the carbonate dissolution rate would at the same time lead to a substantial underprediction of the sedimentary alkalinity release, and so we stick to the carbonate dissolution rate \(CD = 2.7\) mmol C m\textsuperscript{-2} d\textsuperscript{-1}. Accounting for the contributions of all biogeochemical reactions as discussed in this section above, the total alkalinity generation in the sediment \(R_{sed}\) becomes (Figure 12):

\[
R_{sed} = 2r_{CD} + \frac{16 - 1}{106} r_{AR} + \frac{84.8 + 16 - 1}{106} r_{DNF} + \frac{848 + 16 - 1}{106} r_{IR} + \frac{106 + 16 - 1}{106} r_{SR} - 2r_{NIT} - 2r_{SO} - r_{PF},
\]

Note, that all calculations are based on measurements carried out in June and September, and thus needs to be considered if transferring these rates on an annual scale. As we assume no alkalinity flux to deeper sediment layers, the total alkalinity generation in the sediment should match the efflux of alkalinity across the sediment-water interface. The model predicts a total alkalinity production \(R_{sed} = 6.29\) mmol m\textsuperscript{-2} d\textsuperscript{-1}, which is indeed in good agreement with the mean \(A_T\) flux of 6.50 mmol m\textsuperscript{-2} d\textsuperscript{-1} as measured in our flux incubations within the SNS. Positive contributions to the \(A_T\) efflux are due to carbonate dissolution, aerobic respiration, denitrification, sulfate reduction and iron reduction, whereas \(A_T\) is consumed during nitrification, sulfur oxidation and pyrite formation. The most dominant \(A_T\) producing reaction is carbonate dissolution, followed by sulfate reduction and denitrification. The most dominant \(A_T\) consuming reactions are sulfide oxidation and nitrification. The \(A_T\) contribution of iron reduction is small and balances that of pyrite formation.

4.5 System-wide alkalinity budget

Above we have documented how the sediments of the SNS can be a source of \(A_T\) for the water column of the SNS. However, before we can estimate the resulting effect of this benthic \(A_T\) release on the \(pCO_2\) dynamics of the southern North Sea, we first need to assess the \(A_T\) balance of the water column. An efflux of \(A_T\) from the sediment does not necessarily result in an increase of \(A_T\) in the whole system, as in the water column, some biogeochemical processes are opposing the \(A_T\) generation in the sediment. Note however, that all following calculations are based on measurements in June and September and thus not represent an annual average. Here, we identify carbonate formation (CF), primary production (PP), aerobic respiration (AR) and nitrogen fixation (NF) as processes that potentially produce or consume alkalinity in the water column.
As shown above, the dissolution of carbonates in the sediment (Equation 4) forms a strong source of $A_T$, but the production of carbonates in the water column has the opposite effect on $A_T$.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$ (13)

If the annual production of carbonate in the water column matches the carbonate dissolution in the sediments, there will be no net generation of $A_T$ on a system wide scale over a whole seasonal cycle. Note however that when there is a temporal shift in production versus dissolution of carbonates, these processes may still have an impact on the coastal $A_T$ balance on shorter time scales. Here we assume that no net burial or export of solid carbonates occurs in the SNS on an annual scale (de Haas et al., 2002; Thomas et al., 2005; Bozec et al., 2006). Accordingly, the annual benthic carbonate dissolution must be fully compensated by carbonate production in the water column, hence carbonate production in the water column will consume 5.4 mmol m$^{-2}$ d$^{-1}$ of $A_T$.

A second process which consumes alkalinity in the water column is primary production. This occurs mostly pelagic, but also benthic in some very shallow waters of the SNS. If we assume that nitrate is the main nitrogen source, primary production can be described by the reaction equation:

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow OM + 138O_2$$ (14)

Joint and Pomroy (1993) estimated primary production in the southern North Sea to be 199 g C m$^{-2}$ yr$^{-1}$, or equally, 45.40 mmol C m$^{-2}$ d$^{-1}$, thus producing 7.28 mmol m$^{-2}$ d$^{-1}$ of $A_T$. Note, that Joint and Pomroy (1993) estimated annual primary production rate, whereas rates estimated in this study are based on summer measurements. In general, primary production rates are expected to be greater than the annual average in summer. Furthermore, Joint and Pomroy (1993) includes new, as well as regenerated production in their estimation. However, for a net $A_T$ change due to primary production, regenerated production is not relevant, as the $A_T$ generated by primary production is canceled out by the $A_T$ consumption by respiration.

Aerobic respiration in the water column can be described by the opposite reaction equation of primary production (Equation: 14). To estimate the total respiration rate we need to account for two different sources of the organic matter that is being respired. The majority of the organic matter is derived from local primary production, while a smaller part originates from riverine input of terrestrial compounds. It has been estimated that about 80% of the locally produced organic matter respires in the water column, whereas the remaining 20% sinks down to the sediments (Radach and Moll 1993; Moll 1998). The value of $R_{min} = 10$ mmol m$^{-2}$ d$^{-1}$ as derived in the previous section, compare well with this assessment, as it comes down to 22% of the PP value of 45.45 mmol C m$^{-2}$ d$^{-1}$ as estimated above. The pelagic mineralization rate derived from local net primary production hence becomes 35 mmol C m$^{-2}$ d$^{-1}$. Additionally, organic matter input from land also fuels respiration,
either in the water column or in the benthic compartment. The total riverine input of organic matter in the SNS was estimated by Kühn et al. (2010) to be in the range of 1.0 mmol C m\(^{-2}\) d\(^{-1}\), which is hence small compared to the local net primary production. Accordingly, the total respiration rate in the water column must be 36.45 mmol C m\(^{-2}\) d\(^{-1}\), thus consuming 5.85 mmol m\(^{-2}\) d\(^{-1}\) of \(A_T\). Finally, the loss of fixed nitrogen due to denitrification in the sediment can be compensated by nitrogen fixation in the water column. However, the salinity of the North Sea is too high for diazotrophic cyanobacteria and too cold for open ocean cyanobacteria (Stal, 2009). Thus, we consider \(N_2\) fixation in the North Sea to be negligible.

Similar as was done for the sediment, we can define the total alkalinity generation in the water column \(R_{wc}\) as:

\[
R_{wc} = \frac{17}{106}r_{PP} - \frac{17}{106}r_{AR} - 2r_{CF} - r_{NF} ,
\]

which hence leads to a total consumption of 3.96 mmol m\(^{-2}\) d\(^{-1}\) of \(A_T\).

Based on the analysis above, we can now write an alkalinity balance for the combined sediment and water column of the SNS:

\[
\frac{d}{dt} \left[ \int_0^{L_{sed}} A_T(z) dz \right] = -F_{sed} + R_{sed}
\]

\[
\frac{d}{dt} \left[ \int_0^{L_{wc}} A_T(z) dz \right] = F_{river} + F_{sed} - F_{out} + R_{wc}
\]

In steady state, the net generation of alkalinity amounts to \(R_{net} = R_{sed} + R_{wc} = 6.29 - 3.96 = 2.33 \text{ mmol m}^{-2} \text{ d}^{-1}\) or 139 Gmol yr\(^{-1}\). As shown in table 5, 26% can be attributed to sulfur and iron cycling (i.e., anoxic mineralization taking place in the sediment) and the remaining 74% is linked to nitrogen cycling (this part is dominated by denitrification in the sediment). Furthermore, the riverine input of alkalinity was estimated by Pätsch and Kühn (2008) as \(F_{river} = 1.5 \text{ mmol m}^{-2} \text{ d}^{-1}\), based on a river load compilation for the years 1977 to 2002. Accordingly, the \(A_T\) export flux from the SNS to the rest of the North sea (SKNT and NNS) is \(F_{out} = F_{river} + R_{sed} + R_{wc} = 1.5 + 6.29 - 3.96 = 3.83 \text{ mmol m}^{-2} \text{ d}^{-1}\) or 460 Gmol yr\(^{-1}\). Additionally, \(A_T\) from the Wadden Sea might increase the \(A_T\) budget of the SNS. Schwichtenberg (2013) estimated that \(\approx 68\%\) of the yearly \(A_T\) change in the German Bight is due to \(A_T\) export from the Wadden Sea. Thomas et al. (2009) estimated an \(A_T\) flux from the Wadden Sea into the SNS of 9.6 mmol m\(^{-2}\) d\(^{-1}\). However, as the Wadden Sea is a fully mixed system, any net \(A_T\) generation in that area induces an atmospheric \(CO_2\) uptake.

Consequently, water masses of the Wadden Sea are in equilibrium with the atmosphere and thus \(A_T\) generation in the Wadden Sea plays no role in context of an air-sea \(CO_2\) exchange of the SNS.
Considering that, and in absence of reliable Wadden Sea to SNS \( A_T \) flux estimations, possible \( A_T \) inputs from the Wadden Sea were ignored.

As shown in table 5, the different terms that contribute to net generation of alkalinity in the SNS have been attributed to four different types of elemental cycling (carbon, nitrogen, sulphur + iron, phosphate). This analysis reveals that no alkalinity is associated with carbon and phosphate cycling, but that 26\% can be attributed to sulfur and iron cycling (i.e., anoxic mineralization taking place in the sediment) and the remaining 74\% is linked to nitrogen cycling (this part is dominated by denitrification in the sediment). Sedimentary denitrification is hence the most prominent driver of net alkalinity generation in the SNS. Applying our estimated mean denitrification rate (1.9 mmol N m\(^{-2}\) d\(^{-1}\)) to the whole SNS, this implies a removal of 228 Gmol N yr\(^{-1}\) of bioavailable nitrogen, which is roughly twice as high as the denitrification estimate of Pätsch and Kühn (2008) of 119 Gmol N yr\(^{-1}\) for the whole North Sea. However, whereas our estimation covers mainly the summer months, Pätsch and Kühn (2008) calculated an annual average rate. Accounting that the sediments of the SNS are the prime locations for denitrification, our estimates of denitrification rates and the associated alkalinity generation rate in the SNS seems to be in line with previous studies.

### 4.6 Impact on water column pCO\(_2\) dynamics of the SNS

Figure 13 shows the associated DIC and \( A_T \) budget of the water column in SNS. The direction of a \( CO_2 \) flux between the surface water and the atmosphere is determined by the \( pCO_2 \) gradient between water and atmosphere, which is ultimately governed by the ratio of internal DIC over internal \( A_T \) release (Frankignoulle 1994, Egleston et al. 2010, Hu and Cai 2011b). As shown above, the net generation of alkalinity amounts to 2.3 mmol m\(^{-2}\) d\(^{-1}\). Similarly the net generation of DIC amounts to 1.0 mmol m\(^{-2}\) d\(^{-1}\). As we assume that organic matter burial is negligible, there is no net internal net DIC generation due to respiration of locally produced organic matter (the respiration of autochthonous organic matter in both water column and sediment matches the primary production of autochthonous organic matter in the water column). However, as noted above, riverine input of organic matter, and so, respiration of this organic matter releases 1.0 mmol C m\(^{-2}\) d\(^{-1}\) of DIC. At constant atmospheric \( CO_2 \) and retaining a constant alkalinity, one can calculate that the addition one mole \( A_T \) to seawater will lead to an addition of 0.85 mole of DIC. This calculation was carried out in R using the package AquaEnv, utilizing Millero et al. (2006) as the first and second dissociation constant of carbonic acid in seawater (Hofmann et al. 2010), and assuming mean parameters of the SNS for the time of sampling (salinity: 34 PSU, temperature: 16.3 \(^\circ\)C, \( A_T \): 2270 \( \mu \)mol kg\(^{-1}\)) and an atmospheric \( CO_2 \) concentration of 392 ppm). Accordingly, a net internal alkalinity release of 2.3 mmol m\(^{-2}\) d\(^{-1}\) will hence lead to an associated DIC increase of 1.96 mmol C m\(^{-2}\) d\(^{-1}\). Of this, 1.0 mmol C m\(^{-2}\) d\(^{-1}\) is already supplied by internal DIC generation, and so, the remainder of 0.96 mmol m\(^{-2}\) d\(^{-1}\) will be supplied by \( CO_2 \) uptake from the atmosphere. The \( CO_2 \) uptake for the SNS as a whole amounts to 115 Gmol C yr\(^{-1}\), which is around 21\% of the total \( CO_2 \) uptake of the
entire North Sea (Thomas et al., 2004; Egleston et al., 2010). This value is in good agreement to the estimate by Thomas et al. (2009), who calculated that sedimentary $A_T$ can potentially facilitate up to 25% of the total $CO_2$ uptake of the North Sea. This latter estimate was not based on direct flux measurements, but derived from an $A_T$ budget for the North Sea, where $A_T$ generation in Wadden Sea sediments was introduced as a closure term.

The idea that internal alkalinity generation in the SNS can drive atmospheric $CO_2$ uptake is further supported by previous $CO_2$ studies, although significant seasonality has been observed in the atmospheric $CO_2$ uptake. Thomas et al. (2005) reported an uptake of $CO_2$ for the months February to August (-0.52 mmol C m$^{-2}$ d$^{-1}$), while the SNS was reported to be a source for $CO_2$ between September and January (+0.60 mmol C m$^{-2}$ d$^{-1}$). Bozec et al. (2005) described the SNS as a strong source for $CO_2$ with fluxes of 0.8 to 1.7 mmol C m$^{-2}$ d$^{-1}$ in late summer, while on an annual scale, the SNS was characterized as a sink of $CO_2$ with an air-sea flux of -0.55 mmol C m$^{-2}$ d$^{-1}$. Due to the temporal variability of $CO_2$ fluxes, and the seasonal cycles of primary production and respiration, it is hard to compare these numbers with our calculated $CO_2$ air-sea flux based on internal $A_T$ generation only, but the estimated impact on the $pCO_2$ dynamics of the SNS by benthic $A_T$ release appears to be in the same order of magnitude as determined in previous studies of the $pCO_2$ dynamics of the SNS. Overall, the $A_T$ release from sediments, driven by denitrification and anoxic respiration of organic matter, seems to play an important role in the atmospheric $CO_2$ uptake of the North Sea.

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References


Figure 1. Map of sampled stations. Red symbols: Southern North Sea, Black Symbols: Skagerrak, Blue symbols: Northern North Sea, Circles: Sampled in September 2011, Squares: Sampled in June 2012. Border of the Skagerrak as defined by the International Hydrographic Organization, border between SNS and NNS roughly represents the 100 m depth isoline.
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**Table 1.** Sampled stations from both cruises in 2011 and 2012 with coordinates and maximum water depth, as well as with sediment characteristics and bottom water characteristics as measured by the CTD.
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Table 2. Fluxes at the sediment-water interface for O<sub>2</sub> (TOU), AT and DIC. (a) Hydes et al. [1999], (b) Thomas et al. [2009]. Units mmol C m<sup>−2</sup> d<sup>−1</sup> (DIC flux); mmol m<sup>−2</sup> d<sup>−1</sup> (AT flux); mmol O<sub>2</sub> m<sup>−2</sup> d<sup>−1</sup> (TOU rate).
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<td>7.32</td>
<td>1.67</td>
<td>NA</td>
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<td>52</td>
<td>5.49</td>
<td>0.83</td>
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<td>56</td>
<td>3.76</td>
<td>1.47</td>
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<td>59</td>
<td>4.94</td>
<td>4.33</td>
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<td>62</td>
<td>4.80</td>
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<td>71</td>
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<td>1.76</td>
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<td>80</td>
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<tr>
<td>88</td>
<td>2.25</td>
<td>1.87</td>
<td>18.8</td>
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Table 3. Comparison between TOU rates as measured by FireSting optodes and diffusive oxygen uptake rates (DOU) obtained from $O_2$ microprofiles. Unit: mmol $O_2$ m$^{-2}$ d$^{-1}$; Oxygen penetration depth (OPD) for cores used for microprofiling in mm. NA indicates that oxygen does not deplete over the measured depth.

![Temperature profiles](image)

Figure 2. Temperature profiles as recorded by a CTD cast for: (a) Station 11 (SNS); (b) Station 65 (SKNT); (c) Station 80 (NNS)
<table>
<thead>
<tr>
<th>Literature</th>
<th>Location</th>
<th>Month and year</th>
<th>TOU</th>
</tr>
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<tr>
<td><strong>North Sea</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>de Wilde et al. (1984)</td>
<td>OG</td>
<td>5,8,9 (1980,1981)</td>
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<td>Cramer (1990)</td>
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<td>5,6 (1986), 8,9 (1987)</td>
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<td>Van Raaphorst et al. (1990)</td>
<td>DB</td>
<td>7,8 (1988)</td>
<td>4.20</td>
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<td>Van Duy et al. (1992)</td>
<td>FF</td>
<td>1,4,5,8,11 (1989)</td>
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<td>Upton et al. (1993)</td>
<td>U1</td>
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<td>FF</td>
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<td>U3</td>
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<td>U6</td>
<td>9,10 (1988), 2,4,6,8,9 (1989)</td>
<td>7-18</td>
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<td>Lohse et al. (1996)</td>
<td>OG</td>
<td>7 (1994)</td>
<td>5.6.6.1</td>
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<td>Boon et al. (1998)</td>
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<td>FF</td>
<td>2,3,4,6,8,11 (1993)</td>
<td>&lt; 48</td>
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<td>Trimmer et al. (2000)</td>
<td>Thms</td>
<td>7,10 (1996), 4,7 (1997)</td>
<td>11.4 - 5.8</td>
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<td></td>
<td>Thms</td>
<td>10 (2001), 7 (2002)</td>
<td>14 - 43.9</td>
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<td>Weston et al. (2008)</td>
<td>OG</td>
<td>9 (2003)</td>
<td>12.6 - 30.6</td>
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<td>Franco et al. (2010)</td>
<td>F115bis</td>
<td>2,4,10 (2003)</td>
<td>5.5 - 18.8</td>
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<td>F330</td>
<td>2,4,10 (2003)</td>
<td>1.2 - 8.7</td>
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<td>Provoost et al. (2013)</td>
<td>F115</td>
<td>9,10,11,12 (2002), 1,2,3,4,5,7,8,9,10 (2003)</td>
<td>4.5 - 32.9</td>
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<td>Braeckman et al. (2014)</td>
<td>BM</td>
<td>2,3,4,5,6,7,8,9 (2011)</td>
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<td>BS</td>
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<tr>
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<td>BS</td>
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<tr>
<td></td>
<td>BS</td>
<td>10 (2011)</td>
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<td><strong>Other coastal systems</strong></td>
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<tr>
<td>Lansard et al. (2008)</td>
<td>MS</td>
<td>06 (2001 &amp; 2002)</td>
<td>3.9 - 25.6</td>
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<td>Nordi et al. (2013)</td>
<td>FS</td>
<td>04 05 06 07 08 (2011) 02 06 07 (2012)</td>
<td>3.3 - 6.8</td>
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<tr>
<td>Archer et al. (1992)</td>
<td>WS</td>
<td>06 (1988)</td>
<td>1.0 - 18.3</td>
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<td>Grebmeier &amp; McRoy (1989)</td>
<td>BC</td>
<td>07 08 09 (1984 - 1986)</td>
<td>0.3 - 16.9</td>
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<tr>
<td>Smith (1974)</td>
<td>SD</td>
<td>10 (1973)</td>
<td>0.4 - 3.9</td>
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<tr>
<td>Boetius &amp; Damm (1998)</td>
<td>AC</td>
<td>08 09 (1993)</td>
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<tr>
<td>Friedl et al. (1998)</td>
<td>BS</td>
<td>Summer (1995)</td>
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<td>Hartnett et al. (2008)</td>
<td>AP</td>
<td>03 06 10 (2000) 02 (2001)</td>
<td>1.5 - 2.1</td>
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<td>Larsen et al. (2013)</td>
<td>CS</td>
<td>07 (2008)</td>
<td>5.8 - 9.0</td>
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<td><strong>This study</strong></td>
<td>SNS</td>
<td>9 (2011)</td>
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<td>SNS</td>
<td>4 (2012)</td>
<td>6.50 - 25.11</td>
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<td></td>
<td>NNS</td>
<td>9 (2011)</td>
<td>0.74 - 6.20</td>
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</table>

**Table 4.** TOU rates (mmol O$_2$ m$^{-2}$ d$^{-1}$) measured in the North Sea and other coastal systems taken from literature compared to this study. OG: Oyster Ground, FF: Frisian Front, DB: Dogger Bank, BF: Broad Fourteens, U1-U3: (near) English Channel, U4-U6: Central North Sea, F115bis, F330, BM, BFS, BS: Belgian Coast, Thms: Thames, USP: Outer Silver Pit, MS: Mediterranean Sea, FS: Faroe Shelf, WS: Washington Shelf, BC: Northern Bering and Chukchi Seas, SD: San Diego Trough, AC: Arctic Continental Slope, AS: Arabian Sea, MB: Monterey Bay, BS: Black Sea, AP: Western Antarctic Peninsula, CS: Celtic Sea, SNS: southern North Sea, NNS: northern North Sea.
### Input parameters

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Expression</th>
<th>Value</th>
<th>Units</th>
<th>A_T release</th>
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</thead>
<tbody>
<tr>
<td>Mineralization rate</td>
<td>$R_{\text{min}}$</td>
<td>10.0</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>—</td>
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<tr>
<td>Aerobic respiration fraction</td>
<td>a</td>
<td>0.15</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Fraction of DNF supported by NI</td>
<td>b</td>
<td>0.8</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Pyrite formation fraction</td>
<td>p</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
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</table>

### Benthic fluxes

- $J_{\text{NO}_3} = (1-b) \ast 0.8 \ast DNF$
- $J_{\text{N}_4} = 0$
- $J_{\text{Fe}^{2+}} = 0$
- $J_{\text{H}_2\text{S}} = 0$

### Balance statements

- $\delta [\text{CO}_2]/\delta t = +R_{\text{min}}$
- $\delta [\text{O}_2]/\delta t = -AR - R_{\text{SO}} - R_{\text{NIT}}$
- $\delta [\text{NO}_3]/\delta t = NIT - 0.8 \ast DNF + J_{\text{NO}_3}$
- $\delta [\text{NH}_4^+]/\delta t = -a \ast R_{\text{min}} - R_{\text{NIT}} + AM + J_{\text{N}_4}$
- $\delta [\text{Fe}^{2+}]/\delta t = 4 \ast IR - (\frac{1}{2} \ast PF + J_{\text{Fe}^{2+}})$
- $\delta [\text{H}_2\text{S}]/\delta t = 0.5 \ast SR - PF - SO + J_{\text{H}_2\text{S}}$

### Pelagic processes

<table>
<thead>
<tr>
<th>Pelagic process</th>
<th>Expression</th>
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<th>Units</th>
<th>A_T release</th>
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</thead>
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<td>Primary production</td>
<td>PP</td>
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<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+7.28</td>
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<tr>
<td>Aerobic respiration</td>
<td>WAR</td>
<td>36.45</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>-5.85</td>
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<tr>
<td>Carbonate formation</td>
<td>CF</td>
<td>2.70</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>-5.40</td>
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<tr>
<td>Nitrogen fixation</td>
<td>$N_F$</td>
<td>0</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>0</td>
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### Diagenetic processes

<table>
<thead>
<tr>
<th>Diagenetic process</th>
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<th>Value</th>
<th>Units</th>
<th>A_T release</th>
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</thead>
<tbody>
<tr>
<td>Carbonate dissolution</td>
<td>$CD = CF$</td>
<td>2.70</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+5.40</td>
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<td>Aerobic respiration</td>
<td>$AR = a \ast R_{\text{min}}$</td>
<td>1.50</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+0.21</td>
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<td>Ammonification</td>
<td>$AM = \frac{1}{a} \ast R_{\text{min}}$</td>
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<td>mmol N m$^{-2}$ d$^{-1}$</td>
<td>—</td>
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<td>Nitrification</td>
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<td>-3.02</td>
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<td>Denitrification</td>
<td>$DNF = \frac{1}{a} \ast NIT \ast \frac{\text{NIT}}{n_{\text{NIT}}}$</td>
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<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+2.22</td>
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<tr>
<td>Sulfate reduction</td>
<td>$SR = (R_{\text{min}} - AR - DNF)/(\frac{1}{2} \ast p + 1)$</td>
<td>6.10</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+6.97</td>
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<tr>
<td>Pyrite formation</td>
<td>$PF = 8 \ast IR$</td>
<td>0.33</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>-0.31</td>
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<tr>
<td>Pyrite formation</td>
<td>$PF = 0.5 \ast p \ast SR$</td>
<td>0.33</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>-0.31</td>
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<td>Sulfide oxidation</td>
<td>$SO = 0.5(1-p) \ast SR$</td>
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<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>-5.49</td>
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<tr>
<td>Iron reduction</td>
<td>$IR = \frac{1}{df} \ast p \ast SR$</td>
<td>0.04</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
<td>+0.31</td>
</tr>
</tbody>
</table>

### Alkalinity generation

- See text

### Total oxygen uptake

- $TOU = AR + 2 \ast NIT + 2 \ast SO + 0.25 \ast PF$
- $RQ = \frac{R_{\text{min}} \ast CD}{TOU}$

### A_T turnover Linked to

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Expression</th>
<th>Value</th>
<th>Units</th>
<th>A_T release</th>
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</thead>
<tbody>
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<td>Carbon cycle</td>
<td>$2 \ast CD - 2 \ast CF$</td>
<td>0</td>
<td>%</td>
<td>—</td>
</tr>
<tr>
<td>Nitrogen cycle</td>
<td>$84.8/106 \ast DNF + 16/106 \ast (AR + DNF + IR + SR) - 2 \ast NIT + (16/106) \ast (PP - WAR)$</td>
<td>74</td>
<td>%</td>
<td>—</td>
</tr>
<tr>
<td>Sulphur and iron cycle</td>
<td>$8 \ast IR + SR - 2 \ast SO - PF$</td>
<td>26</td>
<td>%</td>
<td>—</td>
</tr>
<tr>
<td>Phosphor cycle</td>
<td>$-1/106 \ast (AR + DNF + IR + SR) + (1/106) \ast (PP - WAR)$</td>
<td>0</td>
<td>%</td>
<td>—</td>
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</tbody>
</table>

Table 5. Input parameters and rate expressions for all diagenetic and pelagic processes including in our model. Additionally, the impact of the different elemental cycles are expressed in percentages. For details on single reaction rates see section 4.4.
Figure 3. Representative concentrations of $A_T$, DIC and $O_2$ saturation over time for all three regions of the North Sea. Red: Station 11 (SNS); Blue: Station 71 (NNS); Black: Station 65 (SKNT)
Figure 4. Total oxygen uptake rates measured in benthic incubation chambers at two different stirring rates (RPM = Rounds Per Minute); Dashed line: 1:1 line; Solid line: Linear regression; Red symbols: SNS; Blue symbols: NNS. All rates in mmol O$_2$ m$^{-2}$ d$^{-1}$.

Figure 5. Examples of microsensor depth profiles from different regions of the North Sea. (a) $O_2$; (b) pH; Red: Station 11 (SNS); Blue: Station 65 (SKNT); Black: Station 80 (NNS); Solid line: Sediment-Water interface
Figure 6. Correlation plots between DIC-, \( A_T \)-fluxes, TOU rates and water depth, porosity and grain size. Red: SNS, Black: SKNT, Blue: NNS; Spearman’s \( p \)-value given in each plot. Units mmol m\(^{-2}\) d\(^{-1}\) (DIC); mmol m\(^{-2}\) d\(^{-1}\) (\( A_T \)); mmol O\(_2\) m\(^{-2}\) d\(^{-1}\) (TOU);
**Figure 7.** (a) Oxygen Penetration Depth (OPD) plotted versus Diffusive Oxygen Uptake (DOU) rate (b) Correlation between measured OPD and theoretical OPD. Dashed line: 1:1 line; Red symbols: SNS; Blue symbols: NNS; Black: SKNT. For calculation and details see text.

**Figure 8.** (a) Correlation between DIC fluxes and TOU rates. (b) Correlation between $A_T$ fluxes and TOU rates. Dashed line: Line of RQ = 0.77; Solid line: Linear regression; Spearman’s $p$-value given in each plot. TA and DIC fluxes in mmol C m$^{-2}$ d$^{-1}$. TOU rates in mmol O$_2$ m$^{-2}$ d$^{-1}$. 
Figure 9. Sensitivity of the benthic $\Delta T$ flux (dashed line) and the net $\Delta T$ generation (solid line) towards a range of mineralization rates in the SNS.

Figure 10. Directly measured $\Delta T$ fluxes for the SNS compared to $\Delta T$ flux estimations based on Ra measurements. Figure taken from [Burt et al., 2014]. Fluxes in mmol C m$^{-2}$ d$^{-1}$.
Figure 11. Correlation between $A_T$ and DIC fluxes for sites of the SNS from both campaigns. Different lines are representing different reaction stoichiometry. For more explanation and reaction equations see text. Short dashed line: Aerobic respiration; Dotted line: Denitrification; Dotted/Dashed line: Sulfate reduction coupled to pyrite formation and burial; Long dashed line: Carbonate dissolution; Note, that the latter two lines are plotting along similar points and are thus hard to distinguish. $p$: Spearman’s rank correlation coefficient for the correlation of all points displayed in this scatter plot. All fluxes in mmol C m$^{-2}$ d$^{-1}$.

Figure 12. Contribution of different processes to the benthic $A_T$ budget in the SNS. For more details on different reaction rates see text. NI: Nitrification; SO: Sulfide oxidation; PF: Pyrite formation; CD: Carbonate dissolution; DN: Denitrification; SR: Sulfate reduction; IR: Dissimilatory iron reduction; AR: Aerobic respiration. Fluxes in mmol m$^{-2}$ d$^{-1}$.
Figure 13. DIC and $A_T$ budgets of the water column in the SNS. Bold arrows: Fluxes; Dashed arrows: Reaction rates. $F_{\text{sed}}$: Net flux from the sediments; $F_{\text{river}}$: Riverine input; $F_{\text{out}}$: Flux into the NNS/SKNT; $F_{\text{air}}$: Atmospheric DIC uptake; $R_{\text{pp}}$: Primary production rate; $R_{\text{resp}}$: Aerobic respiration rate; $R_{\text{cf}}$: Carbonate production rate. Unit: mmol C m$^{-2}$ d$^{-1}$.