Nitrogen and organic matter cycling in coastal systems: case studies from the Baltic Sea

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Contents

Summary

The depletion of dissolved oxygen in bottom waters and the expansion of harmful algae blooms (HAB`s) are most common responses of aquatic ecosystems to eutrophication, and thus also to the semi-enclosed, brackish Baltic Sea with high riverine nutrient loads. In the first part of this thesis the historical progression of eutrophication in the Baltic Sea, and the reasons for its sensitivity towards eutrophication are summarized. The northern watersheds, which are sparsely populated and mainly covered by boreal forests, were compared to the southern watersheds, which are surrounded by highly industrialized and densely populated areas that are mainly in agricultural use. The evaluation of long term data sets and model results indicates that in addition to changes in nutrient inputs, increased temperature and precipitation are likely to become important forcings for the Baltic Sea. Moreover, it has been suggested that lagoons and near shore areas remove large quantities of riverine nitrogen, but will only be able to do so as long as they remain oxic meaning that this system service is threatened due to increasing coastal hypoxia. In the second study the nitrogen removal processes in the adjacent coastal areas of the Oder and Nemunas rivers were characterized during peak outflow, by means of dual stable isotopes measurements in nitrate ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) and nitrate uptake rates, since nitrate is highly bioavailable and the dominant nitrogen component delivered by these rivers. Results show that the isotopic signal of nitrate is dominated on the one hand by mixing and assimilation in the surface waters and on the other hand by denitrification in the near bottom waters. Calculated fractionation factors ($^{15}\varepsilon$ and $^{18}\varepsilon$) of around 10‰ in the near bottom waters infer that the isotopic enrichment from sedimentary denitrification may be higher in permeable, sandy than in muddy sediments. So far, permeable sediments with low organic content were mainly considered to contribute little to the biogeochemical cycling. However, the isotope data of nitrate from this study indicate that denitrification in these sediments may be an important process. Because permeable sediments account for up to 70% of the continental shelf area their contribution to the Baltic Sea loss budget as well as to the global nitrogen loss budget should be reevaluated.

Large quantities of nitrogen are also delivered to the Baltic Sea in form of dissolved organic nitrogen (DON) via rivers and nitrogen fixation. However, the role of DON in the nitrogen cycle is still poorly understood and its impact on eutrophication has not been further considered in nitrogen load reductions. Therefore, in the third study the major aim was to evaluate the role of DON as a potential nutrient source for surface plankton in summer when dissolved inorganic nitrogen (DIN) concentrations are low. Two different ^{15}N labeled bulk DON substrates were produced and DON uptake rates were determined along a salinity gradient from the North Sea to the Baltic Sea. Uptake rates in the Baltic Sea (184 to 1213 nmol N l^{-1} h^{-1}) were an order of magnitude higher compared to rates in the North Sea or the Chesapeake Bay (USA). The findings from this study indicate that DON is an important component of plankton nutrition and can fuel primary production and therefore also contribute to eutrophication. Additionally, the conservative versus non-conservative behavior of dissolved organic matter (DOM) including DON and DOC (dissolved organic carbon) was tested along the same salinity gradient and the share of terrestrial DOM to the total DOM pool was determined by means of $\delta^{13}C$ values in the fourth study. Results indicate that up to 83% of the DOM is derived from terrestrial sources in the Baltic Sea and that substantial amounts of DOM (>50%) delivered by rivers are degraded near the coastline. Since eutrophication is a global problem, results from this thesis can be translated to other coastal zones of temperate climate with similar nitrogen loads. Overall, it seems necessary to reevaluate the role of sediments for the nitrogen turnover and its nitrogen removal capacity and to consider dissolved organic substances as potential nutrient sources.

Zusammenfassung

Die Verarmung an gelösten Sauerstoff im bodennahen Wasser und die Ausbreitung von toxischen Algenblüten sind die am häufigsten auftretenden Folgen von Eutrophierung in aquatischen Ökosystemen, so auch in der Ostsee, einem der größten Brackwassergebiete der Welt mit hohen Nährstofffrachten aus Flusseinträgen. Der erste Teil dieser Doktorarbeit umfasst eine Literaturstudie in der die geschichtliche Entwicklung der Eutrophierung und die Gründe warum die Ostsee besonders sensibel auf die vom Menschen verursachte Belastungen reagiert, zusammengefasst sind. Hierbei wurden die nördlichen Einzugsgebiete der Ostsee, die nur dünn besiedelt und hauptsächlich von Wäldern bedeckt sind, mit den südlichen Einzugsgebieten, die stark besiedelt und von Industrie und Landwirtschaft geprägt sind, verglichen. Die Auswertung von Langzeitdatenmessungen und von Modelierungsstudien ergab, dass wahrscheinlich neben sich ändernden Nährstoffeinträgen auch steigende Temperaturen und Niederschläge in Zukunft eine größere Rolle in der Ostsee spielen werden. Außerdem wurde vermutet, dass Haffe, die normalerweise große Mengen an über Flüsse eingetragene Stickstofffrachten entfernen, dies nur so lange bewerkstelligen können wie die Küstengebiete oxisch bleiben. Durch die zunehmende Sauerstoffverarmung in Folge der Eutrophierung in Küstengebieten ist diese Funktion aber gefährdet. Im zweiten Teil dieser Arbeit wurden Prozesse die Stickstoff aus dem angrenzenden Küstengebieten der Flüsse Oder und Nemunas während der Hauptabflusszeit im Frühjahr entfernen, charakterisiert. Da Nitrat zu dieser Jahreszeit die Hauptstickstoffkomponente ist, erfolgte dieses mit Hilfe von Messungen an stabilen Isotopen im Nitrat ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) und Nitrat Aufnahmeraten. Ergebnisse zeigen, dass das Isotopensignal von Nitrat auf der einen Seite im Oberflächenwasser durch Mischung und Nitrat Aufnahme dominiert ist und auf der anderen Seite im Bodennahem Wasser durch Denitrifizierung. Berechnete Fraktionierungsfaktoren ($^{15}\varepsilon$ and $^{18}\varepsilon$) von 10‰ im bodennahmen Wasser lassen darauf schließen, dass die Anreicherung in den Isotopen durch Denitrifizierung in permeablen Sedimenten höher ist als in feinen Sedimenten. Bisher fanden permeable Sedimente mit niedrigem organischem Gehalt in biogeochemischen Kreisläufen wenig Beachtung, aber die Daten von den Isotopenmessungen lassen darauf schließen, dass auch diese Sedimente durch Denitrifizierung einen wichtigen Anteil zur Stickstoffentfernung beitragen. Da permeable Sedimente bis zu 70% der Kontinentalen Schelfmeere ausmachen, müsste ihr Beitrag sowohl in Stickstoff Budgets der Ostsee wie in globalen überdacht werden.

Stickstoff wird nicht nur in Form von gelöstem anorganischem Stickstoff (DIN) über Flüsse und Stickstoff Fixierung in die Ostsee eingetragen sondern auch in Form von gelöstem organischem Stickstoff (DON). Die Rolle von DON im Stickstoffkreislauf ist immer noch wenig verstanden und in Bezug auf Eutrophierung fand es bisher wenig Beachtung. Deshalb wurde in der dritten Studie dieser Doktorarbeit die Rolle des DON im Sommer, wenn alle anorganischen Stickstoffquellen verbraucht

sind, als potentielle Nährstoffquelle für das Plankton im Oberflächenwasser untersucht. Zwei unterschiedliche ^{15}N markierte DON Substrate wurden produziert und Aufnahmeraten von diesen beiden Tracern entlang eines Salinitätsgradienten in der Nord- und Ostsee bestimmt. Die Aufnahmeraten (184 to 1213 nmol N l^{-1} h^{-1}) in der Ostsee waren doppelt so hoch wie die in der Nordsee oder auch im Vergleich zur Chesapeake Bay (USA). Die Ergebnisse dieser Studie lassen darauf schließen, dass DON eine wichtige Komponente in der Nährstoffversorgung von Plankton spielt und daher auch die Primärproduktion antreiben und somit auch zur Eutrophierung beitragen kann. In einer vierten Studie wurde das konservative gegen das nicht-konservative Verhalten von gelöstem organischem Material (DOM), welches DON und DOC (gelösten organischen Kohlenstoff) einschließt, entlang desselben Salzgehaltsgradienten getestet. Zusätzlich wurde der terrestrische Anteil vom DOM am Gesamt DOM mit Hilfe von $\delta^{13}C$ Werten über Mischungsmodelle berechnet. Hier sprechen die Ergebnisse dafür das bis zu 83% des DOM in der Ostsee aus terrestrischen Quellen stammen und das der größte Anteil (>50%) vom DOM, das aus Flüssen stammt, in den Ästuaren und angrenzenden Küstengebieten abgebaut wird. Eutrophierung ist nicht nur ein Problem in der Ostsee, sondern weltweit und daher lassen sich einige Ergebnisse dieser Doktorarbeit auch auf andere Küstengebiete in den gemäßigten Breiten mit hohen Stickstofffrachten übertragen. Insgesamt ist es nötig die Rolle von Sedimenten in Bezug auf die Stickstoffentfernung zu überdenken und gelöste organische Substanzen als potentielle Nährstoffquellen zu berücksichtigen.

1. Introduction

1.1 Ecological problems of coastal eutrophication

At present, more than 40% of the world`s ocean are strongly influenced by human activities (Halpern et al. 2008). Human population growth and its associated activities like fossil-fuel combustion, production of nitrogen fertilizers (Haber Bosch process) and cultivation of nitrogen-fixing legumes have increased the flux of nitrogen and phosphorus to aquatic and terrestrial ecosystems alterating global cycles of both nutrients (Gruber and Galloway 2008, Galloway et al. 2003, 2004, Howarth 2006, 2008, Vitousek et al. 1997, Pickney et al. 2001). As a result of increasing nitrogen and phosphorus inputs the accumulation of organic matter by primary production has increased, which is defined as eutrophication (Nixon 1995). Selman et al. (2008) identified more than 400 areas worldwide which experienced symptoms of eutrophication (Fig. 1.1). Especially in coastal waters eutrophication has become the biggest pollution problem (e.g Vitouseket al. 1997, Syvitski et al. 2005, Rabalais 2002, Howarth et al. 2000), since rivers deliver large amounts of excess nutrients (Boyer et al. 2006, Dumont et al. 2005). It has been shown that nutrient river runoffs directly reflect human population density and activity in the watersheds (Peierls et al. 1991).

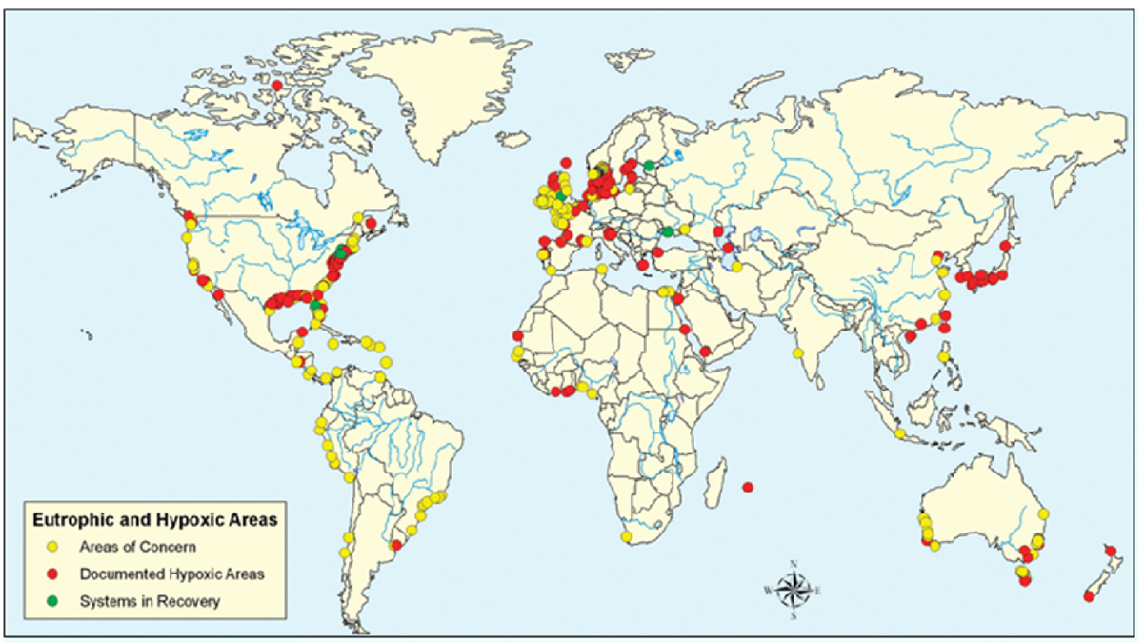

Figure 1.1: Map of 415 eutrophic and hypoxic coastal systems worldwide. The map was compiled by R. Diaz, M. Selman and Z. Sugg (http://www.wri.org/map/world-hypoxic-and-eutrophic-coastal-areas).

Besides increasing primary production, effects of eutrophication are enhancement of anoxia and hypoxia in deep and coastal waters, harmful algae blooms (HABs), decreasing water clarity and increased fluxes of N_2O to the atmosphere (Nixon 1995, Conley et al. 2009a, 2011, Galloway et al. 2003, Diaz and Rosenberg 2008). Even though hypoxia occurs naturally in many marine environments (like fjords and deep basins (Gustafsson and Nordberg 2000, Zillen et al. 2008)), the so called dead zones have spread exponentially since the 1960s, approximately doubling the number each decade and affecting today more than 240.000 km² of the marine environment (Diaz and Rosenberg 2008). Also HAB`s occur as a natural phenomenon, but over the last decades their extent has increased due to nutrient increases and/or shift in nutrient ratios (Anderson et al. 2002, Glibert et al. 2005, Heisler et al. 2008). These negative effects of eutrophication in turn can lead to loss or degradation of habitats with consequences to marine biodiversity and changes in ecosystem structure and function, such as cycling of elements and processing of pollutants (Vitousek et al. 1997, Rabalias 2002). Much of this eutrophication is driven by nitrogen (Howarth 2008). Due to the growing global demand in reactive nitrogen the pressure on coastal ecosystem may even rise in the future (ENA-book). To improve management and focus on strategies to resolve eutrophication a better understanding of coastal system dynamics is highly needed. This thesis will contribute in numerous ways, since it focuses on two major problems of eutrophoication: dissolved organic matter (DOM) and N-retention and turnover in coastal waters.

1.2 Global nitrogen cycle

The largest pool of nitrogen is found in the atmosphere as dinitrogen gas (N_2) that naturally only becomes biologically available through the process of N_2 fixation, the conversion of N_2 into organic nitrogen. The ability to fix N_2 is widespread in the marine environment, with cyanobacteria fixing 140 Tg N yr^{-1} on a global scale (Brandes 2007, Gruber and Galloway 2008, Fig. 1.2). In terrestrial systems, N_2 fixation accounts for 100 Tg N yr^{-1} (Fig. 1.2).With the onset of industrialization it became evident that the amount of reactive nitrogen (fixed nitrogen, Nr: including nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON)) needed to be increased to sustain the growing population. With the invention of the Haber Bosch process, where nonreactive N_2 is converted to reactive NH_3 (ammonia) it was possible to meet the growing food demand. It has been estimated that nitrogen fertilizers are responsible for feeding nearly 50% of the world's population (Erisman et al. 2008). However, the nitrogen use efficiency for typical cultivated plants like rice, wheat and maize is typically below 40%, meaning that most of the N applied fertilizers is lost to the atmosphere via denitrification or to the aquatic environment via leaching. In the latter it is assimilated into biomass, and therefore fueling eutrophication (Canfield et al. 2010, Erisman et al. 2008). This movement of nitrogen from one effect to another as it cycles through environmental reservoirs is referred as the nitrogen cascade (Galloway et al. 2003). Besides the close links in the nitrogen cycle between watersheds, airsheds and the marine system the nitrogen cycle is closely linked to the carbon and phosphorus cycles (Fig. 1.2), which becomes obvious by the Redfield ratio, the molar stoichiometric relationship between C, N and P (106:16:1) in marine organic matter. Of particulate relevance is the carbon cycle, since atmospheric CO_2 has a central role in controlling climate (Sarmiento and Gruber 2002). The full scale of impacts of additional reactive nitrogen input globally still remains unknown but it is obvious that further intensification in agriculture, increasing energy use and population growth will continue to alter the terrestrial and marine nitrogen cycle and will amplify eutrophication in the future. Together fossil-fuel combustion, production of nitrogen fertilizers and increased cultivation of nitrogen-fixing legumes have doubled the inputs of reactive nitrogen compared to preindustrial times, now exceeding natural nitrogen sources, accounting to 160 Tg N yr^{-1}, (Galloway et al. 2003, Gruber and Galloway 2008, Fig. 1.2). Therefore understanding how human induced ecological change interacts with and affects the structure and functioning of large estuarine ecosystems adjoining coastal waters remains important (Paerl et al. 2006).

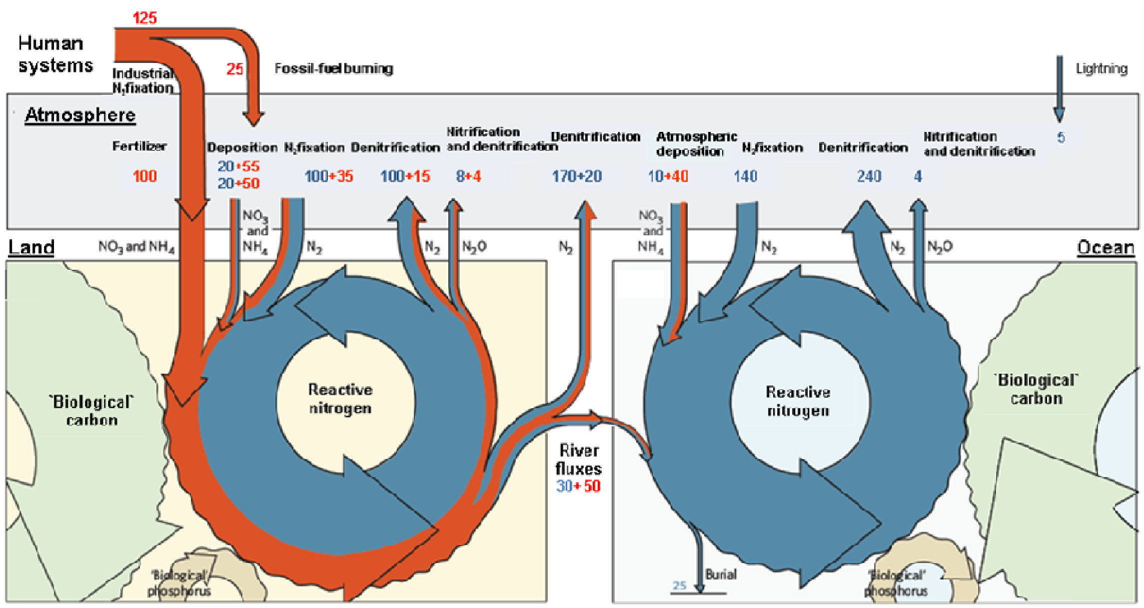

Figure 1.2: Natural and anthropogenic N fluxes on land and in the ocean. The tight coupling between the nitrogen cycles on land and in the ocean with those of carbon and phosphors are shown. Blue fluxes denote natural (unperturbed) fluxes and red fluxes denote anthropogenic perturbation. Redrawn from Gruber and Galloway (2008)

Reactive nitrogen can be assimilated by most organisms and most of the organic nitrogen in the ocean is returned back to nitrate via remineralization to ammonium (ammonification), which is rapidly nitrified and therefore rarely occurs in significant concentrations in oxygenated habitats. The first step in nitrification is the oxidation of ammonium to nitrite by ammonia-oxidizing bacteria and archaea, the second step is the conversion of nitrite to nitrate by nitrite-oxidizing bacteria (Fig. 1.3). Nitrification produces the substrate for denitrification and anaerobic ammonium oxidation (anammox), the only two processes that remove nitrogen permanently from the system by producing N_2. Denitrification describes the conversion of nitrate into N_2 gas through a series of intermediates (NO_2^-, NO, and N_2O) (Knowles, 1982, Fig. 1.3). It takes place under suboxic and anoxic conditions when organic carbon (as electron donor) and nitrate (as electron acceptor) are both available (Knowles 1982, Seitzinger 1988). During anammox NH_4^+ is anaerobically oxidized to N_2 in the absence of organic matter (Dalsgaard et al. 2003, Kuypers et al. 2003, Fig. 1.3) and a recent examination revealed that it could possibly account for 30% to 50% of water column N_2 production (Devol 2003). Apart from the reduction to N_2 through these two processes, nitrate can also be reduced to ammonium during DNRA (Dissimilatory nitrate reduction to ammonium). The importance of DNRA in the water column nitrogen cycling is still widely unknown, but in the Oman Shelf DNRA was found to be an important mineralization pathway for organic matter (Jensen et al. 2011). Current global nitrogen budgets have shown that benthic denitrification and anammox can account for about 70% of the fixed nitrogen loss (Codispoti 2007). But if the nitrogen budget is in balance is still highly controversial (Gruber and Galloway 2008, Zehr and Kudela 2011).

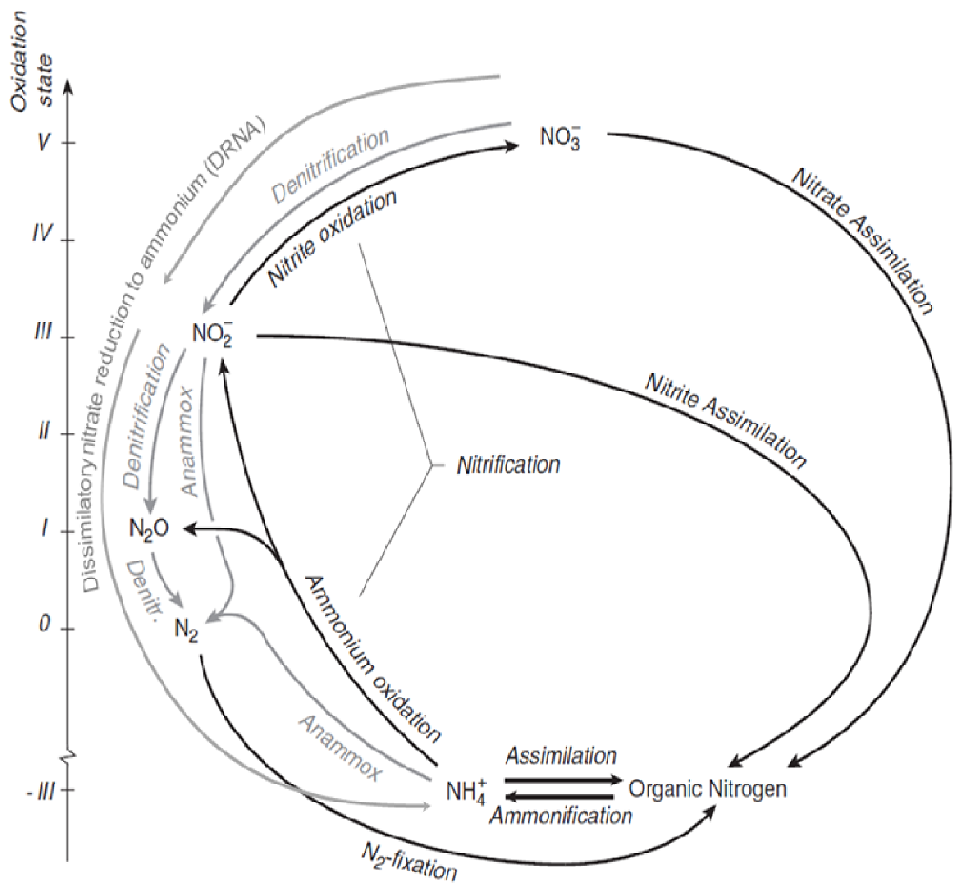

Figure 1.3: The marine nitrogen cycle. The various chemical forms of nitrogen are plotted versus their oxidation state, where nitrate is the most oxidized N species, while ammonium and organic nitrogen comprise the most reduced species involved in the cycle. Processes shown in light grey occur in anoxic environments only (modified from Gruber 2008).

1.3 Dissolved organic matter as part of the nitrogen cycle

Dissolved organic matter (DOM) is a complex pool of organic molecules that pass a filter of nominal pore size 0.2–1 µm (Hedges 2002). It consists of high molecular weight (HMW, weight > 1 kDa) and low molecular weight (LMW, weight < 1kDa) compounds. HMW DOM includes proteins, dissolved combined amino acids, nucleic acids (DNA, RNA), and humic substances. LMW DOM consists of urea, dissolved free amino acids and amino sugars (Bronk 2002, Bermann and Bronk 2003). However, most compounds still remain chemically uncharacterized (Bronk 2002). Recent progress in analytical chemistry like the fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) enable a characterization of dissolved organic matter at the molecular level in unprecedented detail (Koch et al. 2008, Dittmar and Paeng 2009), but still there is a gap in knowledge due to the chemical complexity of the compounds. According to Benner (2002) only 4-14% of DOM have been chemically characterized.

DOM in the marine environment can be from both allochthonous and autochthonous sources. Allochthonous sources include terrestrial runoff, leaching from plant detritus and soils into streams and rivers (Valiela et al. 1990, Tobias et al. 2001), sediments (Burdige 2002), groundwater (Santos et al. 2008) and atmospheric deposition (Duce et al. 2008, Cornell et al. 1995). Most of the allochthonous DOM has passed through several systems and chemical processes like phototransformation by sunlight, bacterial degradation in surface waters and soils as well as chemical changes due to increasing salinities before it reaches coastal regions. Autochthonous sources include release by primary producers (Bronk and Ward 1999, Stedmon et al. 2006) and bacteria (Ogawa 2001), excretion from micro and mesozooplankton (Steinberg et al. 2000), viral lysis of bacteria (Fuhrman 1999) and eukaryotic cells (Suttle 1994), and particle solubilization (Smith 1992) (Fig. 1.4). Main sinks of DOM are heterotrophic uptake, autotrophic uptake and abiotic photochemical decomposition (Bronk 2002) (Fig. 1.4). Small organic compounds like amino acids are taken up through permeases (membrane transport proteins), whereas larger compounds have to be broken down by extracellular hydrolytic enzymes (Anita et al. 1991, Bronk 2002, Mulholland and Lomas 2008 and references therein). For coastal areas terrestrial input via rivers dominates and highest concentrations of DOM are found close to the mouth of rivers (Stepanauskas et al. 2002, Feistel et al. 2008, Bronk 2002). In oceanic systems the major DOM sources are primary production and atmospheric input (Carlson 2002).

DOM is generally characterized in terms of carbon (DOC), nitrogen (DON) and/or phosphorus (DOP). DOC, DON and DOP can function largely independently within many ecosystems and are therefore discussed individually. In this thesis I will mainly focus on the DON components but also DOC will be discussed in face of its distribution and terrestrial background (see chapter 4 and 5 for details). DON represents the largest pool of fixed nitrogen in most aquatic systems with concentrations decreasing from rivers to the open ocean (Bronk 2002). In the past DON has long been ignored as a potential N source, because it was thought to be mainly refractory. However, recent studies have shown that DON can also serve as an important N source for both phytoplankton and bacteria (Veuger et al. 2004, Seitzinger and Sander 1999, Middelburg and Nieuwenhuize 2000, Berg et al. 2001, Bronk et al. 2007), and thus contribute significantly to marine eutrophication (Berman 1997, Seitzinger and Sander 1997). For example, bioassay experiments in nine US rivers indicated that up to 23% of DON is bioavailable and that 43% of the consumed total dissolved nitrogen (TDN) by bacteria is taken up as DON (Wiegner et al. 2006). In general, the bioavailability of terrestrially derived DON is variable at 2-70% (Seitzinger and Sanders 1997, Stepanauskas et al. 2002, Veuger et al. 2004, Wiegner et al. 2006). It is speculated that the bioavailability and the composition of DON may depend on the source (McCallister et al. 2006). DON from anthropogenic sources seems to be more bioavailable than DON exported from forested regions and wetlands (Seitzinger et al. 2002). Especially in summer DON may significantly enhance primary production and its impact on the microbial community and contribution to eutrophication seems to be greater (Stepanauskas et al. 1999, 2002, Berg et al. 2003). Different compounds of DON, like urea or amino acids have been studied in detail (Bronk et al. 1998, Berman and Bronk 2003 and references therein), but studies on the bulk pool are rare (for details see chapter 4).

Like DON, DOC was also assumed to be mainly refractory and therefore unimportant as an energy source for microbes. However, studies in the last decades have shown that DOC is also highly bioavailable. Amon et al. (2001) demonstrated that 30% of fresh, algal-derived DOM was bioavailable in form of DOC for bacteria. Terrigenous dissolved organic carbon was shown to be relatively rapidly remineralized on the continental shelf of the Arctic Ocean (Letscher et al. 2011). In the world ocean approximately 97% of all organic carbon exists in the dissolved phase, which is comparable to the amount of carbon dioxide in the atmosphere (e.g. Siegenthaler and Sarmiento 1993). Every year around 0.25 Gt C are transported as DOC via the rivers to the coastal oceans and a relatively high proportion is degraded after mixing with seawater with turnover rates ranging from days to years (Cauwet et al. 2002). Additionally, only a small fraction of the organic matter within the ocean appears to be land derived (Hedges et al 1997, see chapter 5 for more details). Even though DOC and DON cycling is partly intertwined, it has been shown that DON can be preferentially recycled to avoid nitrogen limitation (Thomas et al. 1999). But still the dynamics of specific compounds of DOM and much less of the bulk pool remains unclear and therefore tracing DOM with stable isotopes can help understanding its cycling (see chapter 4 and 5 for more details).

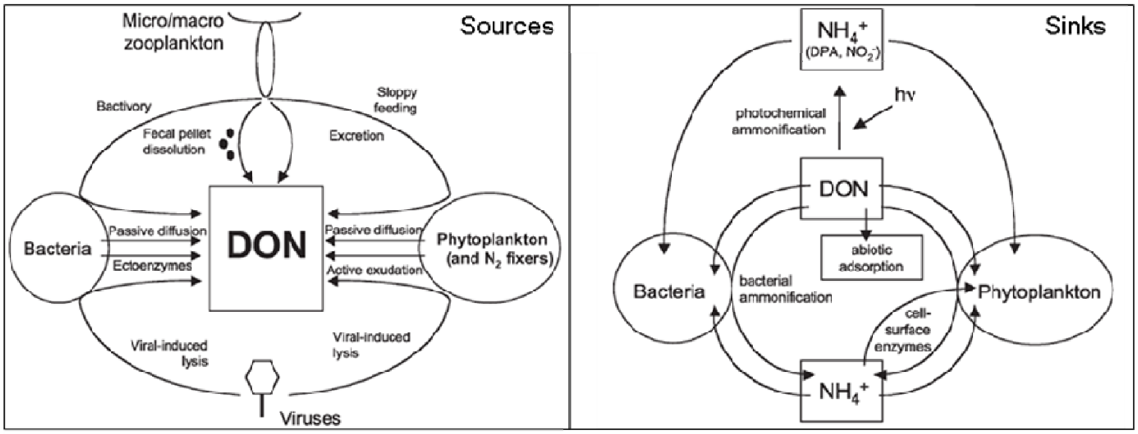

Figure 1.4: Conceptual diagram of autochthonous sources and sinks of DON in the marine environment. DPA stands for dissolved primary amines (Bemann and Bronk 2003, Bronk 2002).

1.4 Stable isotopes as a tool to unravel the nitrogen cycle

To assess nitrogen turnover processes and sources, nitrogen and oxygen isotopes in natural abundance and nitrogen isotopes in artificial labeling experiments were used in many aquatic studies (e. g. Dugdale and Wilkerson 1986, Liu & Kaplan 1989, Brandes et al. 1998, Sigman et al. 1999, Middelburg and Nieuwenhuize 2000, Voss et al. 2000, Sutka et al. 2004, Deutsch et al. 2006, Casciotti et al. 2007, Dähnke et al. 2008, Granger et al. 2008, see chapter 3 and 4 for details). Isotopes are atoms with the same number of protons but different number of neutrons. Stable isotopes are defined as those that are energetically stable and do not decay. Nitrogen has two stable isotopes ^{14}N and ^{15}N, while oxygen has three, ^{16}O, ^{17}O and ^{18}O. In this study ^{17}O is neglected due to its very small abundance in natural sources, but for the mass-dependent $^{16}O/^{17}O/^{18}O$ relationship a correction was always made for ^{17}O. Isotope ratios are expressed in the delta notation ($\delta^{15}N$ relative to atmospheric N_2 and $\delta^{18}O$ relative to Vienna Standard Mean Ocean Water (VSOW)):

$$\delta_{sample}\ (‰) = (R_{sample}/R_{reference}) \times 1000$$

where R is $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of sample and reference, respectively. Stable isotopes values are altered by both equilibrium processes (like evaporation of water) or by kinetic fractionation processes which tend to partition light isotopes (^{14}N and ^{16}O) from heavier ones (^{15}N and ^{18}O) (Kendall 1998). As a consequence, throughout the course of a biochemical reaction, the substrate being consumed becomes progressively enriched with the heavier isotope, while the resultant product becomes relatively lighter. The extent to which a biological transformation fractionates between light and heavier isotopes is given by the isotopic effect, ε (Tab. 1.1).

This value is calculated from the integrated expression of the progress of the reaction according to the Rayleigh model:

$$\delta_{reactant} = \delta_{initial} - \varepsilon[\ln(f)]$$

where f is the fraction of reactant remaining (nitrate/nitrate$_{initial}$), $\delta_{initial}$ is the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of initial reactant pool, and ε is the kinetic isotope effect of the transformation. In practice,ε is the negative slope of the linear relation of $\delta^{15}N$ or $\delta^{18}O$ vs. the natural logarithm of the fraction of the reactant remaining.

Table 1.1: Fractionation factors (ε) for N cycle processes.

Reaction	$^{15}\varepsilon$	$^{18}\varepsilon$	References
Nitrate assimilation ($NO_3^- \rightarrow PN$)	~5‰	$^{18}\varepsilon = {}^{15}\varepsilon$	Wu et al. 1997, Sigman et al. 1999,Altabet 2001, Granger et al. 2004
Nitrification ($NH_4^+ \rightarrow NO_2^-$)	14-38‰	-	Casciotti et al. 2003
Water column denitrification ($NO_3^- \rightarrow N_2$)	22-30‰	$^{18}\varepsilon = {}^{15}\varepsilon$	Brandes et al. 1998, Altabet et al. 1999, Voss et al. 2001
Sediment denitrification ($NO_3^- \rightarrow N_2$)	<3‰	$^{18}\varepsilon = {}^{15}\varepsilon$	Brandes and Devol 1997, Lehmann et al. 2004
N_2 fixation ($N_2 \rightarrow NH_4^+$)	-1,5-0‰	~0‰	Capone et al. 1997, Minagawa and Wada 1986
Ammonification ($N_{org.} \rightarrow NH_4^+$)	~0‰	-	Kendall 1998

1.4.1 Tracking nitrogen in coastal areas

New insights into the nitrogen cycle have been gained from studies that have used stable isotopes in artificial labeling experiments and natural abundances. For example studies using $^{15}N/^{14}N$ isotopic tracers examined the linkages in the cycle of new nitrogen input into the euphotic zone of the ocean, its utilization by phytoplankton, and transport to the deep sea (Altabet and Deuser 1985, Altabet and McCarthy 1985, 1986, Altabet 1988, 1989, Voss et al. 1996). Further on, the distribution of nitrogen isotopes within marine ecosystems can provide a record of the sources of nitrogen supporting biological production and the major pathways and mechanisms moving nitrogen through the biota (Montoya 2008).

Because about 88% of the oceanic fixed nitrogen pool consists of nitrate (Gruber 2008) many studies over the last decades have used ^{15}N isotopes in nitrate to investigate sources and transformation processes (Brandes and Devol 2002 and references therein). Even though, measurements of $\delta^{15}N$ and $\delta^{18}O$ in nitrate in fresh water samples were possible (Silva et al. 2000) the invention of the denitrifier method (Sigman et al. 2001, Casciotti et al. 2002, see chapter 3 for details) enabled researchers to investigate the influence of both cycling and mixing of multiple sources in marine water samples with low nitrate concentrations (e.g. Wankel et al. 2006, Dähnke et al. 2010, Sebilo et al. 2006, Sigman et al. 2003). The advantage of the additional measurement of the O isotopes in nitrate is that now processes overprinting each other when looking at nitrogen isotopes in nitrate can be distinguished. For example, Sigman et al. (2003) were able to distinguish between water column and sedimentary denitrification in the Santa Barbara Basin by using the dual stable isotopes of nitrate. They could furthermore show that sedimentary denitrification accounts for more than 75% of the nitrate loss within that area.

The most significant processes in rivers and coastal areas that cause isotopic fractionation are assimilation, nitrification, and denitrification. Assimilation as well as denitrification results in an increase of $\delta^{15}N$ and $\delta^{18}O$ values in nitrate (Kendall 1998) because plankton and microbes preferentially consume isotopically light nitrate ($^{14}N\text{-}NO_3^-$ and $^{16}O\text{-}NO_3^-$) (Mariotti et al. 1988, Lui & Kaplan 1989, Kendall 1998, Voss et al. 2001, Lehmann et al. 2003). The $\delta^{15}N/\delta^{18}O$ ratio of the remaining nitrate is supposed to be close to 1:1 during assimilation (Granger et al. 2004). The same holds true for denitrification in marine environments (Sigman et al. 2005, Granger et al. 2004), whereas in freshwater ecosystems the ratio seems to be 1:0.5 (Böttcher et al. 1990, Lehmann et al. 2003). But also anomalies from the 1:1 $\delta^{15}N/\delta^{18}O$ relationship can be found in the marine environment (Sigman et al. 2005, see chapter 3 for details). During nitrification the development of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ is decoupled. Nitrification adds isotopically depleted nitrate to the nitrogen pool because nitrifiers preferentially take up isotopically light ammonium (Kendall 1998). In addition to the N isotope effects, also O isotope effects are involved with the nitrification process (Buchwald and Casciotti 2010, Casciotti et al.2010). New O atoms are added from dissolved oxygen (O_2) and water (H_2O) pools, independently of other N cycle processes. While O_2 is incorporated during the oxidation of NH_3 to NH_2OH, H_2O is incorporated during the oxidation of NH_2OH to NO_2 and NO_3 (Buchwald and Casciotti 2010, Casciottiet al. 2010). It was suggested that the $\delta^{18}O\text{-}NO_3^-$ signature from nitrification is dominated by the water $\delta^{18}O$ signal, because 5 out of 6 oxygen atoms in nitrate originate from the water (Casciotti et al. 2002, Sigman et al. 2005). But this only holds true when exchange and fractionation of oxygen isotopes during nitrification are minimal (Casciotti et al. 2011). Casciotti et al. (2010) and Buchwald and Casciotti (2010) could show that in addition to variations in the oxygen isotope value of the O atom donors (O_2 and H_2O), the oxygen isotope value of newly produced nitrate is affected by O isotopic exchange and fractionation. This makes it even more complicated to define a fractionation factor for nitrification and additional work is needed to fully characterize the O isotopic systematics for nitrification (Casciotti et al. 2011).

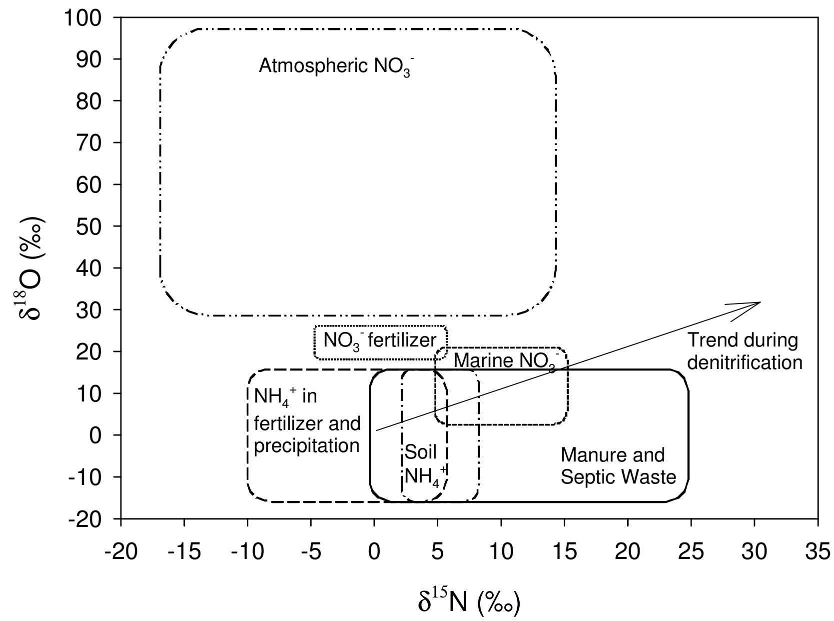

Figure 1.5: Ranges of isotopic compositions of nitrate ($\delta^{15}N$ and $\delta^{18}O$) for major nitrate sources and the expected trend for the isotopic composition undergoing denitrification (adopted from Mayer et al. 2002, Kendall et al. 2007)

The isotope values ($\delta^{18}O$- and $\delta^{15}N$-NO_3^-) resulting from various turnover processes can be used to attribute nitrate to specific sources (Fig. 1.5, Boyer et al. 2002, Mayer et al. 2002, Voss et al. 2006, Deutsch et al. 2006). Enriched $\delta^{15}N$-NO_3^- values indicate sewage input and/or input of fertilizers in agriculture runoff ranging from 7 and 25‰ (summarized in Kendall et al. 2007). Compared to nitrate from natural sources anthropogenic nitrate is enriched in ^{15}N by various processes like ammonia volatilization and denitrification in soils or aquifers. The stable nitrogen isotopic composition of atmospherically deposited nitrogen is highly variable and can be influenced for example by fossil fuel composition or agricultural activities (Kendall 1998, Mayer et al. 2001, Mayer et al. 2002). Synthetic fertilizers and nitrate in natural soils are isotopically distinct from N in the atmosphere and $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- vary between 0 to 3 and 22±3‰ and -3 to 5 and 0 to 14‰, respectively (Kendall 1998). Therefore the isotopic composition of nitrate is a powerful tool to determine both nitrogen transformation processes and its origin (see chapter 3 for details).

1.5 The Baltic Sea and its sensitivity towards eutrophication

The Baltic Sea is one of the most eutrophied coastal seas in the world (Cloern 2001) and anthropogenic eutrophication effects are well studied (Elmgren 2001). Every year about 1000 kt of nitrogen are entering the Baltic Sea from various sources like rivers, N_2 fixation, atmospheric deposition and point sources (Tab. 1.2). In chapter 2 detailed background informations on the Baltic Sea are given. Therefore, only a brief summary in this section about the Baltic Sea is given to highlight why it is an excellent site for studying nitrogen transformation processes in face of eutrophication.

Table 1.2: Nitrogen inputs to the Baltic Sea

Input pathway	Baltic Sea N input [kt N yr^{-1}] in 2000	Reference
Riverine	745	Helcom 2005
Atmospheric	264	Helcom 2005
N_2 fixation	180 to 430	Rolff et al. 2008, Wasmund et al. 2005

The Baltic Sea is a shallow, intra-continental, brackish sea and covers an area of 377.000 km² with a coastline of 8000 km (Sweitzer et al. 1996). Its topography is characterized by a series of basins (e.g. Arkona, Bornholm and Gotland Basins). A positive water balance creates a strong salinity gradient from 2 in the northernmost Gulf of Bothnia to over 20 in the Kattegat and Danish Straits and a permanent halocline separates the deep, saltier water from the surface water in the western and central Baltic Sea. The bottom water of the Baltic proper is only replaced by intermittent inflows of denser, oxygenated water through the Danish Straits from the North Sea. Additionally due to the limited water exchange with the North Sea and long residence times of approximately 30 years, stagnation periods of up to 16 years enhance the natural occurrence of anoxic bottom waters (Elmgren 2001, Conley et al. 2002). Anthropogenic driven eutrophication has increased both the spatial extent and intensity of hypoxia in the deep basins of the Baltic Sea (Conley et al. 2009, Zillen et al. 2008). Recently a study could show that over 115 coastal sites in the Baltic Sea experienced hypoxia, which implies that over 20% of all worldwide known hypoxic sites are in the coastal zone of the Baltic Sea (Conley et al. 2011). The consequences of hypoxia on the biota are mentioned in section 1.1 but also the consequences on the nutrient biogeochemical cycles of the Baltic Sea are substantial leading to increased phosphorus release from the sediments (Mort et al. 2010) and internal loading and circulation of nutrients are intensified. Additionally, eutrophication has led to an increase in the abundance of cyanobacteria and other phytoplankton blooms in the Baltic Sea (Finni et al. 2001, HELCOM 2005, Vahtera et al. 2007).

Another characteristic of the Baltic Sea is that the drainage basin of the Baltic Sea is four times larger than the sea itself and is populated by 85 million people (Sweitzer et al. 1996). The population is heterogeneously distributed with a gradient from high population density in the south (>500 inhabitants/km^2) to low population density in the northern part (< 10 inhabitants/km^2) (Lääne et al. 2005). In the north the land cover is dominated by boreal forests whereas the southern catchment is heavily cultivated. This results in higher riverine inputs of nutrients from the southern part of the catchment (HELCOM 2004, HELCOM 2009, Humborg et al. 2007, Voss et al. 2011). For the Baltic Sea rivers play a crucial role in the total input of nitrogen, accounting for approximately 75% of the total nitrogen input to the Baltic Sea (HELCOM 2005, Rolff et al. 2008, Table 2). The rivers Neva, Vistula, Daugava, Nemunas and Oder supply over 50% of the total nitrogen influx mainly in form of dissolved inorganic nitrogen (DIN) (HELCOM 2004). It is well known that concentrations decrease rapidly offshore in the Baltic Sea but the nitrogen removal processes which lead to the loss of nitrate are still not fully characterized in the estuaries and adjacent coastal areas (see chapter 2 and 3 for details).

To solve the ecological problems of the Baltic Sea, in 1974 seven Baltic coastal states formed the Helsinki Commission (HELCOM). In 2007 the Helsinki Commission (now nine Baltic coastal states) adopted the Baltic Sea Action Plan (BSAP). In the BSAP clear nutrient reduction goals have been allocated to the riparian countries and the main goal is that the Baltic Sea is supposed to be unaffected by eutrophication by 2021. The same is claimed in the European Water Framework Directive (WFD 2000), which implements that in surface waters like coastal water bodies, including the Baltic Sea, good ecological and chemical conditions are to be reestablished. Although recent data indicate a decrease in nitrogen runoff (Wulff et al. 2009), eutrophication remains the single greatest threat to the Baltic Sea environment (HELCOM 2009, Andersen et al. 2011). In a recent study the HELOCM still claims 176 areas out of 189 to be affected by eutrophication (Andersen et al. 2011).

It has been shown that denitrification as the main process that removes nitrogen permanently from the system is estimated to account for 48-73% of external nitrogen removal (Deutsch et al. 2010). Additionally, Hietanan et al. 2008 could show that anammox can contribute 10 to 15% to the total N_2 production in the Baltic Sea. But still the nitrogen budget in the Baltic Sea is not balanced. Additionally, two recent studies suggest that the removal capacity may even decrease when DNRA becomes the most important pathway under hypoxia (Jäntti et al. 2011, Jäntti et al. in press). Therefore studying nitrogen turnover and removal processes in the Baltic Sea is from great importance to make sure that the nitrogen removal capacities are not lost, besides the effort to reduce nitrogen loads.

1.6 Aim of the study

This thesis is part of the international BONUS (Baltic Organization Network for Funding Science) project AMBER (Assessment and Modelling of Baltic Ecosystem Response), which focuses on the implementation and application of an Ecosystem Approach to Management (EAM) to the Baltic Sea in face of eutrophication and climate change focusing on the coastal ecosystem. The aim of the present study is to characterize nitrogen turnover processes in the Baltic Sea and to contribute to the existing knowledge on the role of nitrogen in coastal areas. The study is based on the one hand on in situ rate measurements in artificial labeling experiments and on the other hand on the analyses of natural stable nitrogen, oxygen and/or carbon isotopes in different pelagic compounds like nitrate or particulate organic matter (POM).

In chapter 2 the existing knowledge on the historical progression of eutrophication based on long term data sets is summarized. Additionally, the sensitivity of the Baltic Sea towards eutrophication and future scenarios from climate related change in the Baltic Sea region are examined. Regional differences that lead to major open questions concerning the nitrogen cycle in the Baltic Sea are elucidated. The goals of chapter 3 are to trace the isotopic signature of riverine nitrate in the coastal zone of the Baltic Sea and to determine main nitrate removal processes. Thus nitrate from different sources, including the Oder River in the south, the Nemunas River in the north east and the central Baltic Sea are analyzed by means of dual isotope analysis. Additionally, ^{15}N nitrate tracer techniques were used to quantify the nitrate uptake by in situ measurements. Also the influence of permeable sediments on the N-cycling in the overlying bottom water is studied. This part is based on data from a spring cruise in 2009, when nitrate loads and river runoff reach their annual high. In chapter 4 and 5 the fate of organic matter (DON and DOC) is characterized by means of ^{15}N and ^{13}C tracer techniques along a salinity gradient ranging from 34 to 2. Turnover rate calculations and end-member-mixing-models were used to show the high dynamics of the bulk DOM pool. These studies were performed during summer to account the fact that DON can be a nutrient source, when inorganic nitrogen is limited. Chapters 2 to 5 are presented in a manuscript-like structure and a detailed statement on my contributions to the manuscripts are given at the end of the thesis. In chapter 6 the results of this thesis are summarized and a short outlook is presented.

2. History and scenarios of future development of Baltic Sea eutrophication

M. Voss, J. Dippner, C. Humborg, F. Korth, T. Neumann, J. Hürdler, G. Schernewski, M. Venohr

Estuarine, Coastal and Shelf Science, 92(3), pp. 307-322

2.1a Abstract

Nutrient loads from watersheds, atmospheric deposition, and cyanobacterial nitrogen fixation have led to eutrophication in the Baltic Sea. Here we give the historical evolution of this, detail some of the specific eutrophication features of the Baltic Sea, and examine future scenarios from climate related changes in the Baltic Sea region. We distinguish northern and southern regions of the Baltic Sea. The northern watersheds have sub-polar climate, are covered by boreal forest and wetlands, are sparsely populated, and the rivers drain into the Gulf of Bothnia. The southern watersheds have a marine influenced temperate climate, are more densely populated and are industrially highly developed. The southern areas are drained by several large rivers, including the representative Oder River. We compare these regions to better understand the present and future changes in Baltic Sea eutrophication.

Comparing the future projections for the two regions, we suggest that in addition to changes in nutrient inputs, increased temperature and precipitation are likely to become important forcings. Rising temperature may increase release of dissolved organic matter (DOM) from soils and may alter the vegetation cover which may in turn lead to changed nutrient and organic matter input to the Baltic Sea. For the southern Oder River catchment a model study of nutrient input is evaluated, MONERIS (Modelling Nutrient Emissions in River Systems). The strong correlation between precipitation, flow and nutrient discharge indicates a likely increase in nutrient concentrations from diffuse sources in future. The nutrients from the Oder River are modified in a lagoon, where removal processes change the stoichiometry, but have only minor effects on the productivity. We suggest that the lagoon and other nearshore areas fulfil important ecological services, especially the removal of large quantities of riverine nitrogen but at the same time are threatened systems due to increasing coastal hypoxia.

3. Nitrogen turnover during spring outflow from the nitrate-rich Curonian and Szczecin lagoon using dual isotopes in nitrate

F. Korth, I. Liskow, B. Fry and M. Voss

Submitted to Marine Chemistry

3.1 Abstract

Coastal zones which receive high nitrogen loads from rivers often suffer substantially from eutrophication. This is true for the Baltic Sea, which is well-known for its critical eutrophication status especially along the coastlines. Although the nutrient concentrations decrease rapidly offshore, the uptake and turnover processes near-shore are not well understood. The Rivers Oder and Nemunas, the second and third largest nitrogen contributors, drain into the Szczecin and Curonian lagoon, respectively, before they enter the coastal area of the Baltic Sea. During peak outflow, in March 2009 nutrient concentrations, nitrate uptake rates and dual isotopes ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) in nitrate were measured in the outflows of the lagoons to characterize nitrate turnover processes and its fate in the coastal zone. In the Curonian lagoon outflow the isotopic signature is dominated by mixing, whereas in the Szczecin lagoon outflow the isotope values are influenced by the ongoing spring phytoplankton bloom. Nitrate assimilation is indicated in the surface waters of the Szczecin lagoon outflow by a parallel enrichment of ^{15}N and ^{18}O. In the near bottom waters denitrification seems to be the prevalent process which generates the isotopic signal of nitrate. There a deviation from the 1:1 $\delta^{18}O$-NO_3^- to $\delta^{15}N$-NO_3^- relationship usually associated with denitrification was found. This 1.3:1 ratio suggests that denitrification is not only fueled by nitrate fluxes from the water column into the sediments, but also from nitrate derived from remineralization of particulate matter and coupled nitrification/denitrification. Moreover, the fractionation factors of $^{15}\varepsilon$ of 9.9‰ and $^{18}\varepsilon$ of 10.1‰ in near bottom waters infer that the isotopic enrichment from sedimentary denitrification may be higher in sandy sediment than in muddy sediments.

4. Uptake of dissolved organic nitrogen by size-fractionated plankton along a salinity gradient from the North Sea to the Baltic Sea

F. Korth, B. Deutsch, I. Liskow, M.Voss

Biogeochemistry (DOI 10.1007/s10533-011-9656-1)

4.1 Abstract

The Baltic Sea is known for its ecological problems due to eutrophication caused by high nutrient input via nitrogen fixation and rivers, which deliver up to 70% of nitrogen in the form of dissolved organic nitrogen (DON) compounds. We therefore measured organic nitrogen uptake rates using self produced ^{15}N labeled allochthonous (derived from *Brassica napus* and *Phragmites sp.*) and autochthonous (derived from *Skeletonema costatum*) DON at twelve stations along a salinity gradient (34 to 2) from the North Sea to the Baltic Sea in August/September 2009. Both labeled DON sources were exploited by the size fractions 0.2-1.6 µm (bacteria size fraction) and >1.6 µm (phytoplankton size fraction). Higher DON uptake rates were measured in the Baltic Sea compared to the North Sea, with rates of up to 1213 nmol N L^{-1} h^{-1}. The autochthonous DON was the dominant nitrogen form used by the phytoplankton size fraction, whereas the heterotrophic bacteria size fraction preferred the allochthonous DON. We detected a moderate shift from >1.6 µm plankton dominated DON uptake in the North Sea and central Baltic Sea towards a 0.2-1.6 µm dominated DON uptake in the Bothnian Bay and a weak positive relationship between DON concentrations and uptake. These findings indicate that DON is an important component of plankton nutrition and can fuel primary production. It may therefore also contribute substantially to eutrophication in the Baltic Sea especially when inorganic nitrogen sources are depleted.

5. Tracing inputs of terrestrial high molecular weight dissolved organic matter within the Baltic Sea Ecosystem

B. Deutsch, A. Alling., C. Humborg, F. Korth, C. M. Mörth

Biogeosciences, 9, 4465-4475, 2012
doi:10.5194/bg-9-4465-2012

5.1 Abstract

To test the hypothesis whether high molecular weight dissolved organic matter (HMW-DOM) in a high latitude marginal sea is dominated by terrestrial derived matter, 10 stations were sampled along the salinity gradient of the central and northern Baltic Sea and were analyzed for concentrations of dissolved organic carbon as well as $\delta^{13}C$ values of HMW-DOM. Different end-member-mixing models were applied to quantify the influence of terrestrial DOM and to test for conservative versus non-conservative behavior of the terrestrial DOM in the different Baltic Sea basins. The share of terrestrial DOM to the total HMW-DOM was calculated for each station, ranging from 43 to 83%. This shows the high influence of terrestrial DOM inputs for the Baltic Sea ecosystem. The data also suggest that terrestrial DOM reaching the open Baltic Sea is not subject to substantial removal anymore. However compared to riverine DOM concentrations, our results indicate that substantial amounts of HMW-DOM (> 50%) seem to be removed near the coastline during estuarine mixing. A budget approach yielded residence times for terrestrial DOM of 2.8, 3.0, and 4.5 yr for the Bothnian Bay, the Bothnian Sea and the Baltic Proper.

6. Conclusions and Perspectives

Currently over 40% of the world's population live within 100 kilometers of the coast and since the onset of industrialization the word population has grown to 7 billion people (The state of world population 2011) and will continue to increase. The UK Food and Agriculture Association estimates that the world population will increase to 8.9 billion, by 2050 meaning that global agriculture must increase even further in the next 30 years to sustain this type of population growth. As population density and economic activity in the coastal zone increases, pressures on coastal ecosystems will increase. Also changes in diet are of great importance. Eriksson Hägg et al. 2010 hypothesized that increased protein consumption in the eastern European countries could lead to 16 to 32% increased total nitrogen fluxes to the Baltic Sea making it even more difficult to reduce the nitrogen load by 135000 tons and phosphorous loads by 15250 tons as required by the Baltic Sea Action Plan (BSAP) for the year 2021. Also Krämer et al. (2011) estimated that agricultural nitrogen loads to the Oder Lagoon could increase by as much as 23% in the future considering aspects like cultivation of energy maize and increased animal stocks. Therefore, current and expected future human alterations to the nitrogen cycle make it necessary to understand how nitrogen is cycling through watersheds to assess the consequences of increasing anthropogenic nitrogen inputs.

In the framework of this thesis, the fate of dissolved organic and dissolved inorganic nitrogen were studied in detail in the Baltic Sea. The results indicate that not only inorganic but also organic nitrogen serves as an important nutrient source for phyto- and bacterioplankton and that it is mainly degraded in estuaries and near the coastline. In general, continental shelf ecosystems, such as the Baltic Sea, are characterized by strong gradients in nutrients and organic matter, which are mainly maintained by the continuous supply through river runoff. These gradients imply an intensive nutrient and organic matter cycling within the coastal areas, which contribute a major part to the annual nitrogen demand (e.g. Costanza et al. 1997, Middelburg and Nieuwenhuize 2001, Seitzinger et al. 2006). In the Baltic Sea pronounced regional differences are found according to the land use and population density. In the northern watersheds, which are covered by boreal forests and are sparsely populated, nitrogen discharges from the rivers are lower than in the southern region, where watersheds are densely populated and agriculture and industry are highly developed (Fig.6.1). Additionally, the total nitrogen (TN) composition varies (Stepanauskas et al. 2002). In the northern part organic nitrogen dominates, whereas in the southern part nitrate is the main component of the total nitrogen pool. Moreover, DON from anthropogenic sources is more bioavailable than DON exported from natural regions like forests or wetlands (Seitzinger et al. 2002). Congruently, results of this thesis indicate that the potential of plankton to utilize DON is higher in the southern part of the Baltic Sea, where anthropogenic loads are high and nitrogen limitation occurs (Graneli et al. 1990).

Pronounced differences were found between the North Sea and the Baltic Sea regarding the magnitude of DON uptake rates. In the Baltic Sea, where riverine DON loads are high, DON uptake rates were an order of magnitude higher than in the North Sea. This is the first study were bulk dissolved organic nitrogen (DON) uptake rates were determined by imitating a natural DON source with ^{15}N labeled DON instead of using single DON compounds such as urea or amino acids. Stepanauskas et al. 2002 showed that around 30% of terrestrial derived DON was available to bacteria during bioassay experiments in the Baltic Sea. This thesis adds to the knowledge that besides bacteria also phytoplankton utilizes DON (either directly or following photodegratation or bacterial breakdown).

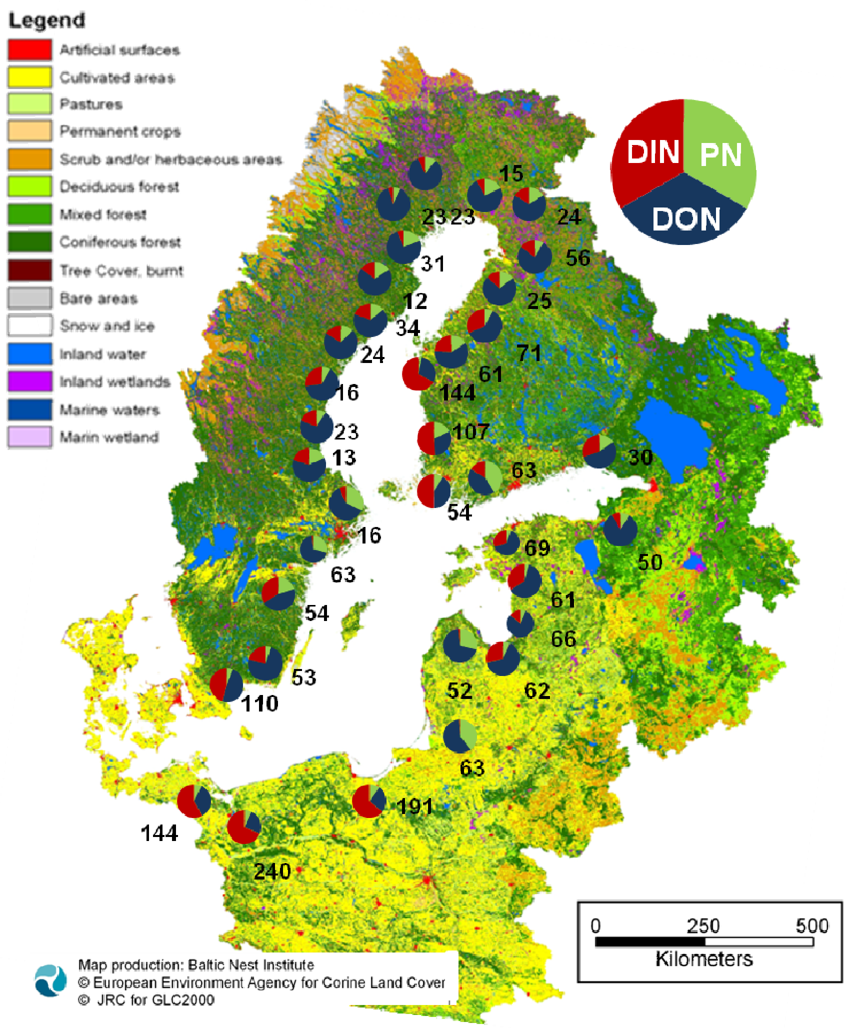

Figure 6.1: The Baltic Sea and its catchment area, which is colored according to the land use. Concentrations of total nitrogen (TN) (µmol l^{-1}) are given for 35 rivers and the percentage of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and particulate nitrogen (PN) (sources Baltic Nest institute and Stepanauskas et al. 2002).

However, riverine loads are the most important allochthonous DON sources. From results of this thesis it was calculated that the share of terrestrial DOM to the total DOM pool in the Baltic Sea is high, ranging from 43 to 83%. Turnover rate calculations showed that terrestrial derived DON must be mainly degraded in near proximity of the coast and that only more refractory compounds remain. Additionally, in this thesis it was demonstrated that also DOC is an important energy source which is also mainly degraded in river estuaries and in the coastal area. The fate of carbon and nitrogen in organic matter can be coupled or decoupled (Veuger and Middelburg 2007, Engel et al. 2002, Bode et al. 2004). Especially under nitrogen limitation the utilization of DON seems to become important. Therefore future studies should trace both DON and DOC to investigate carbon-nitrogen couplings or decoupling. In order to quantify the loss of DON/DOC in the coastal zone, future studies should include measurements of bulk DON/DOC uptake rates along a DOM concentration gradient from the river to the open sea. Since the composition and reactivity of DON depend on its source and DON of different rivers is chemically distinct (McCallister et al. 2006) studies on the fate of DON should be performed in different river systems and over longer time periods, because the reactivity of DON can also vary over the season and even during peak outflow events (Stepanauskas et al. 2000, Wiegner et al. 2009, Bode et al. 2004).

In some regions already today dissolved inorganic nitrogen reductions can be observed due to improved fertilizer, livestock management and/or advanced wastewater treatment (Carstensen et al. 2006), but the productivity has not decreased, which is often attributed to internal nutrient loadings and recycling (Soetaert et al. 2006, Philippart et al. 2007). In the Oder River, one of the most eutrophied rivers of the Baltic Sea, a slight decrease in total nitrogen loads has been observed (Savschuk and Wulff 2009) due to inorganic nitrogen reductions, however around 32% of the nitrogen load is in form of DON and no reduction in DON can be seen. Since this thesis has shown that DON can be an important source for primary production it becomes even more necessary to focus as well on DON dynamics besides DIN and to have a closer look on DON sources and sinks. To evaluate its potential importance in ecosystem-wide nutrient budgets DON should be included as an extra nutrient sources in physical-biogeochemical models. Additionally, as suggested in chapter 2 climate change may lead to massive release of DOC and DON in boreal and arctic rivers since permafrost areas will start to thaw. If this additional DON and DOC will affect the productivity in coastal seas, is not clear yet (Hood and Scott 2008).

Further on, results from this thesis have shown that during cyanobacteria blooms DON release and uptake are closely coupled. Especially under the aspect that the frequency and magnitude of cyanobacteria blooms have increased in the Baltic Sea (Finni et al. 2000, Vahtera et al. 2007) and that climate change is a potential catalyst for the expansion of these blooms (Pearl and Huisman 2008, Meier et al. 2011) it becomes obvious that the understanding of DON dynamics is important to understand how this pool will respond to anthropogenic perturbations and climate change. However, still numerous questions remain concerning dissolved organic substances and its role in the nitrogen cycle. Therefore further studies with ^{15}N tracer techniques, for example by combining nitrogen concentration and stable isotope ratio measurements of DON with the “denitrifier method” are envisioned which can give more insights into processes (Schlarbaum et al. 2010, Knapp et al. 2005, 2011). With the combination of these methods it already have been shown in the North Atlantic and the North Pacific Ocean, as well as in coastal areas like the North Sea, that DON is actively participating in the nitrogen cycle of each region (Schlarbaum et al. 2010, Knapp et al. 2011).

Like organic substances also inorganic nutrients are known to decrease rapidly offshore specifically in the southern Baltic Sea, where the anthropogenic nitrogen isotopic signature is rapidly replaced by the one of nitrogen fixing organisms (Voss et al. 2000, 2005, 2006, HELCOM 2007). However the processes which influence the isotope values in the transition zone of riverine and marine water remained unclear. Therefore measurements of dual isotopes in nitrate were performed for the first time in the outflows of the Nemunas and Oder Rivers, two of the main nitrogen contributing rivers to the Baltic Sea, during peak outflow season, when nitrate loads are highest. Results indicate mixing in the surface water and nitrate assimilation, whereas in permeable sediments, as they are found in the Oder outflow, nitrate is denitrified directly or removed via coupled nitrification/denitrification. So far, permeable sediments were mainly thought to contribute little to the biogeochemical cycling due to its low carbon content thus biogeochemical research has focused on muddy shelf sediments. This study adds to the growing knowledge that permeable sediments can be important sites for nitrogen removal (Jahnke et al. 2005, Janssen et al. 2005). A recently published study by Gao et al. (2012) demonstrated for the North Sea that permeable, sandy sediments, which account for 58-70% of the continental shelf area (Emery 1968), are important nitrogen sinks. They estimated an annual nitrogen removal rate of 745±109 mmol N m^{-2} yr^{-1} for these sediments. Future studies should consider the potential of permeable sediments to regulate the flow of nitrogen at the land–sea boundary in estuaries where nitrate and fresh organic matter loads are high. Consequentley the contribution of permeable sediments to the global nitrogen loss budget need to be reevaluated.

So far denitrification rate measurements in permeable sediments in the Baltic Sea are rare (Deutsch et al. 2010), and have not been performed in the estuaries of the Oder and/or Nemunas River. Future studies should focus on the determination of denitrification rates in these permeable sediments to estimate the amount of nitrate lost in the estuaries and the adjacent coastal zone. Rate measurements should be performed seasonally to determine which major factors are controlling denitrification rates, since the interaction of parameters like substrate availability, temperature, and/or oxygen concentration is still under debate (Seitzinger 1988). Concerning denitrification rate measurements the sample resolution in space and time is relatively low as collecting and incubation by using the isotope pairing technique is time consuming (Nielsen 1992, Risgaard-Petersen et al. 2003). Furthermore, model studies claim that more research is needed on benthic denitrification, since not well understood biogeochemical processes increase the uncertainties of future projections (Meier et al. 2011). Therefore another promising approach would be the use of a needle probe MIMS inlet to measure large sets of N_2/Ar profiles (Hilary and Seitzinger 2003) followed by modeling N_2 production rates.

Both rivers, the Nemunas and the Oder, drain into lagoons before entering the Baltic Sea. Transformation processes within these lagoons have not been a main focus of this thesis but a recent study showed that the Szczecin lagoon act as an important nitrogen sink (Voss et al. 2010). However under hypoxia, which is increasing in the coastal zone of the Baltic Sea (Conley et al. 2011), nitrogen removal rates decrease with reactive ammonium accumulating through the process of dissimilatory reduction to ammonium (DNRA) (Jäntti et al. in press). Denitrification measurements performed during this thesis in muddy sediments of the Szczecin lagoon are the highest denitrification rates so far measured in the Baltic Sea and ranged from 5000 to 7500 µmol N m^{-2} d^{-1} in summer (data not published). Simple budget calculations with the measured denitrification rates show that only 16 to 24% of the DIN load (46 kt DIN yr^{-1}, mainly in form of nitrate (Voss et al. 2010)) entering the lagoon from the Oder river is removed via denitrification. Therefore, still large amounts of nitrogen enter the adjacent coastal zone and these loads may even increase. Since the fate of nitrogen from rivers to the open Baltic Sea still is under debate, results from this thesis provide a valuable basis for future research to further study nitrogen transformation processes in estuaries and adjacent coastal areas to better understand how climate change and increasing direct anthropogenic pressures will influence the Baltic Sea. Projections of combined effects of climate change and eutrophication in general lead to the conclusion that if nothing is changed oxygen deficiencies and phytoplankton concentrations will continue to increase in the Baltic Sea (Meier et al. 2011). Combating eutrophication remains one of the major challenges in the Baltic Sea and worldwide.

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