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Denitrification in sediments as a major nitrogen sink in the Baltic Sea: an extrapolation using sediment characteristics

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Abstract

Rates of denitrification in sediments were measured with the isotope pairing technique at different sites in the southern and central Baltic Sea. They varied between 0.5 µmol m^{-2} h^{-1} in sands and 28.7 µmol m^{-2} h^{-1} in muddy sediments and showed a good correlation to the organic carbon contents of the surface sediments. N-removal rates via sedimentary denitrification were estimated for the entire Baltic Sea calculating sediment specific denitrification rates and interpolating them to the whole Baltic Sea area. Another approach was carried out by using the relationship between the organic carbon content and the rate of denitrification. For the entire Baltic Sea the N-removal by denitrification in sediments varied between 426–652 kt N a^{-1}, which is around 48–73% of the external N inputs delivered via rivers, coastal point sources and atmospheric deposition. Moreover, an expansion of the anoxic bottom areas was considered under the assumption of a rising oxycline from 100 to 80 m water depth. This leads to an increase of the area with anoxic conditions and an overall decrease in sedimentary denitrification by 14%. Overall we can show here that this type of data extrapolation is a powerful tool to estimate the nitrogen losses for a whole coastal sea and may be applicable to other coastal regions and enclosed seas, too.

1 Introduction

Dealing with large quantities of anthropogenic nitrogen inputs is one of the biggest challenges for marine ecosystems and coastal states throughout the world. Every year up to 47.8 Mio tons of reactive nitrogen (N_r) enters the marine ecosystem via the rivers (Galloway et al., 2004) resulting in eutrophication and an extension of dead zones in the coastal oceans e.g. Gulf of Mexico (Turner and Rabalais, 1994), the Black Sea (Mee et al., 2005; Mee, 2006), the Chesapeake Bay (Hagy et al., 2004), or the Baltic Sea (Conley et al., 2009a). A summary of sites with coastal near hypoxic environments is given in Diaz and Rosenberg (2008).

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In the years 2000–2006 an amount of 686 kt a^{-1} N_r entered the Baltic Sea via the rivers and coastal point sources. Atmospheric deposition delivered 201 kt (Wulff et al., 2009). Together with the N-input via nitrogen fixation (434–792 kt a^{-1} in the central Baltic Sea, Wasmund et al., 2001) the total annual N input easily exceeds 1400 kt a^{-1}. Whereas riverine inputs dominate the coastal areas, the study of Voss et al. (2005) showed that inputs via atmospheric deposition and nitrogen fixation strongly influence the central basins. This study also stresses the possible role of coastal sediments as sites of nitrogen removal since the inputs from all sources do not show up in increasing nutrient concentrations of the central Baltic Sea. In the central part the concentrations stayed rather constant since the 70s (HELCOM, 1996).

Heterotrophic denitrification is one process that can permanently remove reactive nitrogen from a system. Denitrifying bacteria reduce nitrate (NO_3^-) via nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O) to the non-reactive dinitrogen gas (N_2) with organic carbon as electron donor (Devol, 2008). It is controlled by a variety of environmental parameters, such as substrate availability, temperature, and/or oxygen concentration, and the interaction between these parameters as well as the reason why the one or the other parameter is dominating is under debate (Seitzinger, 1988). Another important N sink is the Anammox process (anaerobic ammonium oxidation) which can be found in oxygen minimum zones of the oceans (Kuypers et al., 2003, 2005; Lam et al., 2009), as well as in sediments (Dalsgaard and Thamdrup, 2002; Hietanen and Kuparinen, 2008). An increase in N-removal with nitrogen loading has been observed for different coastal ecosystems, counterbalancing excessive nitrogen input (Seitzinger, 1988). Heterotrophic denitrification occurs in sediments as well as in the water column at oxygen levels below 5 µmol L^{-1} (0.112 ml L^{-1}) (Devol, 2008) and can reach rates up to 3400 µmol N L^{-1} h^{-1} in rivers (Laursen and Seitzinger, 2002). For coastal sediments rates of up to 115 µmol N m^{-2} h^{-1} have been reported (Seitzinger et al., 1984). Estimated on a global scale denitrification rates are responsible for a loss of around 40% of the total N inputs (Galloway et al., 2004) and the process is generally considered as the major process removing reactive nitrogen from the world's oceans (Hulth et al.,

2005 and references therein). These losses are even higher when the whole land-sea continuum is considered (Seitzinger et al., 2008).

Little is known about the controlling factors and the general importance of sedimentary denitrification for the Baltic Sea, mainly because investigations of this process are often restricted to specific sub-areas of the Baltic Sea like the Baltic Proper, Gulf of Finland, Bothnian Sea or the Bothnian Bay. However, Hietanen and Kuparinen (2008) and Tuominen et al. (1998) up-scaled their rates for the Gulf of Finland and estimated total N-losses via denitrification and anammox of 39.1 kt a^{-1} and 45 kt a^{-1}. For the Bothnian Sea and the Bothnian Bay Stockenberg and Johnstone (1997) calculated total N-losses via denitrification of 34.5 kt a^{-1} and 14.5 kt a^{-1}, respectively. In the studies that calculated the N-losses from mass balance calculations Shaffer and Rönner (1984) and Eilola and Stigebrandt (1999) gave N-losses via denitrification for the Baltic Proper of 470 kt a^{-1} and 560 kt N a^{-1}, respectively. Voss et al. (2005) applied a stable isotope budget approach to estimate an N-loss via denitrification from the Baltic Proper between 580–855 kt N a^{-1} depending on the isotope enrichment factor they used for isotope fractionation during the denitrification process.

In this publication we present denitrification rates for a variety of different Baltic Sea sediments from different basins and discuss the controlling environmental parameters. For the first time a calculation of the yearly N-removal via sedimentary denitrification was carried out by extrapolation of sediment-specific isotope-pairing rates for the whole Baltic Sea area as well as the sub basins by means of two different sediment distribution maps and a large set of sediment C_{org} contents. Furthermore we evaluate the expansion of the anoxic bottom areas and its influence on the N-removal capacity from the sediments.

2 Methods

Denitrification rates from several sediment types and water depths were measured by means of the Isotope-Pairing Technique (IPT) in 2008 during several cruises and

sampling.

2.1 Sampling

Sediment samples were collected by hand (coastal sandy stations), with a Rumohr corer (Kreidesegler station) or by multi-corer and box-corer (other stations) between May and November 2008. The stations represented shallow mixed and sandy sediments (water depth <0.3 m) and deeper stations with mud, clay, mixed, and sandy sediments (water depth 15–80 m). Water samples for the analysis of $NO_3^-/_2^-$ (Jones, 1984) and O_2 concentrations (Winkler, 1888) were collected from the bottom water overlying the sediment cores and analyzed immediately or within a time frame of maximum three hours. Two extra cores per station were sliced to determine grain size distribution and the organic carbon and nitrogen contents.

2.2 Denitrification measurements

Sediment denitrification was measured using the isotope pairing technique (Nielsen, 1992; Risgaard-Petersen et al., 2003). Three replicate incubation cores (plastic cylinders with a height of 25 cm and ⌀3.6 cm) were taken, half of the core filled with sediment and the remaining with bottom water. The top of the incubation core was closed with a cap, the cores were gently lifted from the sediment, and the bottom was closed. The isotope pairing experiments were performed in the form of a concentration series to verify the assumptions underlying the method and to check for anammox activity. For this, $K^{15}NO_3^-$ solution was added to the cores (3–4 replicates) to reach a $^{15}NO_3^-$ concentration of 25, 50, 100 and 150 µmol L^{-1}, respectively. The cores were then equipped with stirring devices, capped, and incubated in the dark at in-situ temperature for maximum 24 h. For some sediment, the incubation time was reduced to 18 h (Breitling, Gollwitz 1 and 2) and 20 h (Arkona), respectively, to prevent oxygen consumption as a result of high in-situ temperatures (15–23 °C). Oxygen levels were routinely checked using O_2-microelectrodes and remained above 60% saturation during the incubations.

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After the incubation, the sediment of each core was homogenized. Samples of the sediment slurry were taken with a 50 mL syringe and filled in 12 mL exetainers (Labco). 100 µL of zinc chloride solution was added to the samples to inhibit further bacterial activity. Finally, the exetainers were capped bubble-free and stored dry at room temperature prior to analysis. Concentrations of $^{29}N_2$ and $^{30}N_2$ were analyzed at the National Environmental Research Institute in Silkeborg (NERI, Denmark).

For the calculation of denitrification rates, the porosity (ϕ) of the sediment was determined by drying at 60 °C overnight. Calculation was performed following Pettijohn et al. (1973) from fresh and dry weights assuming a solid matter specific density of 2.65 g cm^{-3}.

2.3 Testing the assumptions underlying the IPT

There was no tracer concentration dependency of genuine N_2 production detected at any of the study sites (ANOVA, $p \gg 0.05$). Thus, the assumptions of the IPT that the added $^{15}NO_3^-$ does not interfere with denitrification of in-situ NO_3^- and that labelling of in-situ NO_3^- with $^{15}NO_3^-$ in the water column and in the sediment are homogenous could be validated. At the same time this provides a negative proof of the anammox process for all study sites.

Furthermore, p_{15} showed a significant linear increase with tracer concentration ($R^2 > 0.88$) for all study sites thus confirming the assumption of first order kinetics of denitrification.

2.4 Statistical analysis

The observations were analysed using empirical orthogonal functions (EOFs) analysis (Preisendorfer, 1988). EOFs are a multivariate statistical technique that allows the extraction of the dominant overall pattern in the data set by reducing the dimensionality and the noise. The dimension of the raw data is reduced to few leading eigenmodes that account for the majority of the variance. The noise subspace is neglected. Con-

sider a data vector $\boldsymbol{X}'$ of anomalies:

$$\boldsymbol{X}'(\mathrm{no},\mathrm{st}) = \sum_{i=1}^{R} P_i(\mathrm{no})\alpha_i(\mathrm{st}) + \mathrm{noise} \quad (1)$$

Where "no" is the number of observations and "st" is the number of stations. "P_i" are the leading R eigenmodes depending only on the observations and "α_i" are fitting coefficients for each stations. A correlation analysis is performed between the fitting coefficients of the stations.

2.5 Calculating the annual N-loss

The denitrification rates from this study were used in 5 different approaches to calculate N-removal rates for the entire Baltic Sea or several sub basins.

For the first three approaches two different sediment distribution maps – each of them distinguishing between five different sediment types – were used.

For approach 1 the combined information from a Baltic-wide basin topography (Seifert et al., 2001), a sediment map compiled by B. Bobertz during the project DYNAS (dynamics of natural and anthropogenic sedimentation) and the average distribution of oxygen in the bottom water (1960–1990 means from IOW MOM3/ERGOM model results; T. Seifert, personal communication, 2009) was used. Hence it was possible to exclude all areas from the calculation where oxygen was zero or H_2S present. Sediments are classified according to median diameter into 5 sediment types: silt/clay, fine sand, medium sand, coarse sand and hard rock. Our sampled stations were allocated to a certain sediment type according to their positions on the map. If large discrepancies occurred between the measured sediment characteristics and the allocated sediment type according to the map the station was then allocated according to their sediment characteristics (Table 1).

A mean, maximum and minimum N-removal was calculated. For the calculation of the mean value, the average value of all denitrification rates for the same sediment type

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was used. For calculation of the maximum and minimum N-removal only the highest and lowest denitrification rates of each group were used, respectively.

The dataset used for the approaches 2 and 3 was a sediment map published in the BALANCE interim report No. 10 (Al-Hamdani and Reker, 2007). This map also contains 5 sediment types (mud, hard clay, sand, hard bottom complex and bedrock). The area covered by each sediment type was estimated using GIS. To account for inhibited denitrification in sediments below anoxic water bodies we excluded all sediments in the southern and central Baltic as well as in the Gulf of Finland with water depths ≥100 m.

For approach 3 we estimated the changes in the N removal capacity of the Baltic Sea under increasing anoxic bottom areas. For this approach we simulated a rise in the oxycline from 100 m water depth which is close to the recent state to 80 m by excluding all areas in the Baltic Proper and the Gulf of Finland with water depths ≥80 m.

For both approaches the allocation of the stations to a certain sediment type was performed the same way as for the first approach (Table 1). The calculation of the mean, maximum and minimum N-removal was performed in analogy to approach 1 as well.

For the approaches 4 and 5 we used a correlation between our measured denitrification rates and the C_{org} contents of the surface sediments. A large dataset of C_{org} [%] measurements of surface sediments ($n = 551$) was available for this approach (Leipe et al., 2009). The C_{org} data were arranged into 6 groups (C_{org}: 0–1%, 1–2%, 2–3%, 3–4%, 4–5%, >5%) and a map showing the C_{org} contents was created (Fig. 2). This map was digitalized and the area of every C_{org} group was calculated using GIS. Since the C_{org} data only covered parts of the Skagerrak, the Kattegat, and the western, southern and central Baltic (total area: 110 482 km^2) we only calculated an N-removal rate for this area. The calculated areas for the different C_{org} concentrations were: 0–1%: 10 120 km^2, 1–2%: 18 538 km^2, 2–3%: 20 947 km^2, 3–4%: 23 070 km^2, 4–5%: 16 411 km^2, and >5% 21 396 km^2. For those parts of the area which are not represented by the C_{org} map (mainly the coastal regions) we arbitrarily assumed a C_{org} content of 0–1% (approach 4) or 1–2% (approach 5). This assumes that sediments

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classified as sand may be respectively more or less winnowed by waves and currents acting to reduce their organic carbon content (e.g. Sakamaki and Nishimura, 2007). The significant regression between denitrification and organic carbon was used to calculate a mean, max and min denitrification rate for every C_{org} group. For the calculation of the mean denitrification rate the median C_{org} values were used (for group 0–1%: 0.5, for group: 1–2% 1.5, and so on), the maximum and minimum denitrification rates were calculated by means of the maximum (1%, 2%, 3%, 4%, 5%, 6%) and minimum (0%, 1%, 2%, 3%, 4%, 5%) values of each group. As described for approaches 2 and 3 we excluded all sediments with water depths ≥100 m in the southern and central Baltic and the Gulf of Finland.

3 Results

3.1 Rates of sedimentary denitrification and environmental parameters

Highest denitrification rates were found at the central station in the Arkona Basin (ABBoje: 28.71 µmol N_2 m^{-2} h^{-1} in summer and 24.42 µmol N_2 m^{-2} h^{-1} in autumn; Fig. 3) and there was no significant difference in the rates between the two sampling dates (2-tailed t-test, $p \gg 0.05$). At the two other stations with muddy sediments Kreidesegler and NS13 denitrification rates were lower with 20.58 and 12.58 µmol N_2 m^{-2} h^{-1}, respectively. The silt stations NS10 and NS11 showed rates between 16.37 and 13.40 µmol N_2 m^{-2} h^{-1}. At the two stations in the Gotland Basin NS6 and NS7 rates were significantly lower with 6.75 and 6.08 µmol N_2 m^{-2} h^{-1} (2-tailed t-test, $p < 0.05$), and the lowest denitrification rates were measured in sandy sediments from the edge of the Arkona Basin (NS12: 4.49 µmol N_2 m^{-2} h^{-1}) and from the near shore stations Breitling (2.5 µmol N_2 m^{-2} h^{-1}), Gollwitz 1 (0.5 µmol N_2 m^{-2} h^{-1}), and Gollwitz 2 (1.1 µmol N_2 m^{-2} h^{-1}).

Physico-chemical characteristics of the study sites are shown in Table 2. Bottom water temperatures varied from approximately 5 °C (Kreidesegler, NS6 and NS7), to

15 °C (Gollwitz 1, Gollwitz 2 and ABBoje) and 23 °C (Breitling), respectively. Oxygen was present in the bottom water of all study sites, with lowest concentrations (80.8 to 99.1 µmol L^{-1}) in the central Baltic at stations NS6, NS7 and ABBoje during summer and highest concentration above saturation at stations Gollwitz 1 and Gollwitz 2 (354.1 µmol L^{-1}). During the November sampling campaign oxygen concentrations were 206.4–309.2 µmol L^{-1}, with lowest concentrations found at station NS11 and highest concentrations present at NS12. Nitrate concentrations in the near-bottom water were close to detection limit at the coastal stations Breitling, Gollwitz 1 and Gollwitz 2 (0.3–1.1 µmol L^{-1}). Highest concentrations were found in the Gotland Basin at station NS6 and NS7 with 6.6 and 6.3 µmol L^{-1}, respectively. Summer and autumn concentrations of NO_3^- at ABBoje were only slightly different with 5.2 and 4.3 µmol L^{-1}, respectively. Organic carbon content varied according to sediment type, with highest values found at the mud stations ABBoje, Kreidesegler and NS13 (5.54–3.75%), followed by the mixed sediments NS6, NS7, NS10, NS11 (0.79–3.76%) and sandy sediment stations Breitling, Gollwitz 1, Gollwitz 2 and NS12 (0.06–0.46%).

A significant correlation between the denitrification rate and the possible controlling environmental parameters could be found for the organic carbon content of the surface sediments (denitrification = $1.3061 \times C_{org} + 0.8903$, $R^2 = 0.67$, $p < 0.001$).

After noise reduction denitrification rate is significantly correlated with C_{org} ($R = 0.83$, $p < 0.001$, $n = 12$), N_{org} ($R = 0.79$, $p < 0.01$, $n = 12$), C:N ratio ($R = 0.62$, $p < 0.05$, $n = 12$) and grain size ($R = -0.63$, $p < 0.05$, $n = 12$) (Fig. 4). Since the latter four variables correlate with one another for general sedimentological reasons, C_{org} depicting the highest coefficient of correlation and for which areal information is available in the Baltic Sea was chosen to extrapolate rates to areas.

3.2 Calculation of the annual N-removal

The results of all approaches together with the calculated sediment specific denitrification rates are summarized in Table 3. For the approaches by means of the sediment types (1, 2 and 3) which were performed for the entire Baltic Sea area, the highest

N-removal was calculated from approach 1 with a mean of 652 kt N a^{-1}. The maximum and minimum values were 899 and 380 kt N a^{-1}, respectively. For approach 2 the mean N-removal rate was 426 kt N a^{-1} (max: 618 kt N a^{-1}, min: 287 kt N a^{-1}), which is 35% lower compared to the mean rate calculated by approach 1.

A rise of the oxycline from 100 to 80 m water depth and the resulting spread out of the anoxic sea bottom areas as simulated in approach 3 would lead to a N-removal rate of 367 kt N a^{-1} (max: 532 kt N a^{-1}, min: 247 kt N a^{-1}). Compared to 426 kt N a^{-1} this is equivalent to a reduction of 14%. For the approaches 2 and 3 it was possible to estimate the N-removal for the several sub basins of the Baltic Sea shown in Table 4. The highest N-removal rates were found in the sub basin "Baltic Proper", followed by the "Bothnian Sea" and the sub basin "Kattegatt". It also becomes obvious that a rise in the oxycline only influences the N loss from the sub basins "Baltic Proper" (reduction of 30%) and to a much lesser extent the "Gulf of Finnland" (reduction of 4%).

The approaches 4 and 5 were carried out by means of the C_{org} distribution map for the western, southern and central Baltic only. The mean rates were 297 kt N a^{-1} (max: 379 kt N a^{-1}, min: 232 kt N a^{-1}, Table 3) when the remaining area outside the C_{org} distribution map is calculated with a C_{org} content of 0–1%. If the outside area is calculated with a C_{org} content of 1–2%, the mean N-removal rate increases up to 374 kt N a^{-1} (max: 474 kt N a^{-1}, min: 326 kt N a^{-1}).

4 Discussion

Since denitrification in sediments is assumed to be the dominating N-removal process for the Baltic Sea (Shaffer and Rönner, 1984), the understanding of the controlling factors and an estimate of the total N-removal rate for the entire Baltic Sea basin is a major need for evaluating the current status (in terms of nutrient input and sequestration) and future development of this ecosystem.

4.1 Factors controlling the rate of denitrification in Baltic Sea sediments

It has been shown that benthic denitrification can be controlled by temperature, nitrate availability, and supply of organic carbon (Nowicki et al., 1997; Kana et al., 1998) but very often a combination of various parameters is responsible for controlling the rate of denitrification in sediments (Seitzinger, 1988; Piña-Ochoa and Álvarez-Cobelas, 2006). An increase in temperature for instance not only leads to an increase in the rate of denitrification but also to an increase in the nitrification rate which automatically results in an enhanced supply of nitrate (Seitzinger, 1988). A seasonal variation in denitrification can be observed very often, and is reported for Baltic Sea sediments (Tuominen et al., 1998; Sundback et al., 2000; Hietanen and Kuparinen 2008), as well as for other regions (Nowicki et al., 1997; Cabrita and Brotas, 2000; Dong et al., 2000). The causes for these seasonal variations are likewise mainly combinations of several controlling environmental parameters like higher temperatures and an increased supply of organic carbon in post-bloom-periods (Nowicki et al., 1997), and it can be expected that at our stations a seasonal variation in denitrification exists as well.

We could not detect any seasonality on our rates mainly because our investigations were all carried out during late summer and autumn. Moreover our rates suggest that the rates are primary controlled by the organic carbon content of the surface sediments. This was also reported by Trimmer and Nicholls (2009) for a study from the Irish shelf to the North Atlantic where they found a positive correlation between sedimentary denitrification and C_{org} content of surface sediments.

We did not find a correlation between the rate of denitrification and the concentration of nitrate in the overlying water which indicates that denitrification at most stations was fueled by nitrate which was generated during nitrification in the overlying sediment. This assumption was supported by the fact, that the share of the coupled nitrification-denitrification (D_n) to total denitrification was over 70% at 8 out of 12 stations (data not shown) which implies that an intense coupling between remineralisation of the organic matter in the sediments and the denitrification took place at almost all stations.

4.2 Nitrogen removal calculated from different sediment maps

The total N-loss via sedimentary denitrification for the Baltic Sea estimated from our approaches by means of sediment distribution maps (approaches 1 and 2) ranges between 426 and 652 kt N a^{-1} (Table 3). This means that between 48 to 73% of the annual N-input delivered by rivers, coastal point sources and atmospheric deposition to the Baltic Sea is removed via sedimentary denitrification. A direct comparison with studies from other regions is difficult, because a similar approach has nowhere been applied so far. Boynton et al. (1995) estimated with their conceptual model for the Chesapeake Bay system a total N-loss via denitrification of 40 kt N a^{-1} which is 26% of the total N inputs and lower than our estimates.

The mean rate calculated from approach 1 is 226 kt N higher than the one from approach 2. This difference seems to be the result of a higher areal percentage of muddy sediments in the sediment distribution map from the DYNAS project (50% of oxic area) which was used for approach 1 compared to the map from the BALANCE project (36% of oxic area) used for approach 2 and from the fact that the muddy sediments had highest denitrification rates.

Based on approach 2 it was possible to calculate N-removal rates for single subbasins of the Baltic Sea (Table 4) and to compare them with rates presented from other studies (Table 5).

The annual N-removal of 39 kt N for the Gulf of Finland calculated by Hietanen and Kuparinen (2008) matches very well with our estimated annual N loss for the same area (38 kt). For the same area Tuominen et al. (1998) estimated a removal of 45 kt N, which is slightly higher, but as well in the range of our calculated minimum and maximum N-removal rates (26–53 kt N). The rates for the Bothnian Bay (15 kt N) and Bothnian Sea (35 kt N) by Stockenberg and Johnstone (1997) were much lower than our calculations (35 and 63 kt N, respectively). In that study denitrification rates were measured with the "acetylene block" method which is known to underestimate denitrification rates compared to the nowadays standard "Isotope Pairing Technique" because of an acety-

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lene inhibition of the nitrification process which can be an important source for nitrate in the denitrification pathway (Seitzinger et al., 1993; Lohse et al., 1996; Steingruber et al., 2001). The coupled nitrification-denitrification in sediments (D_n) often exceeds that type of denitrification that is based on the diffusion of nitrate from the overlying water into the sediment (D_w) and can reach a contribution of more than 90% on total denitrification (Lohse et al., 1996; Tuominen et al., 1998; Hietanen and Kuparinen 2008) similar to our findings. Therefore it cannot be excluded that the rates measured by Stockenberg and Johnstone (1997) were lower than the real rates and that the extrapolated N-removal was underestimated.

All three available studies (Shaffer and Rönner, 1984; Eiola and Stigebrandt, 1999; Voss et al., 2005; Table 5) that calculated an N-loss via denitrification for the Baltic Proper did not distinguish between sedimentary and water column denitrification, and are therefore hardly comparable with our results. Especially because the largest hypoxic water-body of the Baltic Sea is located in that area, and water-column denitrification might play an important role for the total N-losses from the system.

As a rough estimate of total water column denitrification in the Baltic Proper we extrapolate the rates reported by Brettar and Rheinheimer (1991) measured with the "acetylene block" method. They found in the Central Gotland Basin 110 and 44 nmol N L^{-1} d^{-1} in 1986 and 1987, respectively. Since denitrification was measurable at oxygen concentrations between 0–17.8 µmol L^{-1}, we calculated a total N-removal rate in the water column for the water body with oxygen concentrations between 0 to 17.8 µmol L^{-1}. This gives us a total volume of 524.39 km^3 (period between January 2005 to December 2006; Source: Baltic Nest Institute, Stockholm), where we assumed a mean denitrification rate of 77 nmol N L^{-1} d^{-1} and a maximum rate of 110 nmol N L^{-1} d^{-1}. The mean and maximum annual N-removal then accounts for 206 and 294 kt N, respectively. Adding our sedimentary rates from approach 2 this gives a total mean and maximum N-removal by denitrification for the Baltic Proper of 397 and 571 kt N, allocating equal parts of denitrification to sedimentary and water column processes. These numbers are in the same order of magnitude as the rates reported

from the other studies (Shaffer and Rönner, 1984; Eiola and Stigebrandt, 1999; Voss et al., 2005).

Since detailed data about N-inputs via nitrogen fixation – an important N-source not only for the central Baltic Sea – are not available for the entire Baltic Sea we set up a total N budget only for the Baltic Proper (Fig. 5). For this budget we used data about N inputs via rivers, coastal point sources and atmospheric deposition from Wulff et al. (2009). Data for N-input via N_2-fixation by cyanobacteria were taken from the study of Wasmund et al. (2001), the N-loss via burial of nitrogen in the sediments was taken from Emeis et al. (2000), and the import and export of nitrogen to and from other basins was taken from Savchuk (2005). For calculation of water column denitrification we extrapolated the mean and maximum denitrification rate measured in the water column in the central Gotland Basin by Brettar and Rheinheimer (1991). The budget was also calculated with both, the mean and the maximum sediment denitrification rate from approach 3. The results show that for the Baltic Proper the N removal performed by denitrification in the sediment is equivalent to the N-removal via water column denitrification. Furthermore, and keeping the roughness of the made extrapolations in mind, it seems that the budget is nearly balanced if calculated with the maximum denitrification rates (difference of ~90 kt N between inputs and outputs). If calculated with the mean values there exists an N-excess of 263 kt which might be buried into the sediments.

Our simulated rise in the oxycline from 100 to 80 m water depth leads to an expansion of the area with anoxic sediments on the order of 30 000 km^2, mainly muddy sediments. These obtain conditions non-favorable for sedimentary denitrification, which result in a total decrease of the N-removal rate of 14% (Table 4). Influenced by this reduction are the Baltic Proper with a reduction of 30% and the Gulf of Finland (4%). All other areas are not impacted by this increase in the oxycline either because they are too shallow like the western Baltic or they do not have strong stratified water columns like the Bothnian Sea and Bothnian Bay.

It is widely accepted that besides the climate the enhanced nutrient inputs are responsible for the expansion of the hypoxic and anoxic areas of the Baltic Sea in the

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last decades (Conley et al., 2009a). Furthermore it is obvious, that a reduction of the anoxic areas is only possible when the nutrient inputs into the Baltic Sea are strongly reduced. Although it can be assumed that an increase of hypoxic areas would lead to an increase of N-removal via water column denitrification (Conley et al., 2009a), our results demonstrate that anoxic sediment surfaces will lead to a drastic reduction of the N-removal via sedimentary denitrification. This could be observed in the Gulf of Mexico, where sedimentary denitrification was remarkable reduced at oxygen concentrations in the overlying water below 31.2 µmol L^{-1} (Childs et al., 2002). Furthermore it could be observed that at highly reducing conditions dissimilatory nitrate reduction to ammonia (DNRA) becomes more and more important, and seems to outcompete denitrification (Karlson et al., 2005).

4.3 Uncertainties

Our calculations are based on several uncertainties such as non-consideration of *seasonal variations* in denitrification, the question whether our sediment-specific denitrification rates are *representative* or not, and finally our choice of the *100 m depth line* to separate between areas with oxygenized waters above the sediment surface (denitrification in sediments) and anoxic waters above the sediment surface (no sedimentary denitrification).

As stated above seasonality in the denitrification rate was observed in many studies. For the Gulf of Finland Hietanen and Kuparinen (2008) found a seasonal cycle with higher rates during autumn and early winter, whereas Tuominen et al. (1998) measured the highest rates in late summer and early autumn. Kähler (1990) measured the highest rates in the Kiel Bight during spring. The rates used in this study were – with the exception of two stations – measured from late summer to late autumn. This seems to be a period where the denitrification rates in Baltic Sea sediments reach high rates implying that our calculated N-removal rates represent an upper estimate of N-removal for the Baltic Sea.

The second uncertainty regarding our N-removal calculations addresses the repre-

sentativeness of our "sediment-specific" rates of N-removal. Here, the rates measured in the sandy sediments (NS12, Gollwitz and Breitling) might underestimate the true rate. The main reason for this is that the conditions during incubation of the IP experiments do not reflect the in-situ conditions. Permeable sediments are strongly influenced by pore-water advection, which is completely interrupted during IP incubations. Gihring et al. (2010) reported higher denitrification rates for sands measured in intact sediment cores, when the cores were permanently percolated with water compared to non-percolated cores. However, their reported maximum rate was 4.1 µmol N m^{-2} h^{-1} and well in the range of the rates measured in our sandy sediment (station NS 12: 4.5 µmol N m^{-2} h^{-1}). In contrast to that Gao et al. (2009) measured potential denitrification rates of 320 µmol N_2 m^{-2} h^{-1} in the sandy sediments of a sand flat in the German Wadden Sea by means of slurry incubations. These rates are 70 times higher than our measured rate of 4.5 µmol N_2 m^{-2} h^{-1} in the sandy sediment. Even if slurry incubations are known to overestimate the true rates these potential rates suggest that N-removal from sandy sediments can be much more effective. For all other stations, our sediment-specific denitrification rates are in the range reported from other studies in the Baltic Sea (Koop et al., 1990; Tuominen et al., 1998; Hietanen and Kuparinen, 2008; Table 6).

As written above the external supply of nitrate can enhance the denitrification rates (Kana et al., 1998). Although this was not important in our investigation ($D_w > 70\%$ at most stations) it must be assumed that there are areas in the Baltic Sea – presumably in close vicinity to the coast – which are highly influenced by enhanced nitrate inputs and thus show high rates of N-removal. How strong the N-removal from these areas influences the total N-removal is unclear.

Furthermore, bioturbation is known to enhance denitrification (Pelegri et al., 1994; Gilbert et al., 2003). This issue has not been addressed, while theoretically, due to reduction of organism size with decreasing salinity, sediments further north-east would not bear the same potential for bioturbation-enhanced benthic denitrification as similar sediments located below saltier water in the west.

The third crucial point in our calculations from approaches 2–5 is the use of the

100 m-depth line to separate between areas with benthic denitrification (areas<100 m water depth) and anoxic areas without benthic denitrification (areas≥100 m water depth) in the Central Baltic and the Gulf of Finland. The oxic area we calculated by using the 100 m depth line is ~389 000 km^2, which is very close to the oxic area calculated from the DYNAS project for approach 1 (~392 000 km^2). In the Central Baltic and the Gulf of Finland prevail usually permanent anoxic conditions with the appearance of H_2S below water-depths >100 m, whereas in waters above 100 m depth anoxia occurs temporarily (Conley et al., 2009b). Furthermore, our calculated area shows good agreement with the anoxic areas shown in the latest HELCOM Indicator Factsheet 2008 (Axe, 2008), and with the map showing the Baltic Sea anoxic areas of 2008 presented on the website of the Baltic Sea Portal (http://www.fimr.fi).

4.4 Calculation of total N-removal from surface sediment C_{org} distribution

With this approach the N removal can only be reliably calculated for the western, southern and central Baltic, since for all other regions no sufficient C_{org} data are available. If we compare the calculated mean N-removal rates from approach 4 where the remaining area outside the C_{org} distribution map is calculated with a C_{org} content of 0–1% (297 kt N) we find an excellent agreement with the mean rates from approach 2 for the same area (total rate minus rate from Bothnian Sea, Bothnian Bay and Gulf of Finland: 290 kt N). If the N-removal in the remaining area is calculated with a C_{org} content of 1–2% the mean N-removal rate increases by ~75 kt N. A C_{org} content of 0–1% for the remaining areas seem reasonable to us, since these are mainly coastal zones with a large proportion of sandy sediments and bedrock (Al-Hamdani and Reker, 2007).

5 Conclusions

With this study we present – to our knowledge – the first N-removal rates via sedimentary denitrification for an entire coastal sea. It could be shown that our way of

combining one-point in situ measurements at different sediment stations with the application of sediment or C_{org} distribution maps is a powerful tool to estimate N-removal via sedimentary denitrification and – if present – via Anammox for an ecosystem. For the Baltic Sea it becomes obvious that the N removal via sedimentary denitrification is high, but may not be high enough to balance all N inputs. And the situation might exacerbate if the extension of the anoxic bottom areas continues and the N-removal via sedimentary denitrification will be further reduced. The question that needs to be answered is whether the pronounced increase in water column denitrification that will occur, might be high enough to compensate the reduction of N-removal via the sediments.

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Table 1. Allocation of our sampled stations to a certain sediment type of the respective sediment map.

Approach 1			Approaches 2 and 3		
Sediment type ($O_2 > 0$)	Area [km^2]	Allocated stations	Sediment type (depth≤100 m)	Area [km^2]	Allocated stations
silt/clay	198 769	ABBoje, Kreidesegler, NS13	mud	142 028	ABBoje, Kreidesegler, NS10, NS11, NS13
fine sand	43 316	NS6, NS7, NS10	hard clay	83 255	NS6, NS7
medium sand	64 367	NS11, NS12	sand	88 826	Breitling, Gollwitz 1 & 2, NS12
coarse sand	20 646	Breitling, Gollwitz 1, Gollwitz 2	hard bottom complex	65 465	Excluded (no denitrification)
hard rock	65 177	Excluded (no denitrification)	bedrock	9887	Excluded (no denitrification)

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Table 2. Stations, sampling date, water depth, temperature, oxygen and nitrate concentrations of bottom water, organic carbon content of the surface sediments as well as median grain size, task sorting coefficient and sediment type.

Station	Date	Depth [m]	Bottom Temperature [°C]	Bottom Oxygen [µmol L^{-1}]	Bottom Nitrate [µmol L^{-1}]	C_{org} content of surface sediment [%]	Median Grain size [µm]	Task sorting coefficient	Sediment Type
ABBoje	Aug-08	46	14.6	85.7	5.22	5.54	10.8	1.3	alluvial mud
ABBoje	Nov-08	46	12.2	183.1	4.30	3.75	11.1	1.4	alluvial mud
Kreidesegler	May 08	15	5.3	236.2	2.50	4.53	9.5	1.2	alluvial mud
NS13	Nov-08	47	12.2	216.2	3.09	4.08	13.3	1.3	alluvial mud
NS10	Nov-08	25	11.3	242.4	1.92	2.58	30.8	1.1	silt/mud
NS11	Nov-08	22	12.4	206.4	4.67	0.79	141.1	0.5	silt/fine sand
NS7	Aug-08	80	5.5	80.8	6.29	3.76	24.5	1.5	Glacial drift, alluvial mud
NS6	Aug-08	75	5.2	99.1	6.62	1.15	42.4 (14.6)	1.3 (1.6)	Glacial drift (boulder clay)
NS12	Nov-08	22	10.1	309.3	0.29	0.06	192.5	0.3	fine sand
Gollwitz 2	Sep-08	0.2	15.3	354.1	1.2	0.46	87.5	0.6	muddy sand
Gollwitz 1	Sep-08	0.2	15.3	354.1	1	0.23	107.5	0.5	sand
Breitling	Jul-08	0.2	22.6	311.5	0.3	0.26	165	0.7	fine sand

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Table 3. Calculated sediment specific denitrification rates as well as calculated mean, maximum, and minimum annual N-removal.

Approach	Area	Used data for interpolation of rates	Calculated mean sediment specific denitrification rates [µmol m^{-2} h^{-1}]	Calculated N-removal from sediments [kt a^{-1}]		
				Mean	Max	Min
1	entire Baltic Sea	Sediment map from DYNAS project, bottom oxygen from MOM3/ERGOM model runs	silt/clay: 21.58±5.95, fine sand: 9.73±4.70, medium sand: 8.94±4.45, coarse sand: 1.38±0.80	652	899	380
2	entire Baltic Sea	Sediment map from BALANCE project	mud: 19.34±6.13, hard clay: 6.42±0.47, sand: 2.15±1.33	426	618	287
3	entire Baltic Sea	same as approach 2	same as approach 2	367	532	247
4	western, southern and central Baltic	Map of C_{org} concentrations of bottom sediment surface	calculated from regression equation	297	379	232
5	western, southern and central Baltic	Map of C_{org} concentrations of bottom sediment surface	calculated from regression equation	374	474	327

Table 4. N-removal via sedimentary denitrification per basin, calculated via approaches 2 (oxycline at 100 m) and 3 (oxycline at 80 m) and the reduction of the N-removal as a result of a rise of the oxycline (mean N-removal from approach 2 minus mean N-removal from approach 3).

Basin	mean N removal from sediments [t a^{-1}] (approach 2)	max. N removal from sediments [t a^{-1}] (approach 2)	min. N removal from sediments [t a^{-1}] (approach 2)	mean N removal from sediments [t a^{-1}] (approach 3)	reduction [%]
Kattegatt	52	79	33	52	0
Belt Sea+western Baltic	24	37	15	24	0
Baltic Proper (excl. Gulf of Riga)	191	277	129	133	30
Gulf of Riga	23	35	14	23	0
Gulf of Finland	38	54	26	36	4
Bothnian Sea	63	85	48	63	0
Bothnian Bay	35	53	23	35	0

Table 5. N-removal rates from other studies for several sub basins of the Baltic Sea.

Area	annual N-removal [kt N]	Sediment/water column	Method	Reference
Baltic Proper	580–855	sediment+water column	stable isotope budget	(Voss et al., 2005)
Baltic Proper	470	sediment+water column	mass balance calculations	(Shaffer and Rönner, 1984)
Baltic Proper	560	sediment+water column	mass balance calculations	(Eilola and Stigebrandt, 1999)
Gulf of Finnland	45	sediment	extrapolation of "Isotope Pairing" rates	(Tuominen et al., 1998)
Gulf of Finnland	39	sediment	extrapolation of "Isotope Pairing" rates	(Hietanen and Kuparinen, 2008)
Bothnian Sea	35	sediment	extrapolation of "Acetylene Block" rates	(Stockenberg and Johnstone, 1997)
Bothnian Bay	15	sediment	extrapolation of "Acetylene Block" rates	(Stockenberg and Johnstone, 1997)

Table 6. Comparison of denitrification rates from Baltic Sea sediments from various studies.

Area	Denitrification Rate [µmol N m^{-2} h^{-1}]	Method	Reference
Bothnian Bay	5–6.7	Acetylene Block	(Stockenberg and Johnstone, 1997)
Bothnian Sea	0–39.2	Acetylene Block	(Stockenberg and Johnstone, 1997)
Gulf of Finland	4.2–27.1	Isotope Pairing	(Tuominen et al., 1998)
Gulf of Finland	3.8–16.7	Isotope Pairing	(Hietanen and Kuparinen, 2008)
Northern Baltic Proper	0.6–12.5	Isotope Pairing	(Tuominen et al., 1998)
Northern Baltic Proper	49	Flux studies	(Koop et al., 1990)
Southern Baltic and Baltic Proper	0.5–28.7	Isotope Pairing	this study

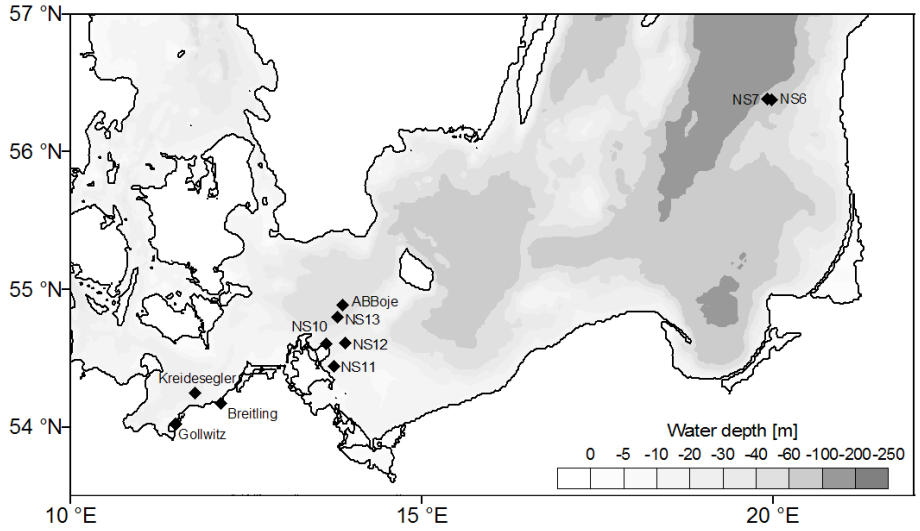

Fig. 1. Map showing the stations in the western and central Baltic Sea.

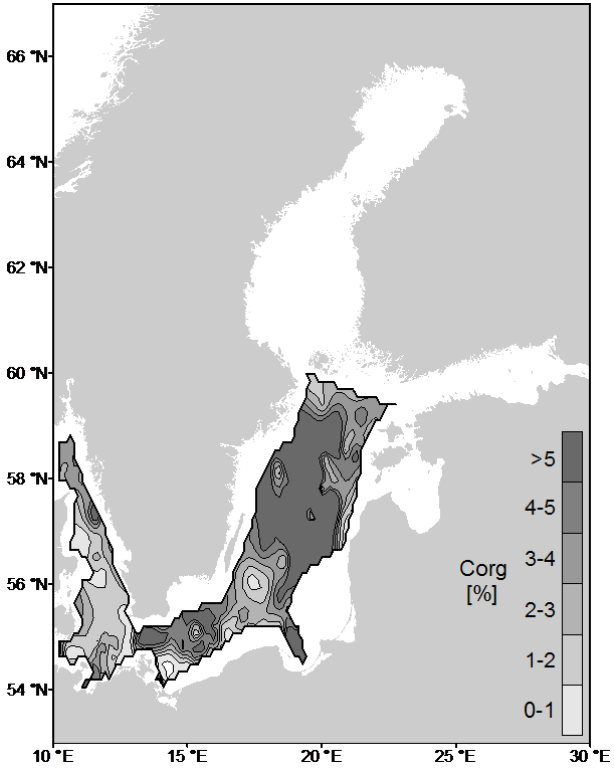

Fig. 2. Map showing the C_{org} [%] distribution for parts of the Baltic Sea.

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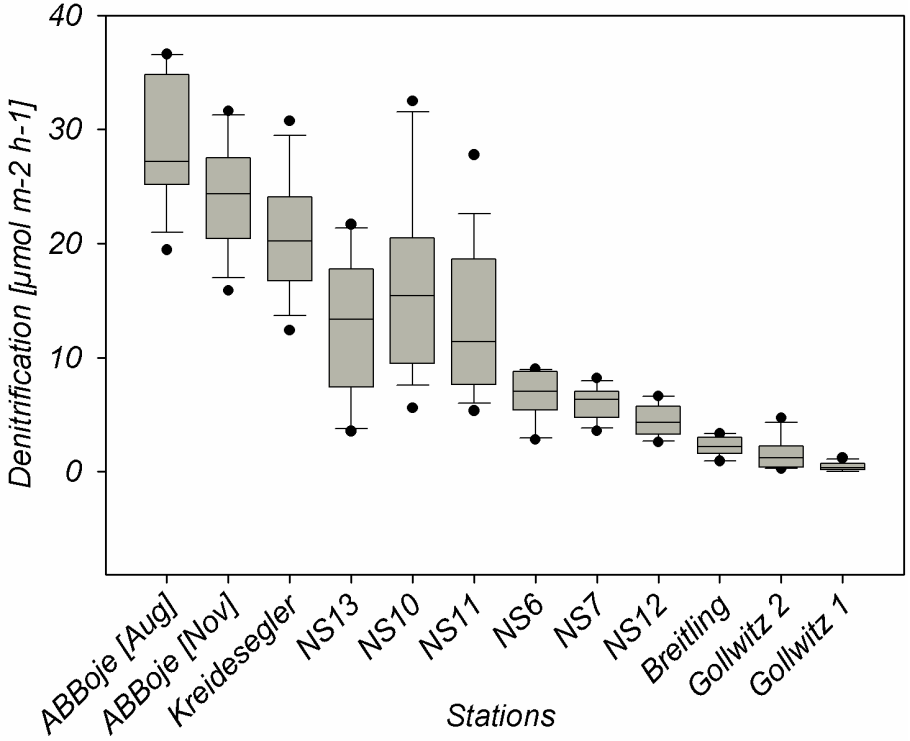

Fig. 3. Box-Whisker-Plots of denitrification rates for all stations, showing the median, lower and upper quartile, the extremes and outliers.

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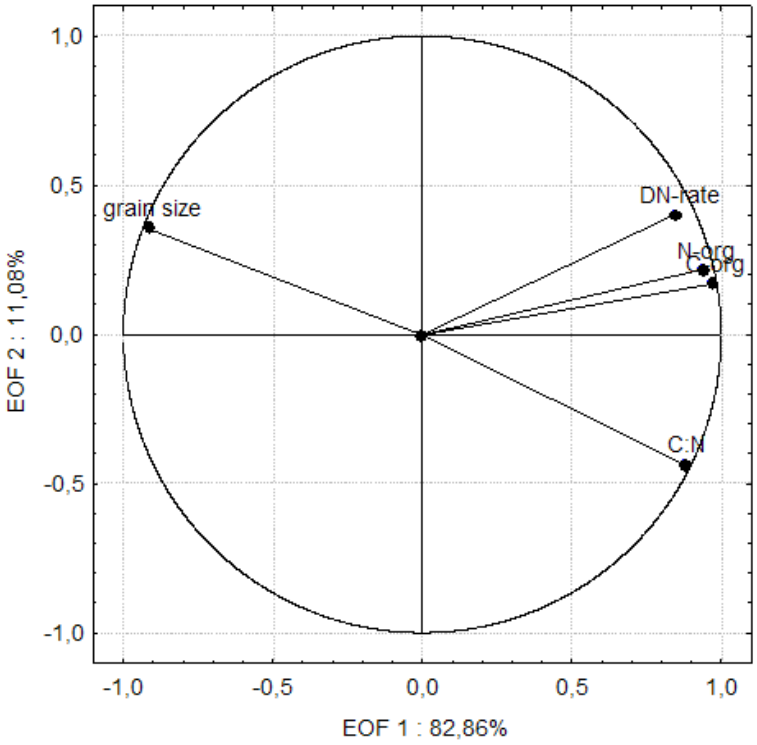

Fig. 4. Projection of the fitting coefficients in EOF coordinates.

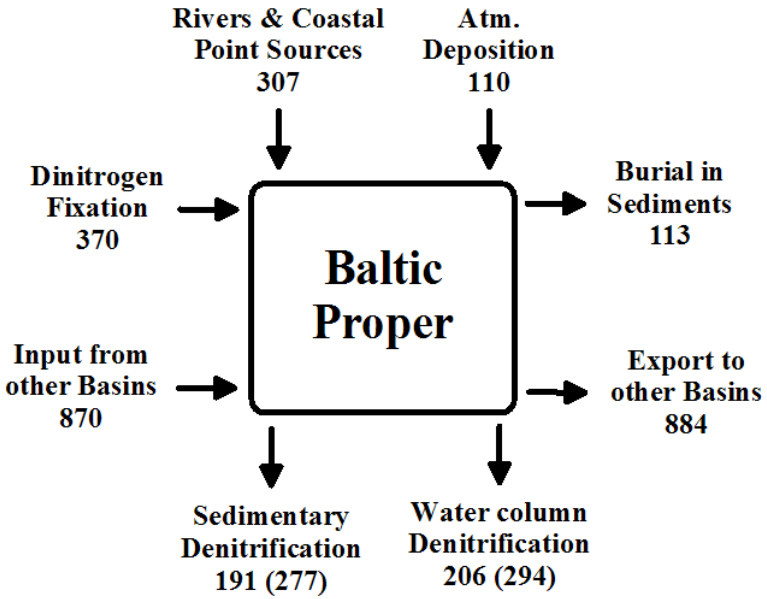

Fig. 5. N-Budget for the Baltic Proper (all values are given in kt N a^{-1}). Mean and maximum removal rates (in parentheses) by denitrification are presented.