Sediment-water exchange of nitrogen compounds and oxygen in the North Sea

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This thesis summarises the research on sediment-water exchange of nitrogen and oxygen in North Sea sediments carried out during a 5 years period at the Netherlands Institute for Sea Research (NIOZ). The research was conducted to study the nitrogen cycle in continental shelf sediments which occupy a central position in the global nitrogen budget. Particular emphasis was put on the spatial and temporal variability of processes involved. Due to its hydrodynamic complexity, the North Sea is characterised by a pronounced seasonal and spatial variation in temperature, nutrient concentrations and primary production. As a result, the flux of organic matter to the sediment is also highly dynamic and variable, both in space and time. Consequently, benthic nitrogen cycling is affected by a number of environmental factors, the most important of them being elucidated in this thesis.

Initially, research concentrated on the seasonal variation of denitrification and nitrous oxide fluxes in intertidal sediments of the western Wadden Sea (Chapter II). Denitrification rates and nitrate concentration in the overlying water showed a similar seasonal pattern. Denitrification was low during the summer months when the water column was nitrate-depleted. In autumn, denitrification rates increased simultaneously with nitrate concentrations, although in an irregular pattern. The absence of distinct pore water maxima of nitrate concentrations throughout the year and low oxygen penetrations during the summer months suggested that nitrification is not an important source of nitrate for denitrification. Additional support for this conclusion followed from nitrate additions to the overlying water. In summer, these enrichments lead to a tremendous (>100-fold) increase in denitrification rates, while in winter, when the nitrate concentrations in the overlying water were high, such an effect was absent.

Nitrous oxide fluxes were coupled to the nitrate concentrations in the overlying water and denitrification. In winter and early spring nitrous oxide was predominantly released by the sediment. These effluxes turned into influxes during the summer months, when the nitrate concentration in the overlying water was low. Addition of nitrate to the overlying water resulted in an immediate high efflux of nitrous oxide in that period. A possible mechanism explaining nitrous oxide influxes follows from the function of this compound as a competitive electron acceptor at low nitrate concentrations. Thus, except photo-dissociation in the stratosphere, microbially mediated reduction to gaseous di-nitrogen may be an additional sink for nitrous oxide. Whether this process can account for the missing sink in the global nitrous oxide budget needs to be addressed in further studies. However, it was determined that the role of intertidal areas as a source adding to the atmospheric nitrous oxide increase is minimal.

A detailed picture of benthic nitrogen cycling was obtained by studying the interaction of nitrification and denitrification in offshore and coastal areas of the North Sea (Chapter III). These investigations revealed a pronounced seasonal difference in the coupling of both processes and the accompanying sediment-water fluxes of inorganic nitrogen compounds. The thickness of the oxic layer appeared to be the predominating factor controlling inorganic nitrogen cycling. This layer was 2 to 3 fold thinner in August compared to February, due to increased carbon and nitrogen mineralisation in the summer. Nitrification was clearly stimulated by the enhanced ammonium availability in August, despite the decreased thickness of the oxic layer. This suggested that the zone of maximum nitrification activity was located close to the oxic-anoxic boundary, where ammonium concentrations were highest. Except in the mud deposition area of the inner German Bight, nitrate pore water concentrations peaked in the oxic layer of the sediment and sediment-water fluxes unequivocally showed the release of nitrate to the overlying water. Hence, nitrification in the sediment rather than the overlying water was the predominant source of nitrate for denitrification in North Sea sediments. The most striking result of this study was the apparent de-coupling between nitrification and denitrification due to the very steep nitrate concentration gradients between the nitrification zone and the overlying water. Although nitrification rates were higher in August compared to February, most of the produced nitrate (i.e. ~95%) diffused along the steepest concentration gradient to the overlying water instead of becoming denitrified in anoxic layers. In February, nitrification rates had decreased and the zone of maximum activity had moved deeper into the sediment. At the same time, nitrate concentrations in the overlying...
water had increased, thereby diminishing the concentration gradient between the nitrification zone and the overlying water. As a result, coupled nitrification-denitrification became more efficient, although even then not more than 25% of the produced nitrate was denitrified. Enhanced diffusive transport in the oxic layer of the sediment, as reported in Chapter VI, may have supported the release of nitrate to the overlying water. The de-coupling of both processes may be representative for continental shelf sediments overlain by a well-oxygenated water column low in nitrate concentrations.

The significance of the overlying water as a nitrate source for denitrification was demonstrated in the depositional area of the inner German Bight where anoxic, sulfidic sediments prevented the occurrence of nitrification in August. Even though thin oxic layers sustained nitrification activity in February, the overall flux of nitrate was towards the sediment. This situation compares to other continental shelf sediments with high nitrate concentrations in the overlying water. In these sediments, steep nitrate gradients exist between the overlying water and the denitrification zone and, as a consequence, all nitrate produced by nitrification diffuses downward along this gradient to become denitrified. In conclusion, the thickness of the oxic layer and the nitrate concentration in the overlying water were the most important factors controlling the efficiency of coupled nitrification-denitrification. Further, it was ascertained that non-depositional North Sea sediments regenerate nitrogen compounds to the overlying water, rather than being a sink.

In chapter IV, sediment-water exchange of inorganic nitrogen compounds was related to the deposition of organic matter on the North Sea shelf. The location of sampling stations was chosen along the prevailing transport route of water masses and suspended material in the North Sea. The major depositional areas (i.e. the inner German Bight and the Skagerrak) as well as areas characterised by temporal deposition were included. Analysis of the grain size spectrum and the organic carbon content of the bottom deposits corroborated with the hydrodynamic regime of the North Sea. Three clusters were distinguished: I) depositional areas with a median grain size < 50 μm; II) transition areas characterised by temporal deposition and grain size between 80 and 180 μm, and III) non-depositional areas characterised by a medium grain size of > 280 μm. Porewater profiles of oxygen, nitrate and ammonium as well as total nitrogen mineralisation corresponded to this clustering. In February 1992, i.e. just before the onset of the spring phytoplankton bloom, the spatial differences in nitrogen mineralisation between these three clusters were much less pronounced than in August 1991, when benthic processes were stimulated by deposition of preceding plankton blooms. In August, nitrogen mineralisation rates at stations belonging to cluster II and III were 2 to 3-fold higher than in February. Stations in the depositional areas (cluster I, Skagerrak and the German Bight) had to be divided in two subgroups in order to explain the 40-fold higher mineralisation rates in the inner German Bight in August compared to February. It was argued that nitrogen mineralisation in the German Bight is controlled by the deposition of fresh organic matter delivered from authochthonous sources. On the contrary, deposition of organic matter in the Skagerrak stations is dominated by the input of refractory material, winnowed from the southern North Sea shelf. This conclusion was supported by the absence of seasonal variations in nitrogen mineralisation at those stations. Consequently, the shelf-slope transition in the Skagerrak does not represent an area of intensified nitrogen mineralisation.

The necessity to verify and calibrate techniques commonly applied to study benthic denitrification rates was addressed in Chapter V. Two independent methods, isotope pairing and acetylene inhibition, were applied simultaneously to estimate denitrification rates in North Sea shelf sediments overlain by a well-oxygenated water column low in nitrate concentrations. Nitrification was the predominant source of nitrate in the investigated sediments. Both techniques were able to detect coupled nitrification-denitrification, however, denitrification rates calculated from the nitrous oxide accumulation in acetylene amended cores were only detectable during the first 60 minutes of incubation. Continued incubation resulted in decreasing rates, suggesting that nitrous oxide was consumed despite the presence of acetylene. Denitrification measured by the isotope pairing method revealed constant production of single-labelled $^{14}$N$^{15}$N relative to double labelled $^{15}$N$^{15}$N isotopic species, indicating that the added $^{15}$NO$_3^-$ rapidly mixed with the indigenous $^{14}$NO$_3^-$ pool. Denitrification rates obtained from isotope pairing were twice as high as initial rates derived from the acetylene inhibition technique. The contemporaneous examination of nitrate and ammonium fluxes across the sediment-water interface confirmed previous measurements in North Sea sediments, which showed that the prevailing part of deposited nitrogen is
returned to the water column as ammonium and nitrate. The results also demonstrated that earlier measurements of denitrification using the acetylene inhibition technique may have underestimated true rates (Chapter II).

The research presented in chapter VI focused on transport processes mediating sediment-water exchange of solutes. While it is generally assumed that the transport of solutes through pore waters and the diffusive benthic boundary layer takes place by molecular diffusion, clear evidence was found for the occurrence of turbulent diffusion or advection in the upper millimetres of North Sea sediments. Oxygen pore water profiles measured with microelectrodes in sandy sediments revealed the presence of a subsurface layer characterised by enhanced diffusive transport. In general, enhanced diffusivity was shown in coarse, permeable sediments intrinsically characterised by relatively low oxygen consumptions. These sediments were predominantly located on the southern North Sea shelf, while silty, impermeable sediments as found in the depositional area of the Skagerrak did not seem to be influenced by enhanced diffusion. Additionally, enhanced diffusive transport was more pronounced in periods characterised by low oxygen uptake of the sediment. Quantitative evaluation of the pore water profiles by a diffusion-reaction model revealed that the effective diffusion coefficient in the subsurface layer to be 1.5 to >100 times higher than the molecular diffusion coefficient in order to account for the observed curvature of the oxygen profiles. The time-depending adaptation of oxygen porewater profiles to changes in bottom friction velocity suggested that bottom currents generated by diurnal tidal motion may induce an oscillating oxic-anoxic interface in sandy North Sea sediments. Repeated shifts from anoxic to oxic conditions may promote organic carbon mineralisation and minimise burial of organic carbon, thereby offering a additional explanation for the low organic carbon contents in North Sea sediments.

A theoretical examination of transient steady-state oxygen profiles adapting to a new flow regime above the sediment surface demonstrated the implications of confined benthic chambers in studying sediment-water exchange in sandy, permeable sediments. The decrease of effective diffusivity in the sub-surface layers of the sediment and the re-establishment of molecular diffusion as the dominant transport mechanism inside benthic chambers may lead to an underestimation of the true oxygen flux between 30 and 60%. As a consequence, previous measurements of benthic oxygen consumption in permeable, sandy shelf sediments may have severely underestimated the benthic oxygen consumption.