NITROGEN CYCLING IN THE SOUTHERN NORTH SEA – ASSESSMENT BY STABLE ISOTOPES

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Zusammenfassung

In die Deutsche Bucht werden große Mengen an anthropogenem Stickstoff eingetragen, was zu zunehmender Eutrophierung führen kann. Anzeichen dafür sind die Entwicklung von Sauerstoffminima, Änderungen in der Artenzusammensetzung und zunehmende Algenblüten. Neuerdings wird verstärkt versucht, die Stickstoffeinträge zu reduzieren, um weitere negative Konsequenzen für das Ökosystem der Deutschen Bucht zu vermeiden.

In der vorliegenden Arbeit werden anhand der Isotopensignatur des Stickstoffs Quellen und Umsetzungsprozesse für reaktive Stickstoffspezies im Kontinuum vom Fluss über das Ästuar zum Küstengewässer untersucht. Die vorliegenden Daten zeigen, dass man durch das Stickstoffsignal auf anthropogene Einflüsse schließen kann. Diese Arbeit gliedert sich in drei Teile, die Kapitel 2 bis 4, die unterschiedliche Aspekte des Ökosystems der Deutschen Bucht untersuchen:

Im ersten Abschnitt wird das Hintergrundsignal verschiedener Flüsse mit landwirtschaftlich geprägtem Einzugsgebiet untersucht (Kapitel 2). Die Daten aus fünf in die Deutsche Bucht einmündenden Flüssen zeigen, dass die Isotopenwerte insgesamt erhöht sind, was hauptsächlich auf Einträge aus der Landwirtschaft zurückzuführen ist. Im jahreszeitlichen Verlauf erkennt man aber auch eine Abhängigkeit von biologischen Umsetzungsprozessen in den Flüssen selbst und in ihrem Einzugsgebiet.

Im zweiten Abschnitt (Kapitel 3) wird untersucht, inwiefern dieses erhöhte Isotopensignal als Hinweis auf historische Veränderungen der Stickstoffquellen genutzt werden kann, indem die Werte aus Sedimentkernen als Maßstab für vorindustrielle Einträge genutzt werden. Es werden Isotopensignaturen von Oberflächensedimenten und von datierten Sedimentkernen aus dem Skagerrak, dem wichtigsten Ablagerungsgebiet für Sedimente der südlichen Nordsee, und aus dem Kattegat, einem Gebiet, das große Mengen an reaktivem Stickstoff durch Oberflächenabfluss aus den Anrainerstaaten bezieht, verglichen. Die Sedimente aus dem Kattegat zeigen im zeitlichen Verlauf zunehmend schwerere Isotopenwerte, während im Skagerrak keine Anreichung zu erkennen ist. Möglicherweise wird dementsprechend der schwere flussbürtige Stickstoff in den seichten Küstengewässern der Deutschen Bucht und in den Ästuaren denitrifiziert, bevor er dieses Ablagerungsgebiet erreicht.

Die Rolle von Ästuaren wird in Kapitel 4 untersucht, indem anhand von saisonalen Gradienten im Elbeästuar Stickstoffsenken und –umsetzungsprozesse untersucht werden. Die Isotopenwerte deuten darauf hin, dass heute, anders als noch vor einigen Jahrzehnten, im

Ästuar kaum Stickstoffumsatz stattfindet, so dass sich die Elbe von einer Nitratsenke in eine Nitratquelle verwandelt hat.

Insgesamt liefern die Daten neue Einblicke in Stickstoffumsetzungsprozesse im Küstengebiet, auch wenn deutlich wird, dass weitergehende Untersuchungen nötig sind, um die tatsächlichen Abbauprozesse für den Stickstoff zu klären, der die Deutsche Bucht und die Ablagerungsgebiete erreicht.

Abstract

The Southern North Sea today receives massive anthropogenic inputs of reactive nitrogen, leading to oxygen depletion, changes in species composition of the ecosystem and algal blooms. All of these phenomena are linked to eutrophication. Currently, efforts are made to reduce these nutrient loads to prevent further negative consequences on the German Bight.

In this thesis I use the nitrogen isotopic signature to investigate both sources and turnover processes of reactive nitrogen in the continuum from the river via the estuary to the coastal ocean. In all datasets show visible that isotope signatures can be used as a tracer for anthropogenic nitrogen inputs. This work can be subdivided into three sections that treat different environments of the German Bight ecosystem, subdivided in the Chapters 2, 3 and 4:

The first part discusses the riverine signal in agricultural watersheds (Chapter 2). The data from five German rivers discharging into the German Bight show that the overall isotope signatures are elevated – mainly attributed to runoff from agricultural land – but also show a distinct seasonality accounted for by biological processing in the rivers and their catchment area.

In Chapter 3 the role of this elevated isotope signal as a tracer for historical changes in nitrogen inputs is investigated by using the signal from sediment cores as a gauge for pre-industrial inputs of reactive nitrogen. Isotope values of surface sediments and dated sediment cores from the Skagerrak, the main depositional centre of German Bight sediments, and the Kattegat, a more enclosed basin receiving high amounts of terrestrial run-off, are compared.

In the Kattegat sediments exhibit progressive enrichment in nitrogen isotopes over time, whereas data from the Skagerrak do not show such enrichment, suggesting that large portions of isotopically enriched riverine nitrogen are denitrified in estuaries and shallow waters of the German Bight before reaching this depositional centre.

The role of estuaries is more closely examined in Chapter 4, where seasonal gradients in the Elbe estuary are sampled to provide evidence of internal nitrate processing. Isotopic values suggest that hardly any turnover takes place in the estuary, which is contrasted by historical data. Apparently, the estuarine function has changed drastically over the last decades, turning the Elbe estuary from a significant nitrate sink into a source of nitrate to the German Bight.

Altogether, the data provide additional insights on nitrogen turnover processes in the coastal zone and stress the importance of further measurements to evaluate the eventual fate of anthropogenic nitrogen entrained to the German Bight and its depositional centres.

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List of Papers

This thesis is based on the following scientific publications which have been published in peer-reviewed journals:

- Johannsen, A., Dähnke, K., and K. Emeis: Isotopic composition of nitrate in five German rivers discharging into the North Sea. *Organic Geochemistry* (2008), doi:10.1016/j.orggeochem.2008.03.004

- Dähnke, K., Serna, A., Blanz, T., and K. Emeis: Sub-recent nitrogen-isotope trends in sediments from Skagerrak (North Sea) and Kattegat: changes in N-budgets and N-sources? *Marine Geology* (2008), doi:10.1016/j.margeo2008.04.017

- Dähnke, K., Bahlmann, E., and K. Emeis: A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary. *Limnology and Oceanography* (2008), **43:** 1504-1511.

1. Overview and Synopsis

1.1. General introduction

One of the most striking problems in coastal ecosystems worldwide is the increased input of nutrients from human activities. This additional nitrogen derives from industrial fixation of atmospheric nitrogen – a large reservoir of nitrogen that under natural conditions used to be only available for a small group of nitrogen-fixing micro-organisms. The ability to fix N_2 is widespread in marine environment, with cyanobacteria fixing an estimated 100 Tg N yr^{-1} (Brandes et al. 2007). In terrestrial systems, N_2 fixation usually occurs established symbiosis of higher plants with nitrogen fixing bacteria in root nodules, such as in legumes (symbiosis with *Rhizobia*) or so-called actinorhizal plants like alder (symbiosis with *Frankia*) (Kneip et al. 2007; Madigan et al. 2000).

With the onset of industrialization roughly 160 years ago, it first became evident that the amount of fixed nitrogen in agraecosystems needed to be increased to sustain the growing population. With the invention of the Haber Bosch Process in 1910, it was first possible to utilize the atmosphere as the largest reservoir of nitrogen as a source to create newly fixed reactive nitrogen (rN). The increased cultivation of legumes, fossil fuel combustion and the creation of rN via the Haber Bosch process together led to rN inputs to terrestrial systems that have doubled as compared to pre-industrial times (Gruber and Galloway 2008, cf. Figure 1.1), now exceeding natural nitrogen sources to the earth's ecosystems (Galloway et al. 2003). As the worlds population since the onset of industrialization has grown to approximately 6.6 billions at present (UN 2007), it is obvious that the demand for food and energy will increase in the future. Changes in diet and the demand for alternative fuel will also do their share in further increasing the demand for agricultural production.

The consequences of this additional input of rN to the biosphere on a global scale are yet unclear, although feedbacks on the carbon cycle and therefore global climate seem likely (Codispoti et al. 2001; Gruber and Galloway 2008). The effect of enhanced nutrient fluxes on the coastal ocean is more problematic than that on the global ocean: Near the coast, the additional reactive nitrogen leads to changes in the nutrient ratios, resulting in harmful algae blooms, vast zones of oxygen deficiency causing death of benthic organisms and assemblages, and changes in the species composition in coastal areas (Conley et al. 2007; Laane et al. 2005; Lepoint et al. 2007).

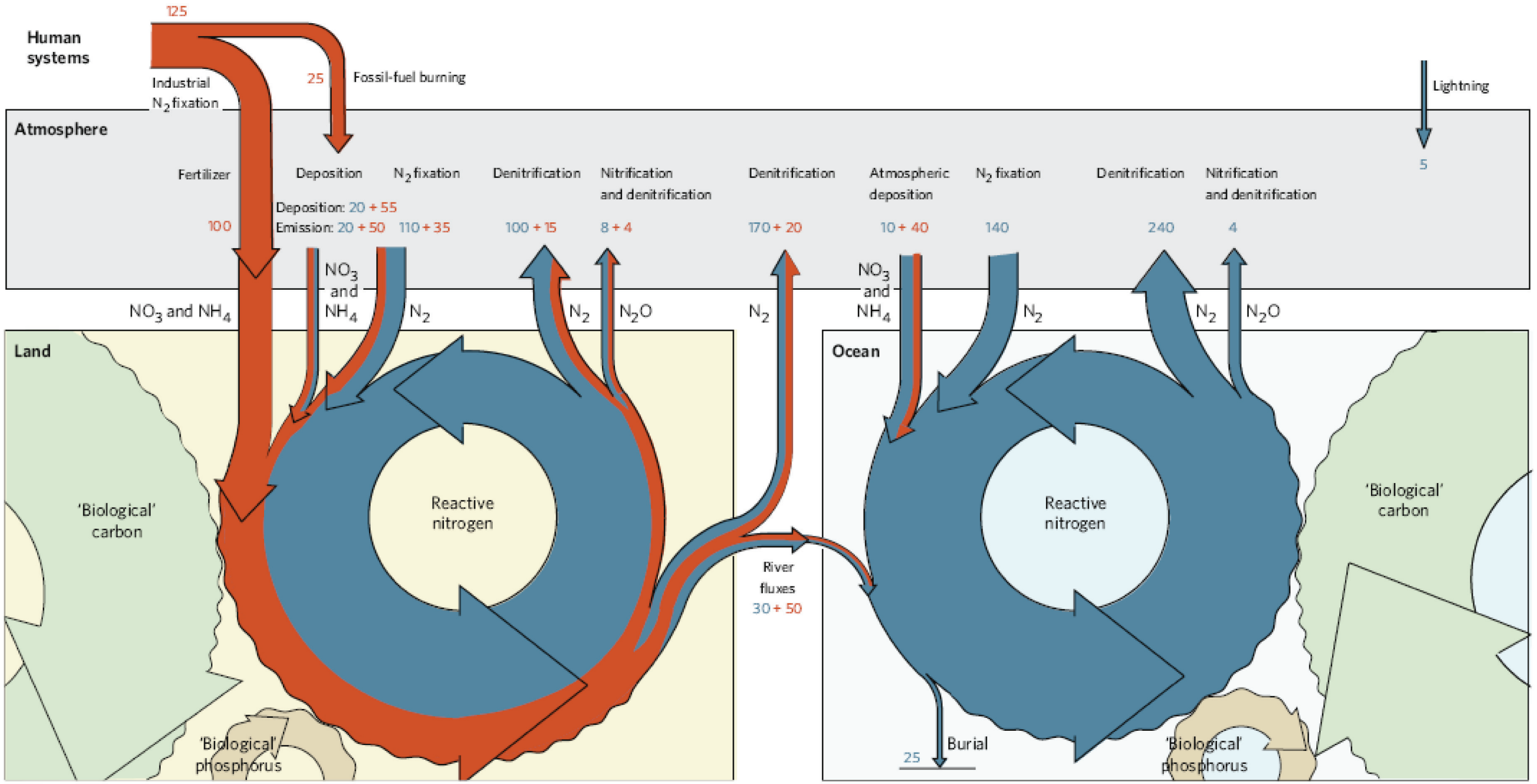

Figure 1.1: Natural and anthropogenic N fluxes to terrestrial and oceanic ecosystems. Source: Gruber and Galloway 2008.

The Southern North Sea receives anthropogenic reactive nitrogen from both the atmosphere and river loads from the densely populated watershed (Beddig et al. 1997; Brion et al. 2004). The water circulation pattern in the German Bight can impede mixing with low-nutrient Atlantic water masses, making this area especially sensitive to eutrophication (Becker 1990). The resulting problems were recognized in the 1980s, and political measures were taken to reduce riverine nutrient loads (Laane et al. 2005). Subsequent implementation of these measures, however, had only limited success: While phosphate loads have decreased dramatically due to the replacement of phosphates in detergents, the problem of elevated riverine nitrate loads in coastal areas, being the predominant form of reactive nitrogen, prevails. Although recent data indicate a gradual decrease in fluvial nitrogen runoff (Carstensen et al. 2006, J. Paetsch pers comm. 2008), the attenuation mechanisms are yet unclear and a prognosis on the future development remains difficult. In the European Water Framework Directive (WFD 2000) it is now implemented that in surface waters like coastal water bodies, among them the German Bight, good ecological and chemical conditions are to be re-established.

Consequently, anthropogenic sources, their impact on the ecosystem, and possible natural attenuation mechanisms should be closely examined for their potential to curb reactive nitrogen loadings to meet the target conditions. This implies that

1) a pristine status of the German Bight/ Southern North Sea is to be defined, to better assess the actual surplus of reactive nitrogen as compared to pre-industrial conditions,
2) the magnitude of riverine rN inputs as the predominant anthropogenic nitrogen source under present conditions has to be assessed through time, and their isotopic fingerprints, if possible, have to be identified as a means to reconstruct past inputs,
3) the role and capacity of natural attenuation mechanisms and sites has to be ascertained.

There are certain analytical challenges in these tasks. First, the main difficulty in assigning a pristine status to any ecosystem is that measurements before the 1960s are scarce, so that the original situation can only be inferred from sporadic, often subjective reports; from modelling approaches that assume certain input boundary conditions or environmental processes and rates in a pristine ecosystem (on land and in the sea); or from archives containing information about conditions under pristine conditions.

Second, rivers receive rN from different sources in the catchment area, and these different sources, internal turnover processes and water mixing complicate a source attribution. This is especially true in the transition zone from freshwater to seawater, the estuaries, which play an outstanding role in nutrient cycling and are held responsible for removal of 50% of phosphate loads and removal of 20-50% of reactive nitrogen (cf. Brion et al. and references therein). This estuarine ecosystem service can thus be expected to contribute substantially to the achievement of the ecological target conditions in the German Bight and deserves closer examination. Traditionally, estuarine turnover of dissolved water constituents has been addressed by mixing of the analyte versus a conservative property, usually salinity or temperature. Given the high turnover rate of reactive nitrogen and the variety of biogeochemical processes involved, in this case a sink within the estuary may be masked by a source that balances out the uptake, or vice versa, which limits the utility of the mixing line approach. An additional dimension in the analysis of estuarine rN cycling is opened through the application of stable isotope techniques.

1.2. Stable isotopes

Stable isotopes of natural elements have been used in many studies that address biological turnover. Most macronutrients present in plants or animals (carbon, hydrogen, oxygen, nitrogen and sulphur) have stable isotopes that, in comparison to the most abundant isotope of each element, have a different number of neutrons. As these isotopes do not decay, they are present in constant whole-earth abundances (Tab. 1.1).

Table 1.1: Elements commonly used in ecosystem studies and their stable isotopes. Given are the most and second abundant stable isotope of each element, the isotope ratio R, and the international calibration standards. Today, the primary standards are exhausted and have been replaced by secondary standard materials (Hayes 1983)

Element	Ratio	Isotope ratio $\times 10^{-6}$	Primary Reference Standard
Hydrogen	$^{2}H/^{1}H$	155.76 ± 0.1	SMOW (Standard Mean Ocean Water)
Carbon	$^{13}C/^{12}C$	11183.0 ± 16	PDB (Pee Dee Belemnite)
Nitrogen	$^{15}N/^{14}N$	3676.5 ± 8.1	AIR
Oxygen	$^{18}O/^{16}O$	2005.2 ± 0.43	SMOW
Sulphur	$^{34}S/^{32}S$	45004.2 ± 9.3	CDT (Canyon Diabolo Triolit)

This study focuses on the use of nitrogen and partly oxygen isotopes in natural abundance to characterize nitrogen turnover processes in the German Bight watershed. The isotope ratios $^{18}O/^{16}O$ and $^{15}N/^{14}N$ in different environments and sources of nitrate of rN will be discussed, Note that, while oxygen has three stable isotopes (^{16}O, ^{17}O and ^{18}O), ^{17}O will be disregarded because of its very small abundance in natural sources.

Due to small absolute changes in relative abundance of stable isotopes in natural materials, the deviations from samples to the standard material (std) are reported in the delta notation:

$$\delta^{15}\mathrm{N} = \left(\frac{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{sample}}}{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{std}}} - 1\right) \times 1000 \qquad (1.1)$$

The standards for $\delta^{15}N$ and $\delta^{18}O$, atmospheric N_2 and VSMOW (Vienna Standard Mean Ocean Water), respectively, both by definition have a δ value of 0‰.

These δ values are altered by both equilibrium processes (like evaporation of water, where the liquid phase is isotopically enriched in comparison to the vapour phase) or by kinetic processes which marginally favour the lighter isotope, whereas the heavier one is sequestered more slowly (Kendall 1998). In an ideal closed system, with continuous assimilation of the progressively enriched substrate, the product will eventually approach the value of the original substrate, so that complete use of the substrate results in no isotopic fractionation. If the nitrate is not taken up quantitatively, though, the reaction product (e.g. N in biomass) is isotopically depleted in comparison to the original nitrate source. The degree of this isotopic enrichment, defined as the fractionation factor δ, is highly variable, depending on the biological pathway, the bacterial species and the environment (Tab. 1.2).

Table 1.2: Important steps in the nitrogen cycle. Anammox is not mentioned because to my knowledge the fractionation factor has not yet been determined. Note that sedimentary processes have much lower fractionation factors in natural environments due to substrate limitation by diffusion.

Process	Reaction	Fractionation factor ε	Reference
Nitrate assimilation	$NO_3^- \rightarrow$ org. N	-6 to -20	Granger et al. 2004
Sediment denitrification	$NO_3^- \rightarrow N_2$	0 to -3	Brandes and Devol 1997; Lehmann et al. 2004
Water column denitrification	$NO_3^- \rightarrow N_2$	-22 to -30	Brandes et al. 1998
Nitrogen fixation	$N_2 \rightarrow$ N org.	0 to -1.5	Brandes and Devol 2002
Nitrification	$NH_4^+ \rightarrow NO_3^-$	-14 to -38	Casciotti et al. 2003
Ammonification	N org. $\rightarrow NH_4^+$	~0	Kendall 1998

Still, the different isotope values resulting from various turnover processes can be used for a source attribution in aquatic systems: Nitrate from anthropogenic sources usually has higher isotope values than nitrate from natural sources because it is enriched by various processes such as ammonia volatilization, harvesting of ^{15}N-depleted plants and nitrification or denitrification in soils or aquifers.

With this additional fingerprinting tool at hand, a new attempt for reconstruction of the pristine status of the coastal ecosystem in the North Sea with regard to land inputs of rN can be made: The comparison of stable isotopes in surface sediments and dated sediment cores can serve as an estimate to gauge changes in the riverborne nitrogen inputs to sediments from pre-anthropogenic times to the present-day situation, provided that the river rN loads are in some way specific in their isotope mixtures.

Furthermore, the role of rivers and estuaries as focal points of nitrogen turnover can be addressed, because different sources vary in their isotopic fingerprint. Additionally, any turnover that is masked by balanced rN concentrations due to internal turnover processes in an estuary will nevertheless lead to changes in the isotopic composition of this aggregated standing stock of rN.

1.3. Nitrogen turnover in the coastal zone

Half of the world's population lives in the coastal zone, and 17 of 24 megacities (over 8 mio inhabitants, Klein et al. 2003) worldwide are in the coastal area (Crossland 2005) even though it represents less than 20% of the world's surface area (Costanza et al. 1997). Thus, the diverse pressures on the coastal environment by human forcing are high: 95% of the world transport is moved by shipping, the coastline is modified for flood protection, the coastal ocean serves as main protein source for approx. 1 billion people (Crossland 2005), to name only a few conflicting interests.

The ecological value of the coastal zone on the other hand is high. In the seminal work of Costanza et al. (1997), the monetary value of the ecosystems belonging to the coastal zone was calculated as 12.6 trillion US\$ yr^{-1}, or 43% of the global ecosystem value. This number was later revised upwards to an even higher percentage of 53% (Sutton and Costanza 2002; Wilson et al. 2004). Regardless of the exact monetary value assigned to different coastal areas in various studies, this highlights the importance of the coastal zone as a whole.

An important property of estuaries, wetlands and continental shelves is their role in nutrient cycling (e.g. Costanza et al. 1997; Middelburg and Nieuwenhuize 2001; Seitzinger et al. 2006). Apart from processes like assimilation of reactive nitrogen by micro-organisms and modifications of reactive nitrogen like oxidation from ammonia to nitrate, the net removal- and input pathways of rN to the biosphere are of particular interest: There is some argument about whether the global nitrogen budget currently is in imbalance (Brandes and Devol 2002; Brandes et al. 2007; Codispoti et al. 2001). The net natural source, biological fixation of dinitrogen, is of minor importance in the German Bight, the Elbe and its catchment because there is no lack of fixed nitrogen. Nitrogen removal processes, on the other hand, are of focal interest because they can contribute to the environmental aim to reduce nutrient loadings. This process - and nitrification, the oxidation of ammonia to nitrate - shall thus briefly be discussed in the following section.

1.3.1. The nitrogen cycle

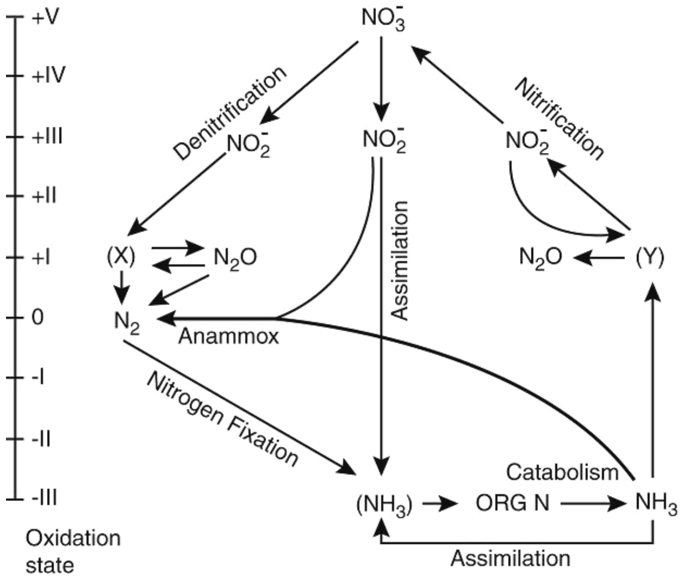

Figure 1.2: The marine nitrogen cycle. X and Y represent intracellular intermediates that are not accumulated in the water column (from Codispoti et al. 2001).

Nitrification:

Nitrification is the oxidation of ammonia to nitrite and nitrate, an oxidative process that is mediated by two different groups of bacteria (cf. Fig. 1.2). The first step, the oxidation of ammonia, is carried out by the *Nitrosomonas* bacteria group. Different bacterial strains from this group have been successfully isolated, and the fractionation that is coupled to ammonia oxidation has been addressed by Casciotti et al. (2003). Less is known about the second step in this process, nitrite oxidation to nitrate. The nitrite oxidizers have long generation times and are difficult to isolate in pure cultures. Therefore, the isotope effect of this reaction step has to my knowledge not yet been investigated.

Nitrification is a key process in soils (Mayer et al. 2001) and rivers (Deutsch et al. 2006; Mayer et al. 2002; Sebilo et al. 2006) and was found responsible for severe oxygen depletion in many rivers (Brockmann et al. 2002; Cebron et al. 2003; Soetaert et al. 2006).

Denitrification

Denitrification (Fig. 1.2) is the reduction of nitrate via nitrite and nitrous oxide to N_2, commonly mediated by *Pseudomonas denitrificans* on the following pathway:

$$4\ NO_3^- + 5\ [C] + 2H_2O \rightarrow 2\ N_2 + 4\ HCO_3^- + CO_2 \quad \text{(Kendall 1998)} \qquad (1.1)$$

It is a key reaction in the global biogeochemical cycle of N (Seitzinger et al. 2006), which takes place under suboxic and anoxic conditions in any kind of aquatic environments where organic carbon is present: in soils, groundwater, sediments, and, in suboxic/anoxic zones of the water column in upwelling areas. While the highly active upwelling zones are limited to specific areas (largest upwelling zones are found in the Arabian Sea, the Eastern Tropical North Pacific and the Eastern Tropical South Pacific (Altabet 2006), denitrification in coastal shelf sediments is much more wide-spread. It occurs in sediments of shelf seas, such as the North Sea/German Bight, and accounts for an estimated 44% of total global denitrification. In these sediments the reaction is independent of water column oxygen concentrations and takes place in a few millimetres sediment depth (Altabet 2006; Schröder et al. 1996). Organic carbon supply in nutrient-rich waters emerging from the river mouths also fuels this process. Often, sedimentary denitrification is coupled to nitrification, thus efficiently removing ammonia (An and Joye 2001; Ogilvie et al. 1997; Sebilo et al. 2006).

While denitrification rate determinations from the North Sea and German Bight are scarce (Lohse et al. 1993), recent model results highlight the importance of sediments in the German Bight for denitrification (Figure 1.3; Paetsch and Kuehn 2008).

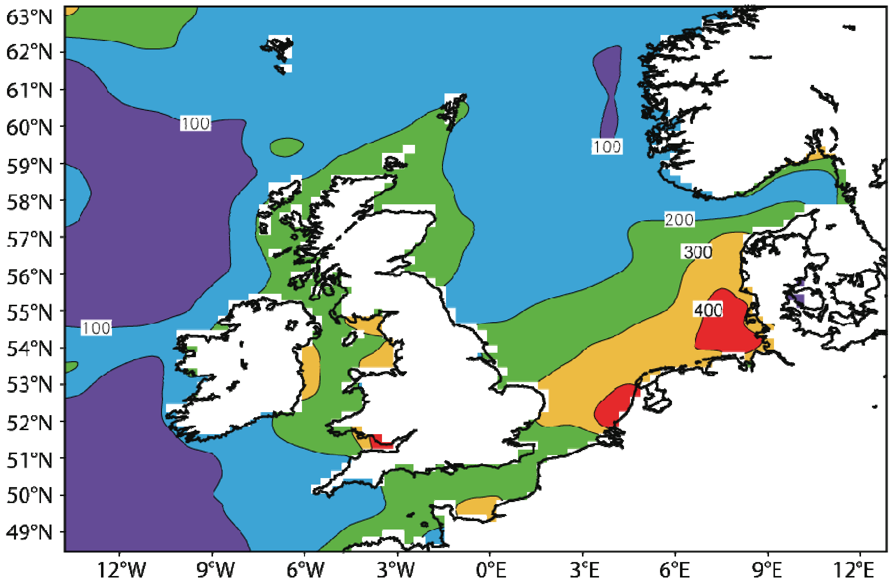

Figure 1.3: Modelled benthic denitrification in 1995. Denitrification rates were calculated from modelled rates of oxygen consumption (Paetsch and Kuehn 2008).

The assessment of sedimentary denitrification by natural abundance isotope measurements is difficult, because the reaction rate is limited by diffusion, which is associated with very low isotopic fractionation. (Brandes and Devol 1997; Lehmann et al. 2004).

A similar microbially mediated process, where reactive nitrogen (in this case nitrite) reacts with ammonia, is the anammox reaction (anaerobic oxidation of ammonia), which in situ often occurs simultaneously with denitrification (Thamdrup and Dalsgaard 2002). While it may on a global scale be equally as important as denitrification (Hietanen and Kuparinen 2008; Thamdrup and Dalsgaard 2002; Trimmer et al. 2006), it is isotopically indistinguishable by mere measurements of $\delta^{15}N$ natural abundance and thus will not be discussed separately in this thesis.

1.4. Thesis outline

This thesis is based on three publications (Johannsen et al. 2008, Dähnke et al. 2008*a*, Dähnke et al. 2008*b*), subdivided in Chapters 2, 3 and 4.

The first publication (Chapter 2) gives an overview of the specific source signature of the most significant anthropogenic reactive nitrogen source to the German Bight, riverine input, by exemplarily investigating the isotope signal of five German rivers discharging into the southern North Sea. For both stable isotope pairs present in nitrate, $^{15}N/^{14}N$ and $^{18}O/^{16}O$, weighted annual means are presented. Furthermore, the nitrate signal is attributed to different sources within the catchment area.

- **Isotopic composition of nitrate in five German rivers discharging into the North Sea (Chapter 2; Organic Geochemistry 2008)[1]**

Johannsen et al. (2008) determined nitrate isotopic signatures and nitrate concentration of five different German rivers that were sampled on a bimonthly basis. The rivers under study (Rhine, Elbe, Weser, Ems and Eider) varied considerably in their monthly nitrate loads and the seasonal variations of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$. These data represent the first seasonal measurements of nitrate isotopes in the above rivers and shall be used to validate the riverine source signature of rivers entering the German Bight and deduce biological turnover processes in the catchment and water column over the course of one year.

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[1] My own contribution to this publication (Johannsen et al. 2008) are
a) establishment validation, and operation of the denitrifier method employed for converting dissolved nitrate into N_2O amenable to mass spectrometric analysis of isotope ratios,
b) Generation of data for the river Elbe for the period from 2006-2007
c) co-work in manuscript preparation

All rivers showed seasonal variations in nitrate concentrations, with low concentrations in summer and higher concentrations in winter. δ^{15}N and δ^{18}O-NO_3^- values were anti-correlated with nitrate concentration, reaching maximum values in summer and minima in winter months.

Nitrate in these rivers was subject to different influences: We found that the high annual mean δ^{15}N values (8.2 to 11.3‰) were directly correlated with the percentage of agricultural land-use in the catchment. This high anthropogenic input of reactive nitrogen also enhanced soil nitrification, which was mirrored by low δ^{18}O values (annual means between 0.4 and 2.2‰) that were especially found at times of heavy rainfall, when nitrate leaching from soils was intensified. The seasonal variation of δ values could be attributed to increasing phytoplankton nitrate consumption in summer. Interestingly, the hydrological regime equally influenced the seasonality: One major river, the Rhine, had a somewhat exceptional role, showing far lesser seasonal variations in both nitrate concentration and isotope values than all other rivers. We attribute this to a much shorter flushing time and a unique catchment area. The Rhine is the only river that in summer continuously receives freshwater from melting water in the Alps, which is likely to mask seasonal variations in agricultural soils in the catchment.

Despite all differences, we conclude that all rivers under study entrain heavy anthropogenic nitrogen to the German Bight. Processing in the estuaries, such as removal of nitrate by sedimentary denitrification, cannot be inferred from this data set, but should not cause a significant alteration of the isotope signal carried by the rivers. The mean values can further be used to validate mass flux models which, in an inverse modelling approach, shall later be used to reconstruct pristine conditions.

- **Sub-recent nitrogen-isotope trends in sediments from Skagerrak (North Sea) and Kattegat: changes in N-budgets and N-sources? (Chapter 3; *Marine Geology* 2008)**

The second publication (Dähnke et al. 2008*a*) focuses on the fate of reactive nitrogen after it has reached the coastal zone.

In many papers on present eutrophication of the Southern North Sea, one analytical problem persists: In order to fully assess current eutrophication, data from a pristine, un-affected situation are needed.

Sediment δ^{15}N values are not altered significantly during diagenesis, and therefore mirror δ^{15}N of particulate material in the water column (Altabet 2006). In areas with high sedimentation rates, changes in δ^{15}N in sediments over time are minimal, so that dated sediment cores can serve as proxies of the past isotopic composition. Sediments from the German Bight are transported to the Skagerrak, one of the main depositional centres of the North Sea (Van Weering et al. 1993). Thus, a change in surface sediments in the German Bight should be reflected by an increase of δ^{15}N over time in sediment cores from the Skagerrak.

We analyzed both surface sediments from the North Sea and sediment cores from the Skagerrak and Kattegat to account for changes in past nutrient fluxes. Surface sediments showed a pronounced enrichment in the German Bight and the Kattegat, while values in the Skagerrak were close to the marine background of ~5‰ (Brandes et al. 2007; Sigman et al. 1997).

At the coring locations in Kattegat and Skagerrak, both short cores with good temporal resolution (multicores) and long cores (gravity cores) were taken. The long cores captured pre-industrial conditions, with sediment age ranging from a few hundreds to thousands of years. The goal was to see if, parallel to industrialization and fertilizer use in Europe, a change in $\delta^{15}N$ in sediment records could be observed.

Such a statistically significant enrichment was only visible in the Kattegat, which showed that the use of sediment cores as archives was a valuable tool to assess changes in nitrogen sources. Here, we interpret this enrichment as increasing terrestrial runoff from bordering countries. In the Skagerrak, no significant trend towards isotopic enrichment was visible. Hence, no anthropogenic nitrogen from the German Bight sediments apparently reached its main depositional centre. This implies that either transport pathways, as they are recognized today, need to be re-assessed, or anthropogenic nitrogen does not reach the Skagerrak because of prior turnover and removal via denitrification in sandy sediments of the German Bight.

The results from this publication showed that the role of estuarine turnover on nitrate reaching the German Bight is still poorly constrained, a gap that is bridged by the third publication (Dähnke et al. 2008*b*), which examines the effect of estuarine turnover on reactive nitrogen loads and isotopes is examined exemplarily in the Elbe estuary. Seasonal sampling campaigns along the salinity gradient are used to elucidate internal processing of nitrate.

- **A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary (Chapter 4; *Limnology and Oceanography* (2008), 43: 1504-1511)**

Dähnke et al. (2008*b*) exemplarily examined the estuarine nutrient retention capacity in the anthropogenically impacted estuary of the Elbe River. The goal of this study was to infer the actual role of estuaries and to evaluate if the measurement of nitrate isotopes allowed insights on the estuarine function that could not be concluded from concentration measurements alone.

In October 2005 and May, June, August and December 2006 the Elbe estuary was sampled from the freshwater to the coastal part of the river. Nitrate concentrations were almost completely conservative at salinities above 2, with little or no trace of the often postulated estuarine removal function. Maximum nitrate removal was no more than 10%. This lack of nitrate removal had previously been addressed to a balanced ratio of nitrate sources and sinks, but the measurement of nitrate oxygen and nitrogen isotopes indicated conservative behaviour of isotope mixing lines also, clearly demonstrating that no active turnover took place in the lower

Elbe estuary. This was in contrast with historical data from the ARGE Elbe archives from the late 1970s, where even concentration data alone indicated massive nitrate uptake or denitrification.

In the upper estuary, in the salinity range from 0 to 2, a significant increase in nitrate concentration occurred, which is commonly attributed to nitrification in sediments. The maximum of nitrate addition was tied to the maximum turbidity zone, supporting this interpretation. Furthermore, measuring the oxygen isotope values of nitrate, we could show that nitrification in this zone was coupled to intense denitrification, which had not been observed previously in the Elbe estuary.

Our data showed that in the past decades severe changes in the estuarine function must have occurred, turning the Elbe estuary from a nitrate sink into a significant source of nitrate. We attribute this change to continuous dredging of bio-reactive sediments to keep the port of Hamburg accessible for large container ships.

2. Isotopic composition of nitrate in five German rivers discharging into the North Sea

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Abstract

We determined concentrations and isotopic composition of nitrate in five German rivers (Rhine, Elbe, Weser, Ems, and Eider) that discharge into the North Sea. Samples were obtained on a biweekly to monthly basis and chemical and isotopic analyses were conducted for the period January 2006 to March 2007 at sampling stations situated before estuarine mixing with North Sea water. We observed maximum nitrate loads in winter and fall, when both discharge and concentration of nitrate are highest. Mean annual isotope values in nitrate ranged from 8.2‰ to 11.3‰ for $\delta^{15}N\text{-}NO_3^-$ and 0.4‰ to 2.2‰ for $\delta^{18}O\text{-}NO_3^-$. The ranges of isotope values suggest that nitrate in these rivers derives from soil nitrification, sewage, and/or manure. These and published data on other rivers in northern Europe and northern America reveal a correlation between agricultural land use (>60% in the catchment areas of rivers examined) and $\delta^{15}N\text{-}NO_3^-$ values. The rivers Rhine, Elbe, Weser and Ems show similar seasonal patterns of the isotopic fractionation of nitrate with increasing $\delta^{15}N\text{-}NO_3^-$ values and simultaneously decreasing NO_3^- concentrations during summer months, indicating that assimilation of nitrate is the main fractionation process of riverine nitrate. Isotopic signals in winter are more depleted than the mean summer isotope values, attributed to less microbial activity and assimilative processes. Load weighted nitrate $\delta^{15}N$ of the riverine input to the German Bight Coastal Water mass before estuarine mixing and processing is 10‰. The high $\delta^{15}N$ value of river nitrate is matched by high $\delta^{15}N$ of nitrate in surface sediments in the German Bight.

2.1. Introduction

According to the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic, nutrient pollution is one of the main environmental problems of the North Sea (OsparCom 2003). The south eastern North Sea, including the German Bight, in particular is facing considerable environmental problems due to high nutrient concentrations and subsequent eutrophication (OsparCom 2003; Van Beusekom et al. 2001) (Fig. 2.1). Because reactive nitrogen (rN) is a limiting factor for primary production in the North Sea (Skogen et al. 2004; Van Beusekom et al. 2001), increase of rN inputs drastically influences primary production rates. Within five decades, the riverborne rN loads to the south eastern North Sea increased 10-fold (Howarth and Marino 2006), the biomass production tripled in many regions (Cloern 2001), and even increased fivefold in the Wadden Sea region (Van Beusekom 2005). In the German Bight, oxygen depletion and phytoplankton blooms in the summer (Brockmann et al. 2002), shifts in the abundance of species (Lancelot et al. 1987), a decline of seagrass beds (Reise et al. 2005), and a massive development of green algal mats (Reise and Siebert 1997) have been attributed to eutrophication.

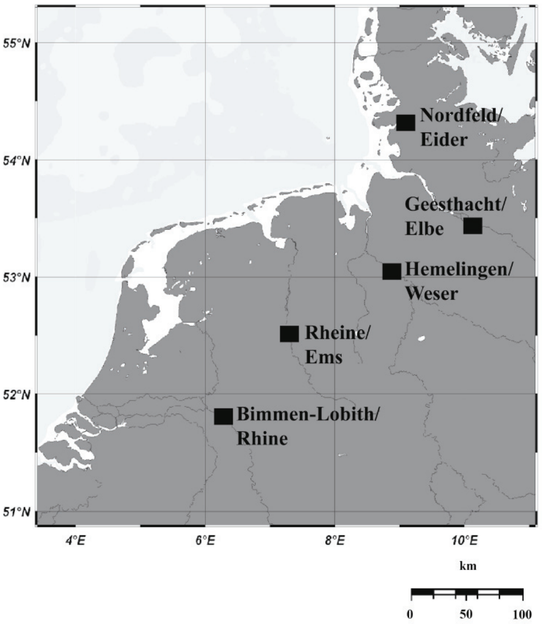

Figure 2.1: Locations of sampling stations at rivers in the northwestern part of Germany.

In an ongoing research project we aim to detect the modern contribution of riverine and atmospheric sources to the reactive nitrogen pool of the North Sea, and to reconstruct the pristine status of the North Sea by means of combined analysis of stable nitrogen isotope records in sediments and N-isotope distribution in an ecosystem model with explicit treatment of nitrogen isotopes under modern and assumed pristine loading conditions (Emeis et al. 2006). In the case of nitrate, which contains the stable isotope pairs $^{15}N/^{14}N$ and $^{18}O/^{16}O$, the stable isotope composition offers a tool for source identification, because the dual isotopic signature of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- of different sources is specific, and is therefore regarded as characteristic of origin (Kendall 1998). However, the isotopic composition of nitrate does not reflect exactly the isotope values of its source, but is altered due to transformation processes (Kendall 1998) like volatile loss of ammonia (Wassenaar, 1995), denitrification (Böttcher et al., 1990, Mariotti et al., 1981) and nitrification (Mayer et al. 2001) or uptake by organisms (Wada and Hattori, 1978). These biological turnover processes may be reconstructed by the measurement of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- (Wankel et al. 2006).

The main goal here is to identify the isotopic signal of riverborne nitrate inputs into the southeastern North Sea, its seasonal variability, and relationships to land use in the catchment and nitrate loads. To do this, we gathered data on riverine nitrogen loads and stable nitrogen and oxygen isotope composition of the rivers Rhine, Elbe, Weser, Ems and Eider discharging into the North Sea covering an annual cycle. We thus establish annual and seasonal loads of nitrate and load-weighted averages of its isotopic signature for later use in coupled mass and isotope balance models of N cycling in the German Bight.

2.2. Materials and Methods

2.2.1. Study area

The North Sea has considerable spatial gradients in biogeochemical character (Thomas 2004) and is subject to different influences on the nutrient budgets of sub-basins (Smith et al. 1997). While the northern part of the North Sea has oceanic characteristics due to water depths of up to 200 m and free water exchange with the Atlantic Ocean, water circulation in the south eastern part of the North Sea (the German Bight that has a maximum water depth of only 35 m) is strongly influenced by freshwater inputs from several large rivers and is hydrographically more isolated, causing an average flushing time of 33 days (Lenhart and Pohlmann 1997). In a numerical simulation of river nitrate fluxes, Radach and Paetsch (2007) found that mean export of total nitrogen (TN) per area for the continental rivers draining into the North Sea was 1685 kg N km^{-2} yr^{-1}, comprising approximately 25% of the mean anthropogenic N input of 7044 kg N km^{-2} yr^{-1} into the watersheds of the North Sea. Among the rivers analysed by Radach and Paetsch (2007) are several that were investigated in the course of this study; together, the five rivers analysed here drain approximately 48% of the 841,500 km^2 and are populated by approximately 53% of the entire population of 184 million persons in the North Sea watershed.

Rhine

With a length of 1320 km and an annual discharge of 69.4 km³ (Frankignoulle and Middelburg 2002), the Rhine is one of the most important water routes in Europe (Lòzan and Kausch 1996) connecting the port of Rotterdam with a highly industrialized hinterland. The catchment area is 185,000 km² (22% of the entire North Sea catchment area), of which 50% is situated in Germany. The Rhine is highly impacted by human activities; approximately 58 million inhabitants live in its catchment area. Average annual nutrient loads of the Rhine are the highest of all German rivers discharging into the North Sea (Behrendt et al. 1999).

Elbe

The Elbe River, one of the main transport waterways of central Europe, runs from the Czech Republic through Germany to the North Sea. The total length of the Elbe is 1165 km and the annual freshwater discharge is about 23 km^3. Its total drainage area is 148,000 km² (17.6% of the entire North Sea catchment area), about 25 million inhabitants live in its catchment area (Lòzan and Kausch 1996).

Weser

The Weser is a stream of 452 km length that drains 46,000 km² (5.5% of the entire North Sea catchment area and including the basins of the headwaters Fulda and Werra; (NLÖ 1995). The river Weser has an annual freshwater discharge of 10.3 km³ and the catchment area is inhabited by 9.3 million people (FGG Weser 2005).

Ems

With a length of 331 km (Lòzan and Kausch 1996), the annual water discharge of the Ems is about 2.5 km³ (Frankignoulle and Middelburg 2002). The catchment of the Ems covers an area of 18,000 km² (2.1% of the entire North Sea catchment area) which is inhabited by 3.8 million people (UBA 2006).

Eider

The smallest river examined in this study is the river Eider with a length of 108 km (Lòzan and Kausch 1996) and an annual discharge of 0.8 km³ (Bakker et al. 1999). The catchment area of 9350 km² (1.1% of the entire North Sea catchment area) is sparsely populated by 0.57 million people. Of the four rivers examined in this study, the Eider is least influenced by industrial waste water (Huntenburg et al. 1995).

2.2.2. Sampling

The water sampling was done at official LAWA (Länderarbeitsgemeinschaft Wasser) monitoring sites located upstream of the transition zone between fresh water and salt water so that alteration of nitrate concentration and isotope values by mixing with marine water can be precluded. Between March 2006 and March 2007 the rivers were sampled monthly (river Eider at the sampling station in Nordfeld) to biweekly (river Rhine in Bimmen-Lobith, river Weser in Bremen-Hemelingen and river Ems in Rheine) by staff of the authorities responsible for the monitoring sites. The river Elbe (Geesthacht) was sampled between January 2006 and December 2006. Sampling sites are indicated in Fig. 2.1.

Water volumes of 50−200 mL were taken from the surface (1−2 m water depth), filtered through PVDF (polyvinylidenefluoride) filters (0.45 µm), then frozen and sent to the GKSS Institute for Coastal Research for further analysis.

2.2.3. Analyses

Nitrate concentrations were measured using a continuous flow analyzer (Bran & Luebbe, Auto Analyzer 3). The nitrate analysis described in Bran & Luebbe Auto Analyzer Method No. G-067-92 Rev.2 (2000) is a modification of the Armstrong et al. (1967) procedure which reduces nitrate to nitrite in a column of copperized cadmium. The nitrite ion is then reacted with sulfanilamide and N-1-naphthylethylenediamine to form a red azo dye. The method has been validated according to DIN 32645 resulting in a detection limit of 5.9 µmol NO_3^- L^{-1} within the expected range of 50−450 µmol NO_3^- L^{-1} for anthropogenically influenced rivers.

Isotopic analyses of nitrogen and oxygen of NO_3^- were carried out using the denitrifier method (Casciotti et al. 2002; Sigman et al. 2001) which is based on the isotopic analysis of nitrous oxide (N_2O) produced by denitrifying *Pseudomonas* strains. The N_2O is concentrated and purified on a Gas Bench (Thermo Finnigan Gas Bench II) and the isotopic composition was determined using an isotope ratio mass spectrometer (Delta Plus XP) calibrated with ultra high purity N_2 gas against air nitrogen. Nitrogen and oxygen isotope ratios are expressed in the delta notation ($\delta^{15}N$ and $\delta^{18}O$) relative to atmospheric nitrogen and Vienna Standard Mean Ocean Water (VSMOW) in the conventional isotope terminology:

$$\delta \text{ sample [‰]} = (\text{Rsample}/\text{Rstandard} - 1) \times 1000 \qquad (2.1)$$

where R is $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of sample and standard, respectively. Results are given in per mil (‰). Analyses of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-were standardized using the internationally distributed KNO_3 reference material IAEA-N3 with an assigned $\delta^{15}N$ value of 4.7‰ versus air N_2 (Böhlke and Coplen, 1995) and a reported $\delta^{18}O$ value of 22.7‰ vs. SMOW

(Revesz et al., 1997). For further quality assurance of the results, we used an internal potassium nitrate standard that was measured with each batch of samples.

Analytical precision (one standard deviation) was better than 0.2‰ for δ^{15}N and better than 0.4‰ for δ^{18}O.

The denitrifier method measures the isotopic composition of both nitrate and nitrite, but nitrite in the examined rivers represents only a negligible portion of reactive nitrogen and has therefore been disregarded in this study.

2.2.4. Annual NO_3^- loads and load-weighted isotopic value

We used our concentration data and discharge rates for the sampling intervals to roughly calculate mass and isotope loads for the rivers examined here. The data of the flow rates used in this study were provided by the authorities responsible for monitoring at the respective sampling dates (Fig. 2.2−2.5).

The annual NO_3^--N loads were calculated by:

$$L(NO_3^- - N) = \sum_{i=1}^{n} |J_i| \times C_i \times flow_i \qquad (2.2)$$

where the whole time interval J of 12 months was divided in n sampling intervals with the duration $|J_i|$, the concentration C_i and discharge $flow_i$. The annual NO_3^--N load L (NO_3^--N) is the sum of the single loads in the sampling intervals J_i (Hebbel and Steuer 2006).

To calculate the load weighted annual isotope values, the isotope values for a certain month were multiplied with the respective concentration and weighted with the loads according to formula (3a, b):

$$\delta^{15}N_{wml} = \sum_i \delta^{15}N_i \times C_i \times flow_i / \sum_i C_i \times flow_i \qquad (2.3a),$$

$$\delta^{18}O_{wml} = \sum_i \delta^{18}O_i \times C_i \times flow_i / \sum_i C_i \times flow_i \qquad (2.3b),$$

where $\delta^{15}N_{wml}$ and $\delta^{18}O_{wml}$ are the load weighted annual isotope values, $\delta^{15}N_i$ and $\delta^{18}O_i$ are the isotope values for a certain month, C_i is the concentration in µmol L^{-1} and $flow_i$ the flow in m³ $month^{-1}$.

2.3. Results

2.3.1. Seasonal variation in concentration of nitrate and its isotopic composition in 2006

Both nitrate concentrations and isotopic composition of NO_3^- (Fig. 2.2−2.6) showed seasonal variations that were similar in all investigated rivers. In all rivers, nitrate concentrations were highest in the winter season with maxima during the months January and April. Highest nitrate concentrations were measured in the river Ems (Fig. 2.2) with a peak concentration of almost 700 µmol L^{-1} nitrate in January 2007. In the river Rhine (Fig. 2.3), the maximum concentration of 260 µmol L^{-1} was measured between January and March 2007. The river Weser (Fig. 2.4) had a maximum value of 380 µmol L^{-1} in January 2007, the river Elbe (Fig. 2.5) reached up to 350 µmol L^{-1} in April 2006, as did the river Eider in February 2006 (Fig. 2.6). Generally, nitrate concentrations were lowest between May and September. During these months, nitrate had minimum concentrations below 150 µmol L^{-1} in the rivers Rhine, Weser and Ems; less than 100 µmol L^{-1} for the river Elbe and below 10 µmol L^{-1} for the river Eider in August and September 2006.

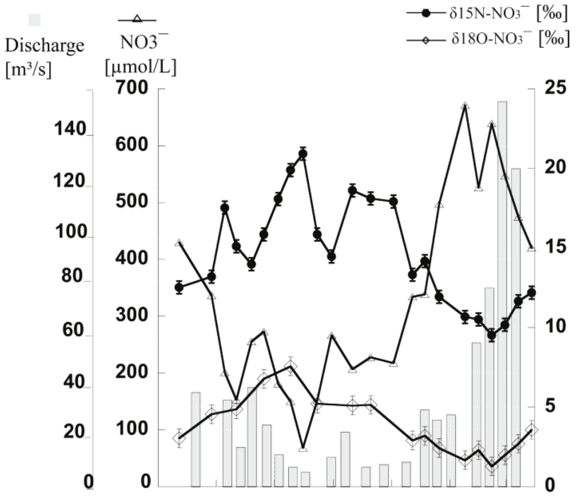

Figure 2.2: The annual cycle of discharge, nitrate concentrations and $\delta^{15}N$ / $\delta^{18}O$ of nitrate for the river Ems, March 2006- March 2007.

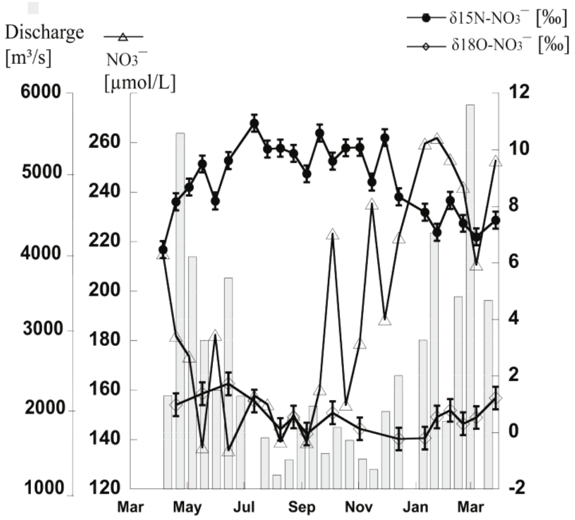

Figure 2.3: The annual cycle of discharge, nitrate concentrations and $\delta^{15}N$ / $\delta^{18}O$ of nitrate for the river Rhine, March 2006- March 2007.

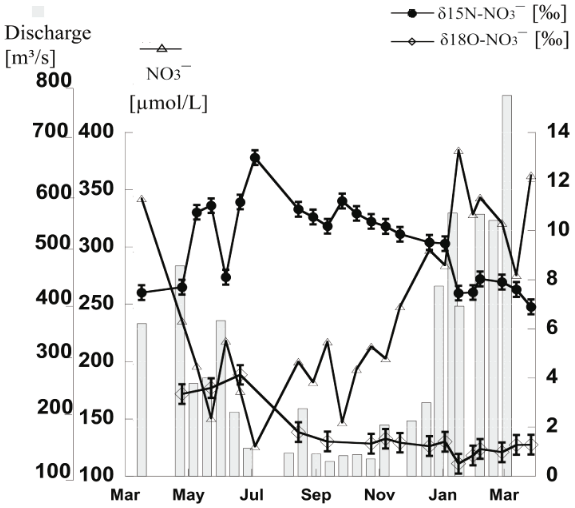

Figure 2.4: The annual cycle of discharge, nitrate concentrations and $\delta^{15}N$ / $\delta^{18}O$ of nitrate for the river Weser, March 2006- March 2007.

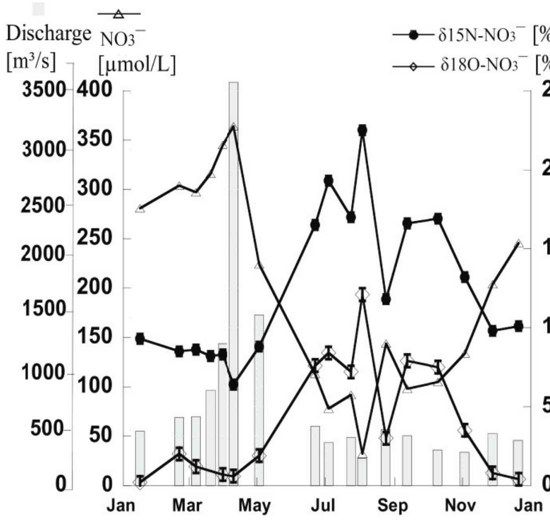

Figure 2.5: The annual cycle of discharge, nitrate concentrations and $\delta^{15}N$ / $\delta^{18}O$ of nitrate for the river Elbe, January 2006- December 2006

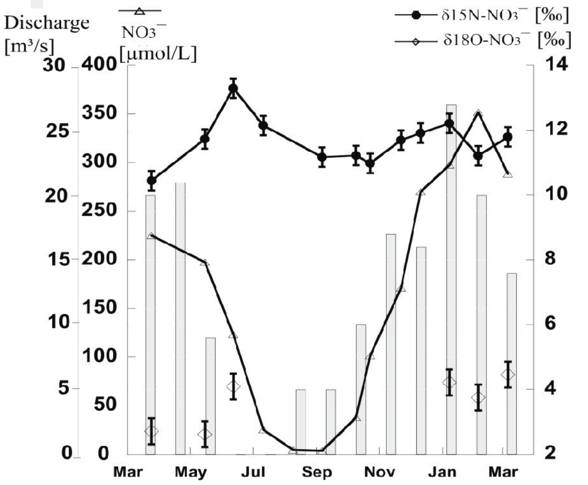

Figure 2.6: The annual cycle of discharge, nitrate concentrations and $\delta^{15}N$ / $\delta^{18}O$ of nitrate for the river Eider, March 2006- March 2007

In general, the $\delta^{15}N\text{-}NO_3^-$ values varied inversely with nitrate concentrations and the $\delta^{15}N\text{-}NO_3^-$ values were higher in summer than in winter (Fig. 2.2−2.5). Maximum values of $\delta^{15}N\text{-}NO_3^-$ were measured in the river Elbe with 22‰ in August 2006, in the Ems with almost 20‰ in July 2006, and in the river Weser with 13‰ in the same month. Also, the river Rhine had a maximum $\delta^{15}N\text{-}NO_3^-$ value of 11‰ in July 2006, when the nitrate concentrations were at their minimum. The river Eider had its maximum $\delta^{15}N\text{-}NO_3^-$ value of 13‰ in June 2006.

The $\delta^{18}O\text{-}NO_3^-$ patterns of the river-borne nitrate were also similar in the course of the year 2006. In the river Ems, highest $\delta^{18}O\text{-}NO_3^-$ values were 7.6‰ in June and July 2006; in the Weser and the Rhine, maximum values of 4.1‰ and 1.7‰, respectively, were measured in

June 2006. The $\delta^{18}O\text{-}NO_3^-$ minimum values were all measured between December 2006 and February 2007: 1.3‰ in the Ems, 0.5‰ in the river Weser, 0.4‰ and -0.2‰ in the rivers Elbe and Rhine, respectively.

2.3.2. Nitrate load and annual isotopic value

Nitrate load

At the sampling site Bimmen-Lobith, the river Rhine had a mean annual flow rate of 2500 m³ s^{-1} for the period March 2006 to March 2007, the highest discharge among the examined rivers, followed by the Elbe with 765 m³ s^{-1} (sampled from January until December 2006), the Weser with 300 m³ s^{-1} in Bremen-Hemelingen and the river Ems with 30 m³ s^{-1} at the sampling site Rheine. The mean flow rates at the sampling site of the River Eider are based on the mean monthly flow rates; accordingly, the Eider has a mean annual flow rate of 13 m³ s^{-1} in Nordfeld, the lowest among the examined rivers.

The discharges in all rivers are highest between January and April, lowest discharges occur during the summer months (Fig. 2.2−2.6). The rivers transport maximum nitrate loads during winter and spring. In annual average, the river Rhine transports the highest loads of nitrate with a mean value of 500 mol s^{-1}, compared with mean values of 200 mol s^{-1}, 85 mol s^{-1}, 15 mol s^{-1} and 3 mol s^{-1} for the Elbe, Weser, Ems and Eider, respectively. The estimated annual NO_3^--N load at the respective sampling sites are 220 kt (kilo tons) for the Rhine, 82 kt for the Elbe, 61 kt, for the Ems, 40 kt for the Weser, and 1 kt for the Eider.

Annual load-weighted isotopic value

Results of the load-weighted annual isotope values of the five rivers are given in Tab. 2.1. Eider and Ems have the highest mean annual isotope values ($\delta^{15}N\text{-}NO_3^-$/ $\delta^{18}O\text{-}NO_3^-$) of 11.2‰ / 2.2‰ for the river Ems, and a mean annual $\delta^{15}N\text{-}NO_3^-$ value of 11.3‰ for the river Eider (for which the mean annual $\delta^{18}O\text{-}NO_3^-$ was not determined). The mean annual isotope values ($\delta^{15}N\text{-}NO_3^-$ / $\delta^{18}O\text{-}NO_3^-$) for the rivers Rhine, Elbe and Weser are similar at 8.2‰ / 0.4‰, 8.5‰/1.3‰, and 8.3‰ / 0.9‰, respectively. We also estimated the load-weighted isotope values separately for the summer season (April to September) and the winter season (October to March) (Tab. 2.1).

Table 2.1: Load weighted annual isotope values in reference to the mean summer- and winter-isotope values

	Mean annual isotope value		Mean summer isotope value		Mean winter isotope value	
River	δ^{15}N-NO_3^-	δ^{18}O-NO_3^-	δ^{15}N-NO_3^-	δ^{18}O-NO_3	δ^{15}N-NO_3^-	δ^{18}O-NO_3
Rhine	8.2	0.4	8.4	0.6	7.9	0.3
Elbe	8.5	1.3	11.7	3.9	7.8	0.8
Weser	8.3	0.9	9.3	1.3	8.1	1.0
Ems	11.2	2.2	14.3	3.2	10.6	1.9
Eider	11.3	n.a.	11.6	n.a.	10.8	n.a.

The data illustrate that load-weighted isotope values are generally lower in the winter season. The mean δ^{15}N-NO_3^- values in summer are 0.5‰−3.9‰ higher than in winter, whereas the mean δ^{18}O-NO_3^- values in summer are 0.3‰−3.1‰ higher than in winter.

2.4. Discussion

In the discussion, we examine our new and published data in relation to land use in the river watersheds, discuss processes responsible for seasonal variations observed, and finally assess the riverine contribution to the nitrate pool of the German Bight.

2.4.1. Influence of watershed land-use on isotopic character

To a first approximation, mixtures of nitrate in the rivers under study reflect land-use patterns in river basins, an observation in line with previous studies (Harrington et al. 1998; Mayer et al. 2002; Voss et al. 2006). When plotting the annual load-weighted δ^{15}N-NO_3^- values of the rivers Rhine, Elbe, Weser, Ems and Eider (Tab. 2.1) versus the respective land use data (Tab. 2.2), and including data presented by Voss et al. (2006) for rivers discharging into the Baltic Sea, and of Mayer et al (2002), for rivers draining watersheds in the northeastern U.S., we find a robust positive correlation (r^2= 0.71, n= 33) between δ^{15}N-NO_3^- values and the proportion of arable and urban land in the catchments (Fig. 2.7). Nitrate-nitrogen (e.g. organic fertilizers) leaching from agricultural soils and nitrate deriving from municipal waste water (sewage) is characterised by high δ^{15}N-NO_3^- values (4−9‰ and more than 10‰, respectively, Grischek et al. 1997), so that the δ^{15}N-NO_3^- values rise with increasing proportion of agricultural and urban land use. The δ^{15}N-NO_3^- values for the river catchments with more than 60% of agricultural and urban land use are all above 7‰. We suggest, therefore, that elevated δ^{15}N-NO_3^- values in rivers draining catchments with significant urban and agricultural land use are caused by nitrate from sewage and/or manure.

Table 2.2: Land use of the sub-basins according to CORINE landcover.

River	Catchment area [km^2]	Sub-basin	Area; Sub-basin [km^2]	Agriculture [%]	Urban [%]	Forest [%]	Others [%]
Rhine	185,000	Lower Rhine	18,900	52.6	17.6	29.1	0.8
Elbe	148,300	Middle Elbe/Elde	16,600	69.5	4.2	23.5	2.8
Weser	46,300	Middle Weser	8,400	69.3	7.5	21.4	1.8
Ems	17,800	Upper Ems	4,800	77	8.9	9.9	4.2
Eider	9,400	Eider/Treene	2,200	87	4	6	3

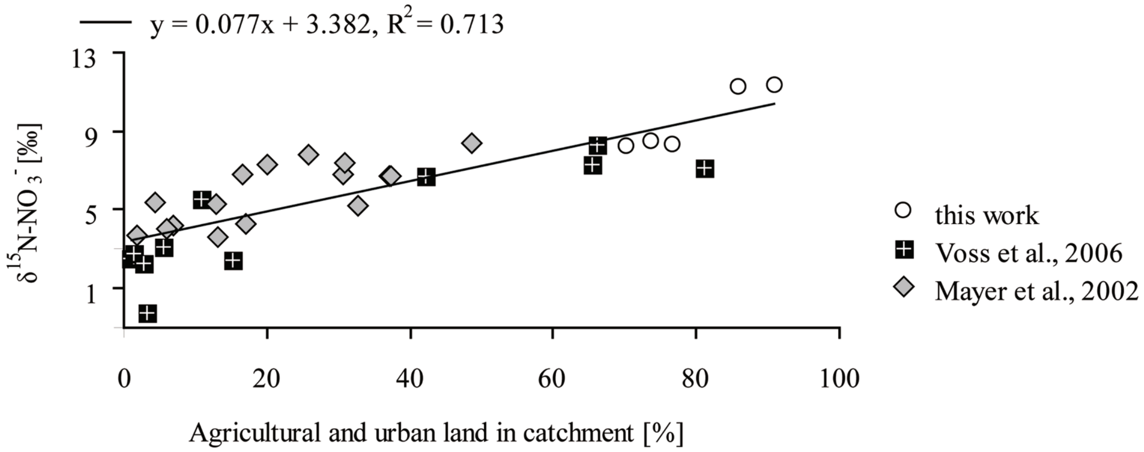

Figure 2.7: $^{15}N\text{-}NO_3^-$ plotted against and urban land use values for rivers in North America and Europe. Land use data for the rivers Rhine, Elbe, Weser, Ems and Eider are based on CORINE data (Table 2.2). Rivers in the Baltic Sea catchment were analysed by Voss et al. (2006). Data for 16 rivers in NE America are from Mayer et al. (2006). Note that, in contrast to the two other data sets, the data presented in Mayer et al. (2006) are not load weighted data.

2.4.2. Identification of nitrate sources and sinks based on the isotopic composition

The isotopic value of riverine NO_3^- is a collective signal of various sources contributing to the nitrate pool in the river. Biogeochemical processes in soils and aquifers affect the isotopic composition of reactive nitrogen inputs before they enter the rivers, so that the direct attribution to the NO_3^- sources is complex (Komor and Anderson 1993). In the rivers under study, isotopically high $\delta^{15}N\text{-}NO_3^-$ values between 8‰ and 12‰, and $\delta^{18}O\text{-}NO_3^-$ values between 0‰ and 3‰ characterize the overall annual signal. The $\delta^{15}N\text{-}NO_3^-$ values are in agreement with data from other rivers of Northern Europe under anthropogenic influence, such as the Oder or the Vistula rivers (Voss et al. 2006), and identify NO_3^- as deriving from sewage, manure and/or soil nitrification (Kendall 1998) (Fig. 2.8).

When binning the mean annual isotopic values into mean winter (October to March) and mean summer (April to September) isotopic values, the load-weighted $\delta^{15}N\text{-}NO_3^-$ are approximately 0.5‰ – 3.9‰, and the $\delta^{18}O\text{-}NO_3^-$ are 0.3‰ – 3.1‰ more depleted in the winter than in the summer season. This is due to seasonal changes in biological activity that causes variations in nitrate concentrations, and is associated with different isotopic fractionation processes. In general, biological processes cause an enrichment of heavy isotopes (^{15}N and ^{18}O) in the residual NO_3^- pool because organisms preferentially incorporate the light isotopes over the heavy isotopes (Kendall 1998). Since biological activity increases at higher temperatures, enrichment of ^{15}N and ^{18}O in the residual NO_3^- pool is to be expected in the summer season.

In regions with excess anthropogenic N input, a dominant source of river nitrate is nitrate leaching from soils (Brion 2004, van Breemen et al. 2002), influencing both the nitrate concentration and its isotopic composition in the rivers. This source is isotopically elevated, because it is a residue of rN that has undergone kinetic fractionation in several processes and locations. After application of organic fertilizers (like manure with a $\delta^{15}N\text{-}NO_3^-$ of 10–20‰; Aravena et al. 1993; Heaton 1996) and mineral fertilizers (with a $\delta^{15}N\text{-}NO_3^-$ of 0±4‰; Kendall 1998) to agricultural soils, ^{14}N is preferentially removed by ammonia volatilization (Wassenaar 1995), by harvesting ^{15}N-depleted crops, or by denitrification in suboxic aquifers (Amberger and Schmidt 1987) and soils (Grischek et al. 1997). The residual ^{15}N-enriched rN pool is in part nitrified in water-unsaturated soils (Wassenaar 1995), making nitrification an important source of nitrate in soils.

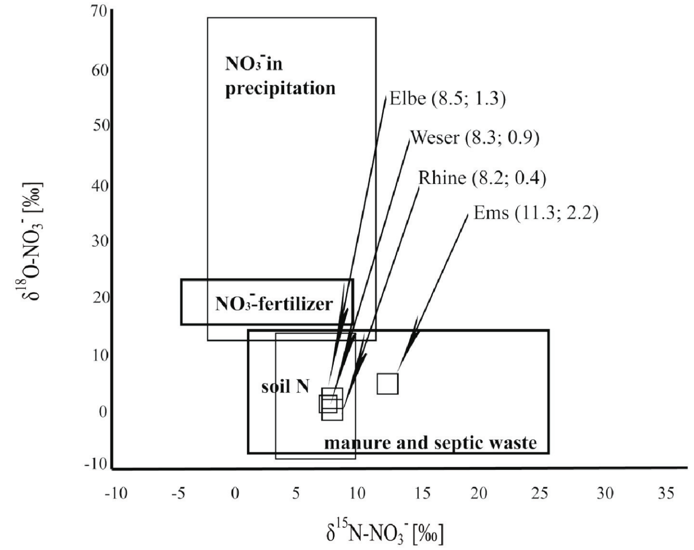

Figure 2.8: General fingerprints of NO_3^- sources in a diagram of $\delta^{15}N$ and $\delta^{18}O$ (modified from Kendall 1998) and character of nitrate isotopic composition in the rivers examined here.

Because nitrification leaves an imprint on $\delta^{18}O$ in nitrate, the data on $\delta^{18}O\text{-}NO_3^-$ for the rivers under study (between 0.4 and 2.2‰) may serve to identify nitrate derived from soil nitrification. Based on the assumption that nitrification acquires three oxygen atoms, two of which are assumed to be derived from ambient water, whereas the third atom comes from dissolved (atmospheric) oxygen (Anderson and Hooper 1983; Yoshinari and Wahlen 1985), the expected range of $\delta^{18}O$ values of nitrate produced by nitrification can thus be calculated from known $\delta^{18}O\text{-}NO_3^-$ values for atmospheric oxygen ($\delta^{18}O\text{-}O_2$) and ambient water ($\delta^{18}O\text{-}H_2O$):

$$\delta^{18}O\text{-}NO_3^- = \tfrac{2}{3}\,(\delta^{18}O\text{-}H_2O) + \tfrac{1}{3}\,(\delta^{18}O\text{-}O_2) \qquad (2.4)$$

(Mayer et al. 2001).

The atmospheric oxygen is known to have a $\delta^{18}O$ value of 23.5‰ (Kroopnick and Craig 1972), and the ambient water, which is expected to be similar to the isotopic value in the river water and in the precipitation, can be derived from previous studies: In the Rhine basin, Buhl et al. (1991) measured $\delta^{18}O\text{-}H_2O$ values of -8‰ in the precipitation, other estimations for $\delta^{18}O\text{-}H_2O$ values in precipitation for the river catchments of the rivers Rhine, Elbe, Weser and Ems range from -8.1‰ and -8.6‰ (Bowen and Revenaugh 2003; Bowen et al. 2005; Bowen and Wilkinson 2002; OIPC 2007). For the period 2002−2007 measured $\delta^{18}O\text{-}H_2O$ of river water for the rivers Rhine, Elbe, Ems and Weser ranged between -7‰ and -9.1‰ (W. Stichler, pers. comm., 2008). Inserting these values into Eq. (2.4) results in an expected value for nitrate from nitrification around 2‰ which is close to the mean $\delta^{18}O\text{-}NO_3^-$ values for the river under study between 0.4 and 2.3‰. Thus, the $\delta^{18}O$ values in nitrate imply nitrification as a dominant source, and soil leaching as an important transport mechanism of nitrate into river water. That soil leaching does indeed influence the isotopic composition of nitrate is suggested by data from a massive spring flood event in April 2006 in the Elbe catchment, when a significant input of soil nitrate is indicated by increased concentrations paired with decreased $\delta^{18}O$ in nitrate (Fig. 2.5). At this time of year biological activity was inhibited by low temperatures, so any changes in the isotopic composition must be a consequence of input from soils.

Our results are in line with a study by Deutsch et al. (2006), who investigated drainage waters from soils in a small river catchment in northern Germany. These waters had concentration-weighted $\delta^{15}N$ and $\delta^{18}O$ in nitrate of 10.4‰ and 4.7‰, respectively, and the low $\delta^{18}O$ was attributed to nitrification. In a mixing model, these authors calculated that 86% of the nitrate in that particular river derived from soil drainage. From the relatively low $\delta^{18}O$ values in nitrate of the rivers under study, we also derive that atmospheric deposition with high $\delta^{18}O$ values in nitrate between 25 and 70‰ e.g. (Durka et al. 1994; Kendall 1998) does not contribute a high share of nitrate. This in line with a study of Mayer et al. (2002) who revealed that the influence of atmospheric deposition to the isotopic composition of riverine nitrate in watersheds with significant agricultural and urban land use is low due to the comparatively low nitrate concentrations in rainwater. In any case the elevated isotopic signature of nitrate inputs from the apparent main sources (soil water, sewage and manure) is further modified by biological activity in the river itself, as inferred from different $\delta^{15}N$ values in the biologically active and inactive seasons (Kendall 1998). We measured relatively depleted $\delta^{15}N$ of riverine NO_3^- in fall and winter, when biological activity in the river itself was inhibited by low temperatures. Because phytoplankton activity is highest in the spring and summer months, significant decreases in river nitrate concentrations and increases in $\delta^{15}N$-NO_3^- characterised the time series from June until September (Fig. 2.2−Fig. 2.5). The characteristic seasonal variation with minimum nitrate concentrations during summer and increase to a late fall or winter maximum is a result of biological uptake, consumption of nitrate and nitrite (Berounsky and Nixon 1985), and reflects the annual phytoplankton production cycle with high nitrate assimilation rates in summer (Van Beusekom and De Jonge 1998).

Nitrate concentrations and its isotope composition are correlated in each river (except Rhine and Eider), but the slope varies amongst the five rivers (Fig. 2.9). The strong correlation of $r^2 \geq 0.77$ for the plot of nitrate against $\delta^{15}N$-NO_3^- and the correlation of $r^2 \geq 0.52$ for the plot of nitrate against $\delta^{18}O$-NO_3^- in the rivers Elbe, Weser and Ems indicates an important influence of changing nitrate concentrations on the isotopic value, suggesting fractionation during nitrate consumption. The expected fractionation of $^{18}O/^{16}O$ and $^{15}N/^{14}N$ with a ratio of 1:1 for assimilation (Granger et al. 2004) is not given for the rivers examined here. We assume that additional transformation processes or additional nitrate sources contribute nitrate with low $\delta^{18}O$ values (e.g. nitrate from soil nitrification) and mask the fractionation caused by assimilation.

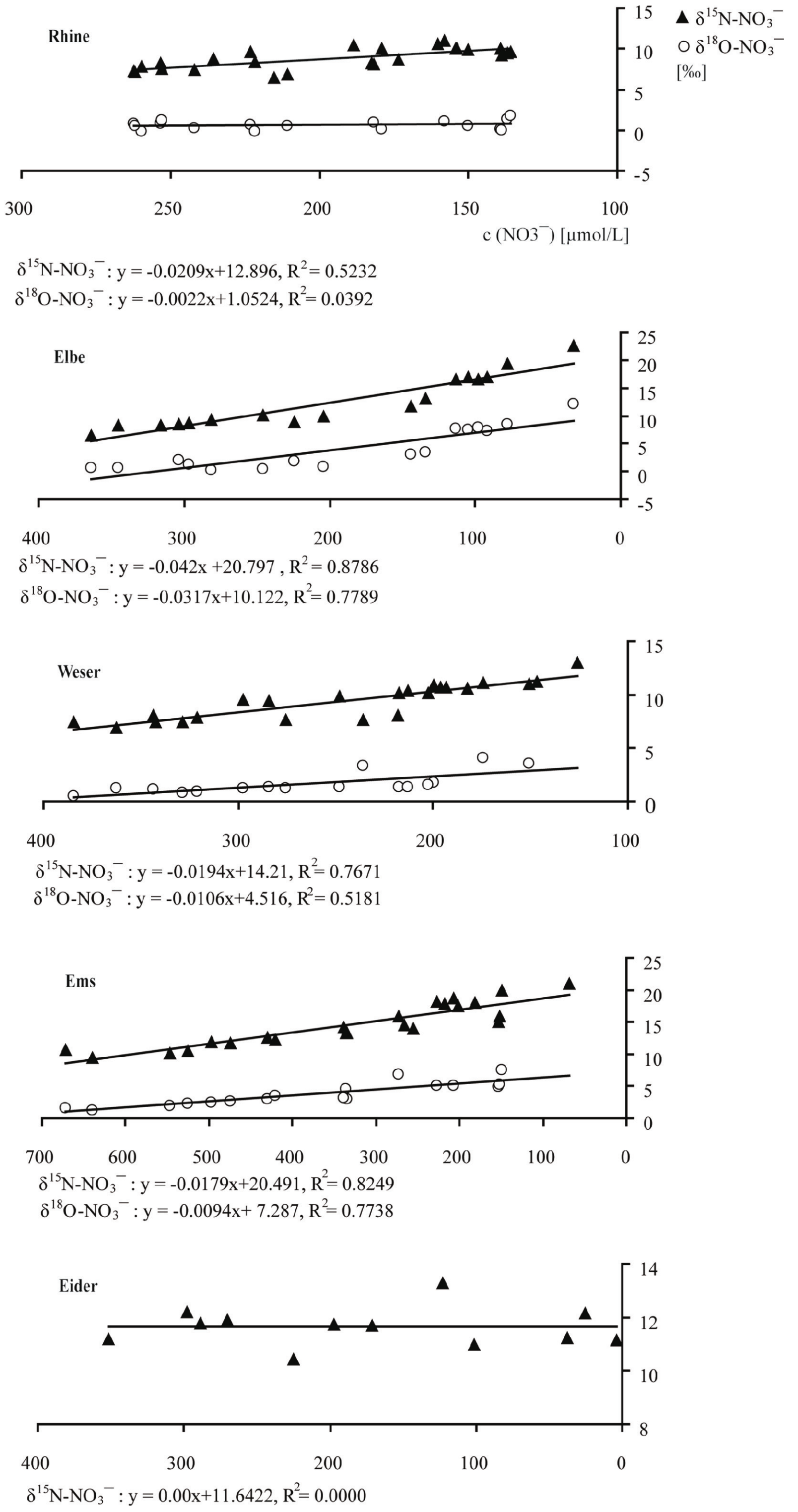

Figure 2.9: Plot of isotopic values against nitrate concentrations. See text for discussion.

In the river Rhine, the correlation between δ^{15}N-NO_3^- values and nitrate concentration is weak (r^2= 0.52, Fig. 2.9). The NO_3^- concentrations show seasonal variations with low nitrate concentrations in summer and high concentrations in winter, whereas the variation of δ^{15}N-

NO_3^- values is low comparing to the rivers Elbe, Weser and Ems. $\delta^{18}O$-NO_3^- values do not vary at all, and show no apparent fractionation (Fig. 2.3 and 2.9). We hypothesize that the hydrodynamic regime of the Rhine influences nitrate concentrations in dependence on season. The discharge of the river Rhine is dominated by two different hydrological regimes: from May to November the greater part of the discharge is derived from the Swiss part of the drainage basin, whereas from December to May the discharge consists largely of water from the German and French parts of the drainage basin because the precipitation in the Swiss Alps is largely retained as snow. Water components from higher catchment areas are still dominant at lowlands of the river Rhine (Stichler et al. 2005). Hence, the summer flow is supported by a base flow of snowmelt and precipitation in the Alps, the winter flow consists of surface runoff from the German/French part of the drainage basin (Davis and Keller 1983). The seasonal behaviour of NO_3^- concentration in the river Rhine can be attributed to the fact that the NO_3^- concentration in the summer snowmelt is lower than the NO_3^- concentration in the winter flow (Dijkzeul 1982), largely derived from surface runoff influenced by leaching of fertilizers from arable land in the drainage basin (Kattan et al. 1986, Probst 1985). Because of the different hydrological regimes, it remains difficult to evaluate the transformation processes influencing the isotopic composition of nitrate. Any kind of fractionation signal is likely to be masked by the varying source signature. Furthermore, we speculate that the high discharge in the river Rhine (Fig. 2.3) associated with a short water residence time is responsible for comparatively low fractionation of NO_3^- in the river Rhine. Water residence time is an important factor in nutrient processing efficiency (Kadlec 1994, James et al. 2006) and the development of plankton communities (Lack 1971, Winner 1975). Generally, phytoplankton abundance increases with higher residence time and reduced velocity (Lack 1971, Jones 1984, Descy et al. 1987). The lower the concentrations of nitrate and the shorter the residence time of micro-organisms in river water, the smaller the fractionation (Kendall 1998).

Considering the river Eider, the seasonal variations of nitrate concentrations are largest among all rivers examined. Nitrate concentrations in summer decrease below 10 µmol L^{-1} from 350 µmol L^{-1} in winter months. It is remarkable that the $\delta^{15}N$-NO_3^- values vary only in the narrow range between 10‰ and 13‰ and do not show the characteristic pattern of maximum isotopic values in summer and minimum isotopic values in winter (Fig. 2.6), suggesting no fractionation and no increase of $\delta^{15}N$-NO_3^- over the course of the year. Because the nitrate concentrations from July until early fall are below 10 µmol L^{-1}, we assume that the nitrate pool is almost completely assimilated in the summer months. In small rivers such as the river Eider, nitrate in river water is generally in close and frequent contact with benthic detritus, biofilms and sediments (Hamilton et al. 2001). Under these conditions, nitrate is presumably rapidly and completely turned over several times. A complete conversion leads to a lack of apparent fractionation (Kendall 1998), which is consistent with our data.

Nitrate, regardless of its source, is subject to denitrification within the riverine ecosystem (Howarth 1996; Kellman and Hillaire-Marcel 1998) in suboxic zones of water and sediments. Bacterial denitrification converts NO_3^- to N_2O and N_2, the fractionation resulting in the progressive enrichment of ^{15}N and ^{18}O in the residual nitrate (Kendall 1998). The process is linked to environments which are oxygen limited with a readily oxidizable carbon source. Because the oxygen concentrations in all rivers examined here significantly exceed the threshold of 0.2 mg L^{-1} (Painter 1970) at all seasons, denitrification in the water column is unlikely to contribute to the seasonal variability. However, denitrification may consume nitrate from the overlying water column (Kaushik et al. 1981) in anaerobic sediments. Benthic denitrification acts as a significant sink since nitrate diffusing across the water-sediment interface is completely consumed irrespective of its isotopic composition (Reinhardt et al. 2006). Sebilo et al. (2003) assessed the feasibility of using $\delta^{15}N\text{-}NO_3^-$ as an indicator of denitrification at the scale of large river systems and hypothesized that benthic denitrification does not affect the isotopic composition of riverine nitrate significantly when the rate limiting step is the diffusive migration of nitrate through the water-sediment interface (^{15}N isotopic enrichment factor about -2‰). We derive from this study and from other studies carried out in different kind of water bodies that denitrification in sediments does not result in apparent fractionation of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ (Brandes and Devol 1997, Lehmann et al. 2003, Reinhardt et al. 2006, Sebilo et al. 2003). Hence, sedimentary denitrification cannot be traced by isotope techniques, and our data are not suited to evaluate this process for the rivers under study.

According to Howarth (1996) and Schröder et al. (1996), benthic denitrification eliminates between 20% and 80% of nitrate input to rivers, whereas recent studies suggest that this rate has significantly decreased (Fulweiler et al. 2007, Savage 2005). Further investigations of processes in sediments are required to give a complete picture of N-cycling in riverine ecosystems.

2.4.3. The riverine contribution of nitrate to the German Bight

Eutrophication of the seas and estuaries in Europe is mainly attributed to nutrient inputs from the land, with rivers as the main carriers (Behrendt et al. 2002). Nitrogen budgets and models of nitrogen in- and output of river systems include different pathways, e.g. point discharges, paved urban areas, atmospheric deposition, tile drainage and groundwater (Bach et al. 1999; Behrendt 1996; Kunkel and Wendland 2006; Luc and Bernhard 2006). A discrepancy between nutrient loading of river systems and the actual nutrient load is a general feature of all budgets, and most of the anthropogenic N loading of the watersheds is lost in transit through the hydrological system before reaching oceans by riverine transport (Howarth et al. 1996; Alexander et al. 2000; Radach and Paetsch 2007). In this study, we only considered the isotopic signals of nitrate in rivers before entering the estuarine transition zones between fresh water and salt water. The turnover of nitrogen is expected to be most intense in this transition zone, because the tidal circulation generally causes a long residence time of water (De Wilde and De Bie 2000). However, the data from this study suggest that river discharge delivers nitrate with high $\delta^{15}N\text{-}NO_3^-$ between 8‰ and 12‰, and with low $\delta^{18}O\text{-}NO_3^-$ between 0‰ and 3‰ to the German Bight. We do not expect considerable change in the isotopic composition of NO_3^- in the main course of the river before reaching the German Bight, because denitrification in the water column, accompanied with fractionation of nitrate, can be excluded. Since denitrification in the sediment does not cause a significant enrichment of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (Lehmann et al. 2003; Sebilo et al. 2003), the isotopic signal measured at the sampling stations before estuarine mixing might be stable along the course of the river. Recent studies in the estuary of the river Elbe doe not suggest alteration of $\delta^{15}N$ and $\delta^{18}O$ in nitrate, because the measured range along the estuary and in the German Bight Coastal Water mass (salinities between 31 and 33) is between 7‰ and 10‰ for $\delta^{15}N\text{-}NO_3^-$ and around 0‰ for $\delta^{18}O\text{-}NO_3^-$ (K. Dähnke, pers. comm., 2007), a clear imprint of riverine nitrate.

2.5. Conclusions

The primary goal of this study was to assess the riverine background signature of rivers discharging into the southern North Sea. We examined the rivers Rhine, Elbe, Weser, Ems and Eider for the period of one year during January 2006 – March 2007. The data give evidence that riverine nitrate of the rivers examined in this study originally derives from anthropogenic input, e.g. sewage and/or manure which is consistent with high agricultural and urban land use in the catchment areas. In the rivers Rhine, Elbe, Weser and Ems we observed seasonal variations of increasing $\delta^{15}N\text{-}NO_3^-$ values with decreasing NO_3^--concentrations during summer, whereas such a variation of the isotopic composition of NO_3^- was not observed in the river Eider. We attribute this concentration-dependent effect to bacterial or phytoplankton nitrate assimilation, which is the dominant nitrate removal process in the rivers during biologically active seasons that coincide with smaller discharges. The isotopic signal is more depleted in ^{15}N and ^{18}O during winter, when riverine nitrate fluxes are maximal, and bears an imprint of nitrate leaching from soils at times of high precipitation. Generally low $\delta^{18}O\text{-}NO_3^-$ values point towards significant nitrate inputs from nitrification in soils, where oxygen derives partly from ambient water and accordingly has a low $\delta^{18}O$ signature.

Future investigations have to verify that seasonal variations of nitrate concentrations and isotopic composition measured during this study are representative and typical for each river. If the data turn out to be robust, we will on the one hand be able to estimate nitrate isotopic composition in river discharges based on land-use patterns in river catchments, which are available. On the other hand, the isotopic mixture of each river may possibly be extrapolated from individual $\delta^{15}N$:nitrate relationships for each river. In light of available data on land-use changes and river loads in past decades, both steps will greatly advance our ability to numerically model nitrogen transport and isotopic mixtures from land to the North Sea in the past. In an inverse modelling approach with a numerical ecosystem model, we then expect to be able to reconcile combined mass- and isotope-balances with data from suitable archives of pristine conditions.

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3. Sub-recent nitrogen-isotope trends in sediments from Skagerrak (North Sea) and Kattegat: changes in N-budgets and N-sources?

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Abstract

We determined $^{15}N/^{14}N$ ratios of total nitrogen in surface sediments and dated sediment cores to reconstruct the history of N-loading of the North Sea. The isotopic N composition in modern surface sediments is equivalent to and reflects the isotopic mixture of oceanic nitrate on the one hand ($\delta^{15}N$ = 5‰) and the imprint of river-borne nitrogen input into the SE North Sea ($\delta^{15}N$ up to 12‰ in estuaries of the SE North Sea) on the other hand. We compare the results with $\delta^{15}N$ records from pre-industrial sediment intervals in cores from the Skagerrak and Kattegat areas, which both constitute significant depositional centres for N in the North Sea and the Baltic Sea/North Sea transition. As expected, isotopically enriched anthropogenic nitrogen was found in the two records from the Kattegat area, which is close to eutrophication sources on land. Enrichment of $\delta^{15}N$ in cores from the Skagerrak - the largest sediment sink for nitrogen in the entire North Sea - was not significant and values were similar to those found in sediment layers representing pre-industrial conditions. We interpret this isotopic uniformity as an indication that most riverine reactive nitrogen with its characteristic isotopic signature is removed by denitrification in shallow water sediments before reaching the main sedimentary basin of the North Sea.

3.1. Introduction

The present-day coastal ocean is loaded with nutrients from continental runoff and from the atmosphere, and both changed nutrient element mass fluxes and inter-element ratios are held responsible for ecological changes observed over the past decades in estuaries, coastal waters, and entire shelf seas (Crossland 2005; Howarth 1996; Nixon 1995; Nixon et al. 1996; Rabalais 2004). As in other coastal seas, a tenfold increase in N-loads of rivers and the atmosphere in the North Sea induced eutrophication, the spread of oxygen deficient conditions in bottom waters, the demise of macrophytes in many coastal settings, increases in harmful algal blooms, and changes in the food web structure (Galloway et al. 2003; Lancelot et al. 1987; OsparCom 2003; Smith 2003; Van Beusekom 2005). An important step to curb the loading of coastal oceans with nutrients originating from river runoff in Europe is the European Water Framework Directive (WFD, 2000), which requires that member states of the EU re-establish good ecological conditions in riverine and coastal environments. In this endeavour the most important challenge is the reduction of reactive nitrogen loads. Whereas the reduction of P loads in many rivers has been quite successful due to replacement of phosphates in detergents and enhanced waste water treatment, success of nitrate reduction measures has been poor, and removal from runoff by biological treatment is significantly more costly.

A further problem in attaining the environmental goals is the definition of the ecological target conditions, because direct observations on nutrient levels and ratios in rivers and coastal oceans are scarce before the 1960s. Instead, numerical models are commonly used to estimate nutrient runoff from pristine river catchments (Behrendt and Opitz 1999; Seitzinger et al. 2002). Here, we evaluate the use of stable isotope ratios in nitrogen of sediments to reconstruct reactive nitrogen discharges from land into the North Sea and westernmost Baltic Sea. This approach has previously been employed in tracing eutrophication through time in the Baltic Sea (Struck et al. 2000; Voss et al. 2005; Voss and Struck 1997) and in individual fjords, estuaries, and embayments of the North Sea (Clarke et al. 2003; Clarke et al. 2006) and elsewhere (Church et al. 2006).

Suitable sediment archives are from sediment accumulations in the Skagerrak and Kattegat sediment basins; they collect material from extended submarine catchments, which in turn received reactive nitrogen that has been produced and cycled in densely populated and industrialised watersheds of NW Europe in the course of industrialisation over the last 150 years.

Our objectives here thus are to establish the present-day pattern of δ^{15}N in surface sediments, and then to trace the history of DIN input from anthropogenic sources by analysing N mass accumulation rates and N isotopic composition in dated sediment records of the last 150 years – the period of industrialization (Galloway et al, 2003) – to obtain an estimate of changes in the N isotopic composition that are coupled to increasing anthropogenic nitrogen input. These data are then compared with those of sediments deposited before the onset of industrialisation and the increasing production of reactive nitrogen. To substantiate results of isotope measurements, we also use the mass accumulation rate of sedimentary nitrogen, and changes in the ratio of nitrogen to alumosilicate material in the samples that provide information on changing N-mass-fluxes due to eutrophication.

3.2. Working Area

The North Sea catchment is home to 180 million inhabitants and is a large export source for reactive nitrogen (Howarth 1996). Inputs of nitrogen vary from year to year, but have increased significantly since the 1950s (Behrendt et al. 2003; Paetsch and Radach 1997). This reactive nitrogen is completely assimilated by organisms, but only a small portion (< 1%) of the biomass is deposited as sediment; the rest is mineralised and recycled (De Haas et al. 2002). On shallow sea floors of the southern, central and eastern North Sea, wind-induced currents, tides, and/or wave action resuspend the sedimented material, and residual currents transport it to depositional areas where energy at the sea floor is low enough to preclude resuspension (Eisma 1990; Puls and Sündermann 1990).

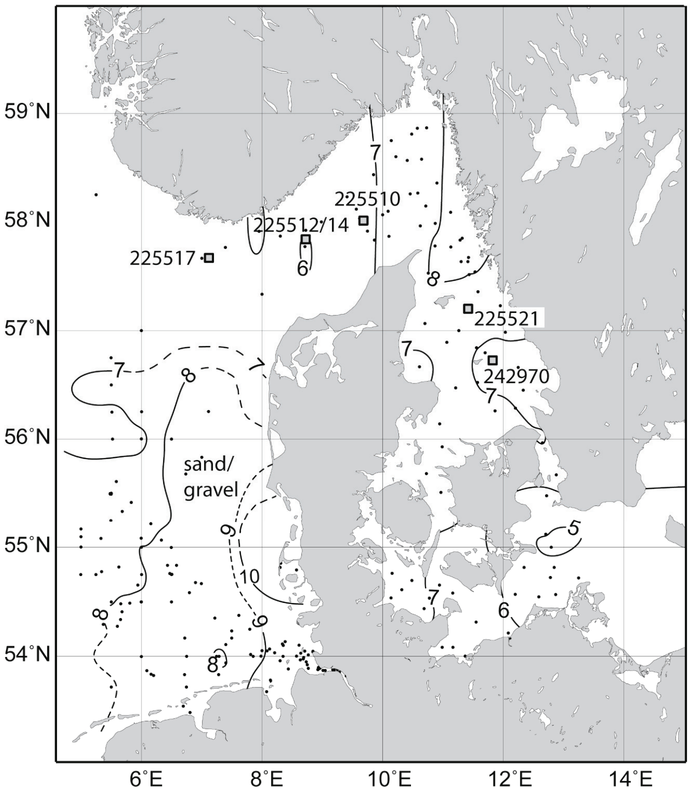

Figure 3.1: Map of δ^{15}N in surface sediments of the North Sea-Baltic Sea area and core locations. Surface sediment data east of 10°E have been previously published by Voss et al. (2005).

Such depositional areas comprise around 1/3 of the sea floor in the North Sea, and the largest depositional centre is the Skagerrak. The Skagerrak is part of the epicontinental North Sea and is connected to the brackish Baltic Sea via the Kattegat (Fig. 3.1). The Skagerrak is a deep basin (maximum depth 700 m) with an average depth of 200 m and a counter-clockwise water circulation (Svansson 1975) that entrains Baltic Sea outflow (salinity of 25 to 30) and North Sea water (salinity 33 to 35). As the water depth increases and the current speed of the cyclonic gyre is reduced, fine-grained sediment is deposited in the northeastern and central parts of the basin (Rodhe and Holt 1996) at a relatively high rate of up to 1 cm per year. The Skagerrak (and Norwegian Trench to the Northwest) account for 50-70% of all the suspended matter permanently buried in the North Sea. One of the major sources for material buried in the Skagerrak is the Southern North Sea (Van Weering et al. 1993), which is subject to most severe eutrophication phenomena and input of river-borne nutrients.

The Kattegat (water depth <70 m) water circulation is characterized by inflow of salty water from the Skagerrak at depth, and outflow of brackish water of Baltic Sea origin at the surface. According to Carstensen et al. (2006) discharge is collected from a total land area of roughly 16,000 km^2 in Denmark and 21,000 km^2 in Sweden. In Denmark 63% of the watershed is arable land and pasture, in Sweden 18%. Sediments in the Kattegat reflect local processes of sediment production and transport. The sea floor is depositional only in deep channels, whereas in shallow waters there is no net deposition (Christiansen et al. 1997). Normally, there is no flux of nutrients from the Skagerrak to the Kattegat (Rydberg et al. 1996). Typically, the winter nitrate concentrations in the Kattegat exceed concentrations expected from mere conservative mixing between Skagerrak and Baltic Sea waters (Rasmussen et al. 2003), which also suggests inputs of nitrogen (and other nutrients) from regional sources on land and from the atmosphere. Therefore, the local nitrogen load from freshwater discharge of bordering countries into the Kattegat area, which has varied between 50 and 150 kt/a in the period from 1989 to 2002 (Carstensen et al. 2006), to a large extent determines the isotope signature of nitrogen in sediment in the Kattegat.

3.3. Materials and Methods

3.3.1. Surface sediments

Analyses of elemental composition and δ^{15}N were done on 214 surface sediment samples (0-1 cm) collected by grab sampling on various expeditions performed by various institutions between 1986 and 2003. All samples had been dried prior to storage. To exclude artefacts of sample storage, we checked that the concentrations of total N had not changed systematically from those measured at the time of sampling. Due to bioturbation in the upper sediment layer, the modern data set smoothes any possible variability over approximately two decades, and thus is comparable to the temporal resolution achieved by dated sediment series. The bulk of the isotope data from the Kattegat has been previously published by Voß et al. (2005).

3.3.2. Multicores and gravity cores

The five multicores (MUCs) and gravity cores (GCs) were collected on expedition R/V Alkor-159 (2000) (Fig. 3.1; see also Tab. 3.1 for core positions). MUCs were extruded on board and sliced in 1 cm intervals, gravity cores were sampled in the laboratory with sawn-off syringes pushed into the core faces. Both types of sediment samples were frozen, freeze-dried and homogenized for subsequent measurements.

3.3.3. Chemical and isotopic analyses of sediment samples

Aluminum concentrations were determined after acid digestion of sample splits and determination of Al with an ICP-OES instrument at IOW (Emeis et al. 1998). For organic carbon analysis the <63 µm sediment fraction was weighed into silver cups, acidified with HCl to remove carbonate, dried at 60°C over night and pressed into pellets. For total nitrogen and N-isotope analysis, tin cups were used, and no acidification was necessary. The sand-free size fraction was chosen because many surface sediment samples were medium to coarse sands with exceedingly low nitrogen concentrations; parallel determinations of $\delta^{15}N$ for a selected set of samples (n=13) on whole sample and the <63 µm fraction showed that there was no significant difference in $\delta^{15}N$.

Table 3.1: Core locations, intervals considered for comparison of $\delta^{15}N$ in multicores (MUC) and gravity cores (GC) and respective averages, means, variability and trends of $\delta^{15}N$ of these intervals. Estimated interval ages are based on 210-Pb dating in the MUCs, and 14-C dating in the gravity core intervals. Only MUC samples within the 210-Pb dated interval are considered. Data from the MUCs below these 210-Pb dated intervals are also displayed in Fig. 3.4. Note that GC 225514 and 225521 did not recover the topmost sediment layer represented by the multicore. T-value and probabilities show that at all locations except 225510, sample sets of MUC and corresponding gravity cores are different at the 95% significance level.

Position	**Depth (m)**	Core	n	**Age interval**		**Average $\delta^{15}N$**	**± 1 sd**	**Trend?**	**Trend**
57°40.04'N 07°05.36'E	293	MUC 225517	9	AD 1870 - 200		6	0.25	yes	0.3‰/100yrs
		GC 225517	22	< 4000 yrs	82 cm: 2185 ± 30 122 cm: 3065 ± 35	5.4	0.44	no	
57°50.22'N 8°41.40E	420	MUC 225512	12	AD 1880 - 2000		6.1	0.14	no	
		GC 225514	21	<3000 yrs	10 cm: 810 ± 30 105 cm: 1165 ± 30	5.7	0.22	no	
58°01.92'N 09°37.17'E	285	MUC 225510	21	AD 1950 - 2000		6	0.17	no	
		GC 225510	20	<350 yrs	232 cm: 550 ± 35	6	0.31	no	
57°12.09'N 11°24.84'E	130	MUC 225521	21	AD 1900 - 2000		6.9	0.24	yes	0.5‰/100yrs
		GC 225521	20	< 1200 yrs	130 cm1025 ± 25	5.6	0.26	no	
56°43.58'N 11°49.80'E	46	MUC 242970	19	?		5.7	0.43	yes	0.7‰/20cm
		GC 242970	38	?		4.9	0.18	no	

Analyses were made on a CE 1108 elemental analyzer (Thermofinnigan) connected to a mass spectrometer (Finnigan 252 for North Sea surface sediment samples at Hamburg University and Delta S for all other samples at the Institute of Baltic Sea Research, Rostock, Germany) via a split interface (Conflow II). The mass spectrometer was calibrated according to international standard procedures with reference gases taken from cylinders with ultra high purity N_2 gas calibrated against nitrogen from air, IAEA standards N1, N2, N3. Isotope data are given in the conventional delta notation as ‰ deviation from air N_2:

$$\delta\ ^{15}N = (R_{sample} / R_{standard} - 1) \times 1000,$$

where R= $^{15}N/^{14}N$ of the sample and the standard, respectively. Every fifth sample was a sediment standard, and one standard deviation for replicate measurements was less than 0.2‰.

3.3.4. Dating

Multicores were dated by the 210-Pb method at the Risoe National Laboratory, Denmark. Chronologies were established by the CRS-method as described in Emeis et al. (2000). Sediment accumulation rates of all multicores except 242970 were determined in the course of the 210-Pb dating process. Long core chronology is based on ^{14}C-AMS dating of the >125 µm size fraction of benthic foraminifers with precisions ranging from ±25 to ±50 years (standard deviation) and was performed at the Leibniz-Labor (Radiometric Dating and Isotope Research) of the University of Kiel/Germany. The exact calendar age in our samples is not crucial for our purpose, because our main concern is to distinguish between industrial and pre-industrial situations. Therefore, we report uncorrected ^{14}C ages determined in the intervals 0-200 cm depth of the long cores. This depth interval spans different time intervals due to different sedimentation rates, but all long cores clearly capture pre-industrial conditions, with oldest sediment layers ranging from >5000 ^{14}C years (station 225517) to <350 ^{14}C years at station 225512/14.

3.4. Results

3.4.1. Regional patterns of $\delta^{15}N$ in surface sediments and multicores

The range of $\delta^{15}N$ in surface sediment samples of our working area is from 5.1‰ to 13.3‰. Markedly enriched (>9‰) are surface sediments in the inner German Bight, where several large rivers discharge and surface waters are both low in salinity and rich in nutrients (Fig. 3.1). In the central Kattegat, surface sediment $\delta^{15}N$ values are >8‰ and decrease both eastward towards the central Baltic Sea, which is attributed to an increasing contribution by fixed nitrogen in this area (Voss et al. 2005), and towards the Skagerrak, where we found values ranging from 6 to 7‰.

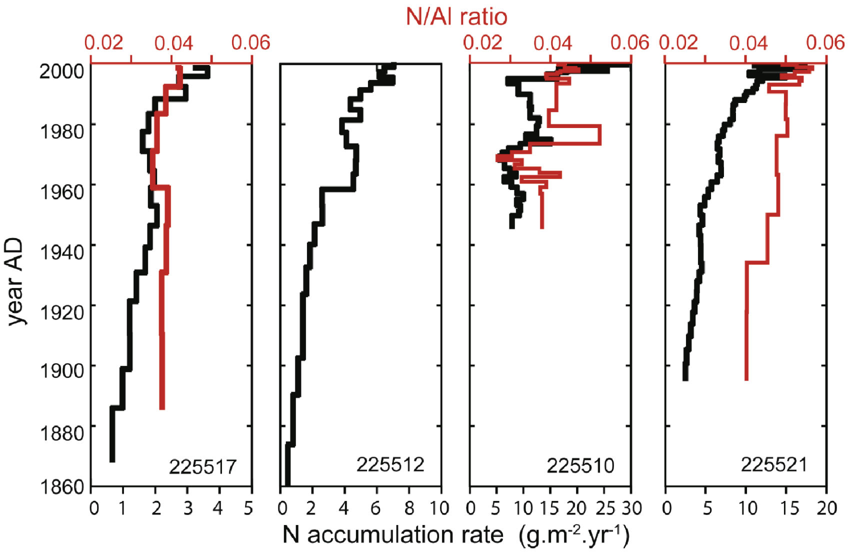

Figure 3.2: Nitrogen accumulation rate (black line, in g/m^2/yr) and N/Al weight ratio (in g/g, grey line) determined in 210-Pb-dated intervals of multicores.

Accumulation rates of N appear to have increased at all locations (Fig. 3.2). This added N-input is also reflected by an increase in the ratio of total nitrogen to aluminium in three records where Al has been measured (Fig. 3.2). This increase in the N:Al ratios excludes a general increase of sedimentation rates as a reason for increased N-burial, because in that case the N:Al ratio should remain the same.

The increased amount of N deposited relative to lithogenic material over the last decades is isotopically enriched, with strongest enrichment of $\delta^{15}N$ in the Kattegat (Tab. 3.1). In 3 of the MUC records, we see increasing $\delta^{15}N$ through time until the topmost sediments (Fig. 3.3). The trend is most pronounced at station 242970 in the Kattegat (increase of 0.7‰ over the 20 cm analysed in the core), even though the depth can only serve as an estimate, because this core has not been dated. The multicore record at station 225521 has a linear trend of 0.5‰ over the last 40 years, and station 225517 of 0.3‰ over the last 100 years. Records at two other stations (225512 and 225510) have no obvious trend in $\delta^{15}N$ (Fig. 3.3).

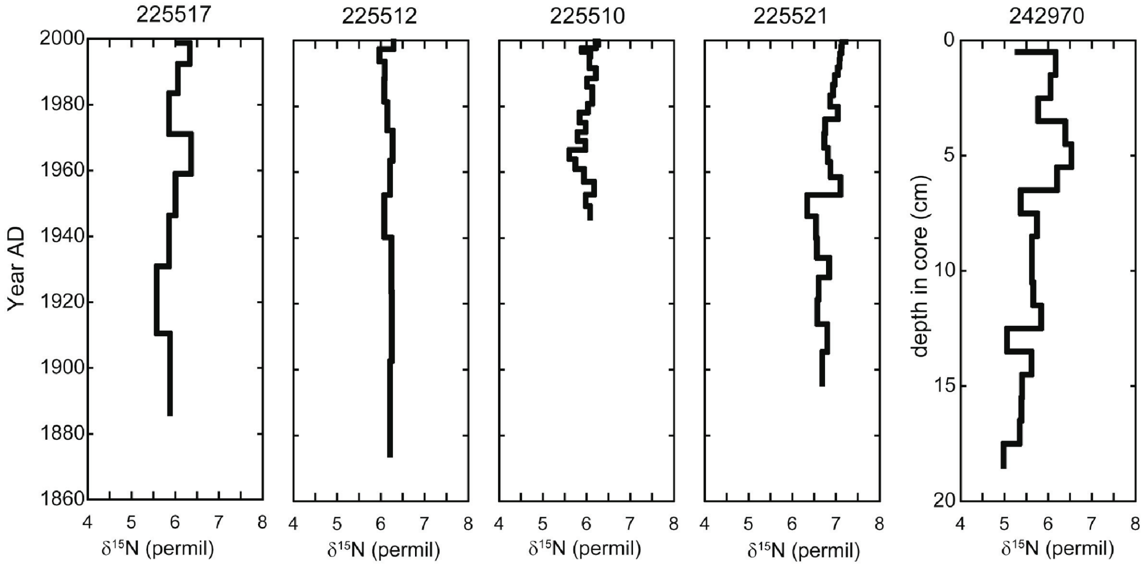

Figure 3.3: δ^{15}N versus age (210-Pb-derived) in multicores. Note depth scale in MUC 242970.

3.4.2. The pre-industrial situation: Gravity cores

To establish the δ^{15}N of sediments under pre-industrial conditions of N-input, we measured samples from longer sediment cores taken at the same locations as the MUCs (Fig. 3.4). The time intervals bracketed by the gravity cores in all cases reach periods that predate industrial use of fertiliser and range from >5000 ^{14}C years (station 225517) to <350 ^{14}C years (station 225512/14). One gravity core in the Kattegat (225521) and one in the Skagerrak (225514) overpenetrated, so there are no time-equivalent surface samples available in these gravity core records that image the sediment record in the corresponding MUC (Fig. 3.4). Thus, part of the top sediment is lost, but as we use the gravity cores to evaluate the pre-industrial situation, this loss of recent sediment is not relevant for our study.

We used Student t-tests and Chi^2-tests to check whether the isotope values in the pre-industrial section of the long gravity cores are significantly different from the modern sediments that are captured by the MUCs. These tests show that the δ^{15}N values of multicore and pre-industrial gravity core samples at each location are statistically different at the 95% probability level, but the differences in the Skagerrak cores are much smaller compared to the cores from the Kattegat (Tab. 3.1). At stations 242970 and 225521 in the Kattegat, the differences in δ^{15}N means of all samples amount to 0.9‰ (242970) and 1.3‰ (225521), respectively (Tab. 3.1). The highest enrichment of younger sediments as compared to pre-industrial sediments in the Skagerrak is at station 225517, where it amounts to 0.6‰. In contrast, at station 225512/14 the enrichment is only 0.3‰, whereas at station 225510 there is no evident enrichment at all in the gravity core as compared to the multicore. Comparing only the maxima of δ^{15}N in MUCs and corresponding gravity core sample sets yields differences of only 0.5‰ for 225517 (6.4‰ in MUC versus 5.9‰ in GC), and 0.2‰ for 225512/14 (6.3‰ in MUC versus 6.1‰ in GC).

3.5. Discussion

The $\delta^{15}N$ of pre-industrial sediment deposits in the North Sea and Kattegat is statistically different from modern sediments at all stations but one. However, in the Skagerrak the differences are small and in part may be due to poor resolution in gravity core records. This small difference between modern and pre-industrial sediments implies that the main depositional centre of N in the North Sea has not received a significant contribution of isotopically enriched river-borne reactive nitrogen over the course of the last 150 years. Unambiguous and significant differences are seen in the two stations in the Kattegat, which suggest an equally significant addition of land-derived N to the sediments. The following discussion of the data centres on the distribution patterns of $\delta^{15}N$ in surface sediments, which reflect variable mixtures of nitrate from different sources. The second section addresses the differences in ^{15}N enrichment in Kattegat and Skagerrak in the course of the last 150 years.

3.5.1. Isotopic composition of N-sources: relation to surface sediments

The $\delta^{15}N$ of inputs of reactive inorganic nitrogen (DIN) to the North Sea is to some degree source specific. As in the oceanic average (Brandes and Devol 2002), $\delta^{15}N_{nitrate}$ in the inflowing oceanic waters is around 5‰ (Dähnke, unpubl. data), with possible historical values around 4‰ or less (Brandes and Devol 2002). This oceanic input is by far the largest source of nitrate to the North Sea (OsparCom 2000). In the surface sediment signal, this is mirrored by low values near 6 per mil in the northwesern part of the study area (Fig. 3.1).

The two sources of nitrate that are subject to anthropogenic influence are atmospheric deposition, which accounts for roughly one third of man-made reactive nitrogen entrained to the North Sea, and riverine input, which makes up for approximately two thirds. Note that we do not consider ammonia in this calculation, because nitrate is the predominant form of dissolved nitrogen in rivers. In atmospheric deposition, ammonia is also present in relevant concentrations, but is not transported over long distances (Spokes and Jickells 2005) and should therefore only play a minor role as contributor of reactive nitrogen to the North Sea.

The nitrate inputs from land, both diffuse runoff and riverine input, are isotopically enriched. Before industrialisation, $\delta^{15}N$ of DIN in rivers may have been between 2 and 4‰, similar to modern rivers draining pristine catchments in the northern Baltic Sea (Voß et al., 2005), but increased N-input from fertilizer use and livestock farming over the last decades led to isotopic enrichment by isotope fractionation processes associated with harvesting of isotopically depleted plants and denitrification in aquifers (Amberger and Schmidt 1987; Seitzinger et al. 2002). Nitrate from rivers entering the German Bight has an elevated isotope signal with riverine signatures ranging from 8 to 12 per mil (Johannsen et al. 2008; Middelburg and Nieuwenhuize 2001). The isotopic fingerprint of river-borne excess DIN characterizes coastal sediments and biota in the vicinity of river mouths (Church et al. 2006; Emeis et al. 2002; McClelland and Valiela 1998; Voss et al. 2005), a pattern that is clearly seen also in $\delta^{15}N$ patterns of North Sea surface sediments (Fig. 3.1). Interestingly, the contours of $\delta^{15}N$ >8‰ match the extent of German Bight Coastal Water that has relatively low salinity and high nutrient concentrations. A second region of high $\delta^{15}N$ is in the Kattegat, where surface sediments are obviously equally influenced by diffuse runoff from land.

In contrast, the isotopic composition of atmospheric deposition is depleted, with values around 1 per mil in Western Europe (Freyer 1991). Therefore, the isotope signals of these two sources may partly cancel each other out. Assuming an overall isotope signal of nine per mil for riverine inputs, and mass fluxes for terrestrial runoff and atmospheric deposition of 800 kt N yr^{-1} and 350 kt N yr^{-1}, respectively (OsparCom 2000), the combined signature has a value of 6.6 per mil. This complies well with what we see in sediment data from the southern North Sea, which have an isotopic value of 6.8‰ (gridded data median $\delta^{15}N$ for area west of 10°E only = 6.8‰, n = 98), and thus are markedly enriched over the marine background of 4.7 per mil. Therefore, in the German Bight, surface sediments can obviously be used as a reliable tracer for anthropogenic nitrogen sources, despite diluting effect from other fluxes.

3.5.2. A view to the past? The sediment record

Isotopic enrichment in the Kattegat

Given that the surface sediments of both Kattegat and German Bight are notably enriched over marine background values, one would expect to see a trend over time in the sediment cores from the Skagerrak and Kattegat area that reflects this increase in enriched nitrogen from terrestrial runoff.

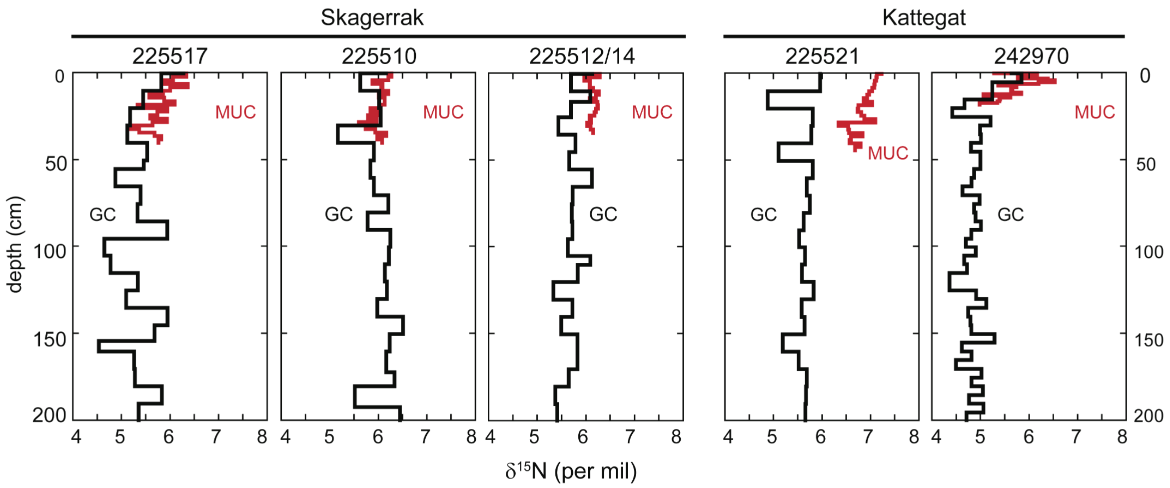

Figure 3.4: δ^{15}N in multicores (top of each panel; grey line) and gravity cores (0-200cm depth interval; black line) from the same locations plotted versus depth in core. Note that gravity cores 225514 and 225521 over-penetrated and that surface sediments recovered by the multicores were not recovered in the gravity cores from these locations.

In the two cores investigated from the Kattegat basin (225521 and 242970), the increase in δ^{15}N values over pre-industrial sediments is statistically significant and amounts to 1.3 and 0.9‰, respectively (Tab. 3.1; Fig. 3.4). We attribute the more depleted isotopic signal at station 242970 to a comparatively larger input of nitrogen (dissolved or particulate) from the western Baltic Sea, where sediments are characterized by low δ^{15}N values (Voss et al 2005, cf. Fig. 3.1). The δ^{15}N in sediments of the gravity cores reflect the pre-industrial reactive nitrogen. N-effluents from land to the Kattegat area today have a δ^{15}N of 11‰ (Deutsch and Voss, 2002), and from a simple mixing line we may estimate the percentage of nitrogen in sediments that derive from land sources. In the case of sediments from station 225521, their average contribution in the period bracketed by samples in the MUC is approximately 20% with a maximum of 30%. At station 242970, the average contribution is 15% with a maximum of 25%.

These estimates are at the lower end of other reconstructions of the eutrophication history in this area. Ellegaard et al. (2006) investigated sediment cores from Mariager Fjord in the Kattegat and found an increase in δ^{15}N from 8‰ in sediment dated to AD 1910 to 11‰ in sediment dated to AD 1960 and a further increase to 11.7‰ by AD 1997.The latter value agrees with that found for dissolved nitrate by Deutsch et al. (2002). In this land-locked fjord that receives agricultural effluents, the man-made increase in δ^{15}N thus amounts to at least 3.7‰. Ellegard et al. (2006) also reconstructed total nitrogen (TN) concentrations in water of Mariager Fjord with micropaleontological methods and suggest that TN doubled from AD 1900 to AD 1990. Clarke et al. (2003) reconstructed eutrophication levels in Roskilde Fjord, a land-locked fjord on the island of Sjelland. Based on diatom transfer functions, they proposed a doubling of coastal nitrogen concentrations in the period from 1950 to 1990, associated with a tripling of N-loading from land. Considering that our stations are situated in the open Kattegat, the estimate of around 20% for excess N over pristine background thus is quite reasonable as a minimum estimate: In our calculation, the lowering of sediment δ^{15}N by depleted atmospheric N deposition has not been factored in; hence the riverine contribution may actually have been significantly higher.

Isotopic uniformity in the Skagerrak

The Skagerrak is the largest sedimentary sink for N in the North Sea. De Haas et al. (1996) calculated accumulation rates of organic carbon in the depositional areas of the Norwegian Trench and Skagerrak of 830 and 170 kt/a, respectively. Of this, only 10% is accounted for by local primary production; the remainder is laterally transported to the depositional centres from their extensive submarine catchment areas such as the southern North Sea. The weight ratio of C:N in sediments is around 12 in the Skagerrak, which implies that burial of organic C is associated with a minimum burial of 120 kt N annually (De Haas et al. 1996; Kunzendorf et al. 1996) This represents 1/3 of all N burial in the entire North Sea.

With exception of a slight enrichment in core 225517, the data from the Skagerrak do not exhibit such an increase in δ^{15}N in industrial times over the pre-anthropogenic background established from gravity cores. It is possible that this lack of enrichment is simply due to dilution of the riverine signal carried from the German Bight with sediments carrying the marine background signal before sediments reach the Skagerrak. However, this is unlikely as there is a continuous transport of sediments along the Danish coast to the Skagerrak, making the Southern North Sea one of the main sources of sediments for the Skagerrak (Van Weering et al. 1993). This transport is also indicated by heavy metals and other elements that derive from the southern part of the North Sea (Kuijpers et al. 1993).

One possible explanation for the apparent lack of enrichment in Skagerrak sediments is that the riverine DIN never reaches the depositional centre, because it is lost to denitrification in estuaries and shallow sandy sea floors of the southern North Sea. Although at present this can only be inferred from circumstantial evidence, lack of isotopic enrichment in young sediments despite the geographical distribution of surface sediment δ^{15}N in the German Bight points in that direction. This implies that the benthic N-cycle has a larger significance in the North Sea than can be deduced from studies on estuarine nitrogen retention, where sediment denitrification is held responsible for removal of 20 to 50 per cent of riverine nitrate loads (Brion et al. 2004; Schröder et al. 1996; Tobias et al. 2003). We speculate that the isotopic gradient away from the river discharge areas is caused by progressive benthic remineralisation and subsequent denitrification of isotopically enriched nitrate at redox boundaries within the permeable sands that are characteristic of sediments of the southern and south-eastern rim of the North Sea. This rim of coarse, permeable sediment may constitute an effective purification site for riverine nitrate discharges and may eliminate the riverine nitrogen load by denitrification or via anaerobic ammonia oxidation before it reaches the open North Sea (Seitzinger and Giblin 1996). This removal is regarded as a common feature of shelf sediments (Cook et al. 2006; Dalsgaard and Thamdrup 2002; Thamdrup and Dalsgaard 2002), removes nitrogen without a large effect on isotopic composition (Lehmann et al. 2004) and has also been found to be responsible for removal of reactive nitrogen in the Baltic Sea (Voss et al. 2005). In our current interpretation, the extent of riverine influence on the N-cycle of the North Sea is limited to the restricted area outlined by enriched δ^{15}N ratios in sediments of the southern German Bight.

3.6. Conclusions

Inputs of reactive nitrogen from rivers to the North Sea and Kattegat are traced by enriched values of δ^{15}N in surface sediments, which are an indirect indicator of eutrophication. Dated sediment cores of the last 150 years from the Kattegat are significantly enriched in δ^{15}N over sediments deposited before widespread use of artificial fertilizer and suggest that present-day N-inputs from rivers contribute between 20% and 25% to the N deposited in offshore sediments in the Kattegat. In contrast, recent sediments cores from the main sedimentary sink of N in the North Sea, the Skagerrak, do not display any enrichment of δ^{15}N over pre-industrial isotope values, although the combined inputs from the atmosphere and rivers have raised the average δ^{15}N in the southern North Sea surface sediments by 1.8‰ in comparison to the marine background. This absence of a clear-cut anthropogenic signal may be due to almost complete elimination of river-borne reactive nitrogen by denitrification in shallow-water and nearshore sediments of the eastern North Sea. Alternatively, current understanding of transport mechanisms of sediment and suspended matter from the North Sea into the Skagerrak may be flawed. In order to fully understand turnover processes of anthropogenic reactive nitrogen and its consequences for the shelf-sea ecosystem of the North Sea, we see a need to investigate and quantify rates of denitrification in typical sea floor sediments of the North Sea. Furthermore, it is necessary to better trace and model particulate matter transport from sources to sedimentary sinks in the North Sea.

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4. A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary

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Abstract

To elucidate the fate of river-borne nitrate in the estuarine environment, we measured nitrate concentrations and $\delta^{15}N$ and $\delta^{18}O$ of nitrate along the salinity gradient in the estuary of the river Elbe, one of the largest German rivers discharging into the North Sea. Nitrate concentrations in river waters ranged from 78 to 232 µmol L^{-1}; $\delta^{15}N$ varied from 8.2‰ to 16.2‰, and the $\delta^{18}O$ values ranged from -0.1 to 3.2‰. The nitrate concentrations in the German Bight were between 2 and 34 µmol L^{-1}, with $\delta^{15}N$ between 8.0 and 12.2‰ and $\delta^{18}O$ between 0.3 and 9.5‰. Both riverine and marine end-member showed seasonal variations, with lower nitrate concentrations and more enriched isotope values during spring and summer compared to winter months. We found no indication in either concentrations or isotopic composition for a significant loss of nitrate within the estuary, but we found a significant increase of nitrate in the maximum turbidity zone in summer. We attribute this to nitrification, reflected in a change in the oxygen isotopic composition. The entire riverine nitrate load is entrained into the North Sea by conservative mixing; this conflicts with both the presumed role of estuaries as effective N-sinks, and with historical data from the Elbe estuary. Fundamental changes in the biogeochemical processes of the estuary have occurred over the past several decades due to extensive dredging and removal of sediment favorable for denitrification in the Elbe estuary that connects the port of Hamburg with the North Sea.

4.1. Introduction

Estuaries have a prominent role in regulating material fluxes from land to sea (Crossland 2005), and the capacity of estuaries for reducing riverine nutrient loads to continental shelf seas has been appreciated as one of the most valuable functions of all global ecosystems (Costanza et al. 1997). According to current understanding of reactive nitrogen transport from land to sea, the estuaries of major rivers are thought to be sites of massive nitrate losses (Brion et al. 2004; Seitzinger et al. 2006), removing up to fifty per cent of reactive nitrogen(OsparCom 2000). In spite of its salient relevance as natural attenuation mechanism combating eutrophication of coastal seas and the intrinsic economic relevance of this specific ecosystem service, the cycling of nitrogen in contemporary estuaries is still subject to open questions. Most older studies are based on tidal input and output, which are prone to a large degree of uncertainty, or are based on mass fluxes alone, which is problematic when sources (e.g., nitrification) and sinks (assimilation and burial, denitrification) may be balanced. A few newer studies suggest that estuarine removal of reactive nitrogen may be significantly overrated, with estimates of removal efficiency ranging from ~5% in the Humber estuary (Jickells et al. 2000) to ~20% in the Rowley estuary (Tobias et al. 2003). More than concentration data alone, measurements of stable isotopes in reactive nitrogen species provide a powerful tool to assess internal turnover and sources in estuaries (Middelburg and Nieuwenhuize 2001; Sebilo et al. 2006). The combined use of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ has recently been acknowledged as a powerful tool for valuation of biological turnover (Wankel et al. 2006).

The goal of this study was to account for nitrate loads from the Elbe River and to assess nitrate losses in the estuary of this river to better constrain the effect of river-borne nutrients on eutrophication in the German Bight and the southeastern North Sea. Differing from previous studies in the Elbe estuary, we used a combined approach based on the mixing curves of nitrate concentration versus salinity and determined $\delta^{15}N$ and $\delta^{18}O$ of nitrate to shed light on possible transformation processes in the estuarine cycling of reactive nitrogen. Faced with unexpected data, we compared the present situation with archival datasets on nitrate concentrations in the Elbe estuary and found that substantial changes must have occurred in nutrient cycles of the Elbe estuary over the past decades.

4.2. Materials and methods

4.2.1. Study site

The Elbe estuary (Fig. 4.1) is a turbid estuary with suspended matter concentration ranging from ~80 mg L^{-1} in the intermediate salinity section to ~200 mg L^{-1} in the maximum turbidity zone (ARGE 2007). The total water residence time is 32 d during mean discharges (Frankignoulle and Middelburg 2002). The entire estuary extends into the German Bight and is bordered by vast areas of intertidal flats. With an average freshwater discharge of 731 m^3 s^{-1} and an annual nitrate load of 79 × 10^6 kg N a^{-1}, the Elbe is one of the most important nitrogen sources to the southern North Sea (ARGE 2005). Whereas phosphate loads have decreased significantly since the 1990s, nitrate loads have shown only a slight downward trend, because diffuse sources, which contribute nitrogen mainly through leaching from soils in the watershed (Johannsen et al. 2008), complicate the attainment of environmental quality goals.

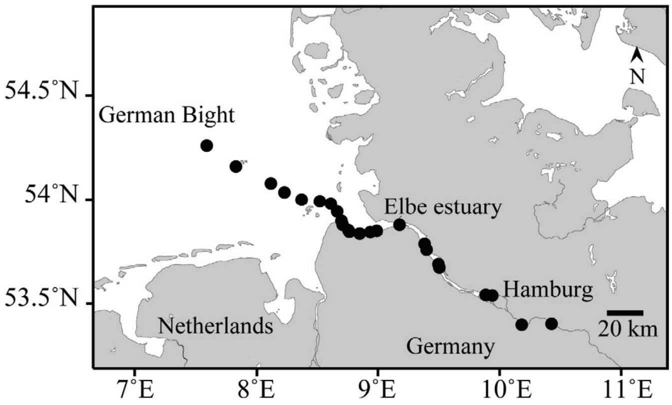

Figure 4.1: Sampling area and stations.

4.2.2. Water sampling along salinity gradients

Water samples in the estuarine mixing gradient were taken on transects spanning the freshwater portion of the river to German Bight Coastal Water with maximum salinities ranging from 27 to 32. This salinity gradient was sampled in different seasons to recognize the range of variability attributable to biological activity.

The first campaign with the RV *Ludwig Prandtl* took place in October 2005. To preclude variations due to mixing behaviour within the water column, both surface and bottom samples were taken. Further sampling campaigns were carried out in May, June, August, and December 2006 (Tab. 4.1). Temperature and salinity were measured on board with a multiprobe (OTS 1500, ME Meerestechnik-Elektronik). Turbidity was measured with a Turbimax W CUS31 turbidity sensor (Endress+Hauser). Due to weather conditions, the samples taken during the cruises in October and December represent only the salinity range from 0.4 to 27 and a marine end-member station only few miles offshore (Fig. 4.1). Sampling of summer cruises also covered salinities up to 31, representing typical German Bight coastal water (BSH 2006).

Table 4.1: Overview of sampling campaigns in the Elbe estuary.

Date	Vessel	No. of stations	Maximum salinity	Temperature range
October 2005	RV *Ludwig Prandtl*	13	27.5	11.1-12.9
May 2006	RV *Uthörn*	20	31.2	7.7-14.3
June 2006	RV *Ludwig Prandtl*	17	31.3	22.2-13.1
August 2006	RV *Ludwig Prandtl*	30	31.4	19.1-21.7
December 2006	RV *Ludwig Prandtl*	22	27.2	7.4-8.1

The river water samples were either taken with a Limnos sampler (Hydrobios) attached to the multiprobe or with the ships' membrane pump. The inlet of the membrane pump is situated at the ship's bow at a depth of 1 m. Water samples were filtered through precombusted GF/F filters immediately after sampling and stored at -18°C until analysis. Data on daily river discharge from the gauge Neu Darchau were provided by the Wasser- und Schifffahrtsamt Lauenburg (WSA Lauenburg).

Archival data on nitrate concentrations were obtained from ARGE Elbe. Salinity was calculated from chlorinity data in the archive data sets by the equation by Knudsen (1902):

$$\text{salinity} = 1.805 \times \text{chlorinity (‰)} + 3\times10^{-2}$$

4.3. Analytical methods

4.3.1. Determination of nitrate concentrations

Nitrate concentrations were determined according to Grasshoff and Anderson (1999). This included reduction of nitrate to nitrite with a cadmium reduction column and subsequent reaction to an azo dye with N-(1-naphtyl-)ethylenediamine, which was then determined photometrically at a wavelength of 540 nm with an auto-analyser AA3 (Bran+Luebbe). The detection limit for our setup was 0.5 µmol L^{-1}. We focused on riverine nitrate loads because the concentrations and loads of both nitrite and ammonia were negligible in comparison to nitrate in the Elbe.

4.3.2. Isotopic analysis of water samples

$\delta^{15}N$ and $\delta^{18}O$ of nitrate were determined with the denitrifier method (Casciotti et al. 2002; Sigman et al. 2001). In brief, the water samples were injected into a suspension of *Pseudomonas aureofaciens* (ATCC#13985) for combined analysis of $\delta^{15}N$ and $\delta^{18}O$, or *P. chlororaphis* for $\delta^{15}N$ analysis only. Both bacterial strains denitrify nitrate under anoxic conditions, but lack nitrous-oxide reductase activity. The resulting N_2O gas was flushed by purging the sample vials with helium, concentrated and purified on a GasBenchII (ThermoFinnigan), and analyzed on a Delta Plus XP mass spectrometer. To avoid concentration-dependent fractionation effects, sample size was adjusted to achieve a final gas amount of 10 nmol. For each sample, replicate measurements were performed, and an international standard (IAEA-N3) was measured with each batch of samples. The contribution of nitrite to the NO_x pool was always <1% and therefore was not considered further in our calculations, because the effect on $\delta^{18}O$ values was negligible (Casciotti and McIlvin 2007).

The standard deviation for IAEA-NO_3 was better than 0.2‰ (n = 5) for $\delta^{15}N$ and better than 0.4‰ for $\delta^{18}O$. For further quality assurance of the results, we used an internal potassium nitrate standard that was measured with each batch of samples. The standard deviation for the internal standard was within the same specification for $\delta^{15}N$ and $\delta^{18}O$ as in IAEA-N3.

Variations in isotope ratios are reported using the common “delta” notation:

$$\delta^{15}\mathrm{N} = \left(\frac{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{sample}}}{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{std}}} - 1\right) \times 1000 \qquad (4.1)$$

The standard for nitrogen is atmospheric N_2 and the accepted standard for oxygen is Vienna Standard Mean Ocean Water (VSMOW), which both by definition have a δ-value of 0‰.

4.3.3. Mixing model

The mixing behaviour of compounds can be assessed using the classical mixing model of Liss (1976):

$$C_{MIX} = f \times C_R + (1-f)C_M \qquad (4.2)$$

where C denotes concentration, the subscripts R and M indicate riverine and marine end-members, respectively, and f denotes the fraction of freshwater in each sample calculated from salinity:

$$f = (31 - \text{measured salinity})/31 \qquad (4.3)$$

where 31 is taken as the salinity (referring to the Practical Salinity Scale) of the marine end-member for coastal water in the German Bight.

Isotopic values of mixed estuarine samples (δ_{MIX}) were calculated using concentration-weighted isotopic values for riverine and marine end-members, respectively (Fry 2002):

$$\delta_{MIX} = [f \times C_R \times \delta_R + (1-f)C_M \times \delta_M] / C_{MIX} \qquad (4.4)$$

In contrast to concentrations, which have linear conservative mixing paths, salinity-based mixing diagrams for isotope mixtures usually show curvilinear mixing that reflects concentration-based weighting of end-member isotopic contributions (Fry 2002).

4.4. Results

4.4.1. Nitrate concentrations and isotopic composition in the Elbe estuary

The freshwater end-member in the estuary determining the initial nitrate concentration of the mixing gradient varied with season. In general, the values of the freshwater end-members in each estuarine gradient corresponded to those measured in the same period landward at the weir Geesthacht. Lowest nitrate concentrations were found in late summer, followed by an increase over the course of the year with maximum nitrate concentrations of 260 µmol L^{-1} in early spring. Further down the estuary, the concentrations decreased as the river water mixed with salt water from the German Bight.

The sampling campaign in December 2006 (Fig. 4.2A) represents a situation of low biological activity in river, estuary and German Bight. Nitrate concentrations in the river end-member were 230 µmol L^{-1}, decreasing to a value of 34 µmol L^{-1} in the coastal waters. The $\delta^{18}O$ values did not change along the salinity gradient and remained stable around 0‰, whereas $\delta^{15}N$ values decreased slightly from 10.5‰ in the river end-member to 8‰ in the marine end-member. Isotopic composition as well as nitrate concentrations behaved strictly conservatively over the entire salinity gradient, ranging from 0.5 to 27.

In May 2006, riverine nitrate concentration was 260 µmol L^{-1} and indicated only limited nitrate consumption upstream at this time of the year. A clear increase in nitrate concentration by about 60 µmol L^{-1}, corresponding to an increase of >20%, was seen in the salinity range from 0.5 to 1.5 This increase was coupled with a slight decrease of $\delta^{15}N$ and a very pronounced decrease in $\delta^{18}O$ of nitrate of 6.8‰. The isotope values stabilized at a salinity of 1.7, and the mixing curves for nitrate isotopes and concentration followed the conservative mixing line further down the estuary (Fig. 4.2B). $\delta^{15}N\text{-}NO_3^-$ values remained stable at 8.1 ± 0.3‰ up to a salinity of 27 and then increased to a value of 11.8‰ in the most saline sample. Using this value at maximum salinity as the marine end-member for calculating the mixing curve, all values show good agreement with a modelled conservative mixing behaviour.

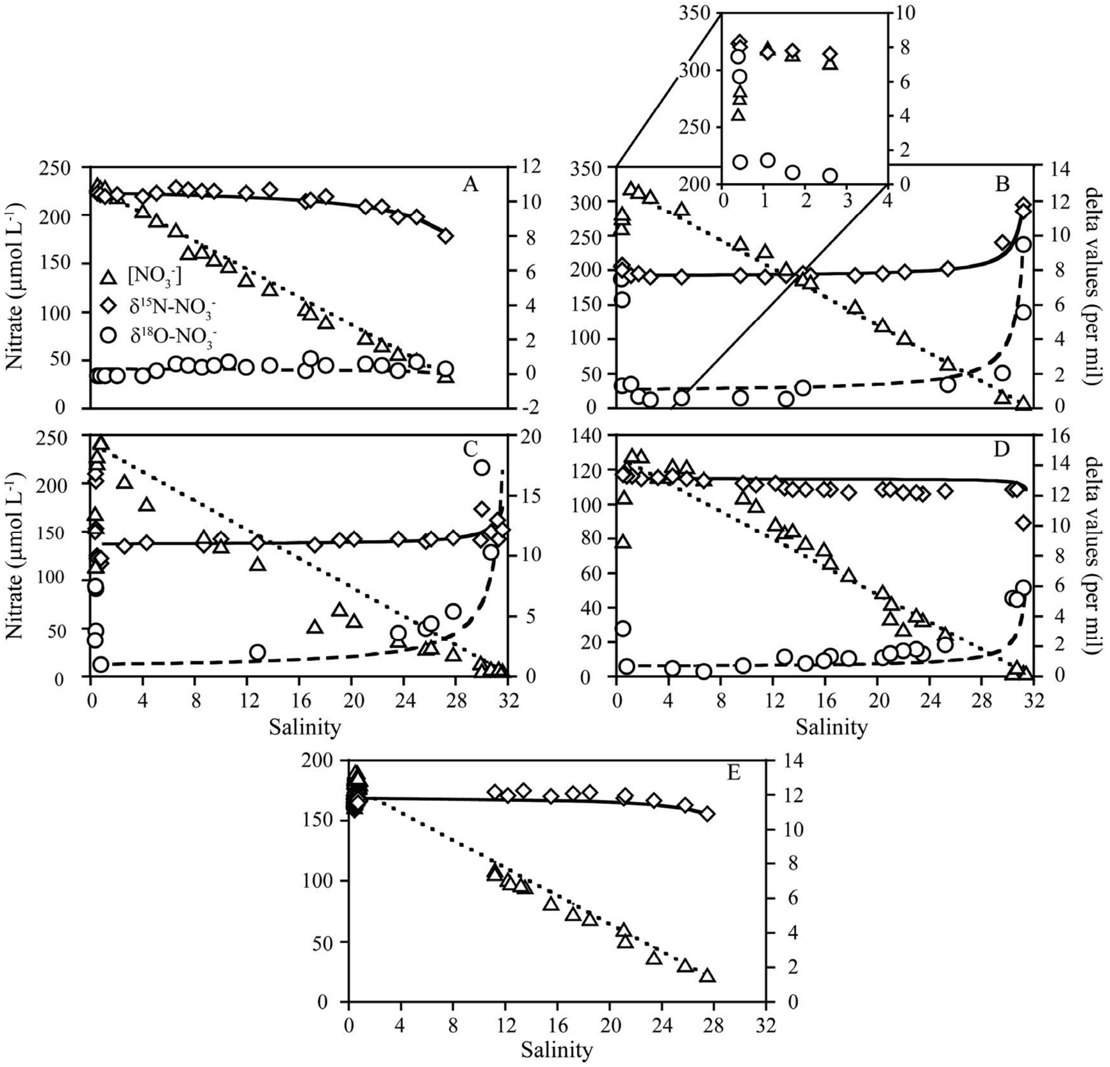

Fig. 4.2: Nitrate concentrations and isotopic values of nitrate along the salinity radient in the Elbe estuary. (A) December, (B) May (insert shows the increase in nitrate concentrations in the upper estuary), (C) June, (D) August, (E) October.

The gradient sampled in June 2006 (Fig. 4.2C) had similar features as that in May, but the range of δ values was somewhat narrower, which is surprising in light of a high mean water temperature of 18.6°C that should have promoted biological activity. Nitrate concentrations rose in the upper estuary (in the salinity range from 0 to 2) from 150 µmol L^{-1} to 240 µmol L^{-1}, while the $\delta^{15}N$ and $\delta^{18}O$ values decreased from 16‰ to 10‰ and 7.5‰ to 1‰, respectively. Mixing at salinities >2 was almost conservative in the isotope mixing model for $\delta^{15}N$, but concentration data suggest a slight nitrate sink within the estuary that may have removed ~5 - 10% of the total nitrate load. $\delta^{15}N\text{-}NO_3^-$ remained stable around 10‰ up to a salinity of 27, then rose to a maximum of 13.9‰, which is in accord with conservative mixing. Apparently the slight nitrate loss was almost neutral with regard to isotopic fractionation, suggesting a fractionation factor of

≤1‰ for δ^{18}O and no apparent fractionation for δ^{15}N. The scatter in the high-salinity samples may be attributed to differences in the water masses sampled due to changing tides.

In August 2006 (Fig. 4.2D), the initial nitrate concentration determined landward of the weir was 104 µmol L^{-1}, decreasing to 78 µmol L^{-1} in the freshwater end-member of the salinity gradient. A significant amount of nitrate was added in the salinity range from 0.5 to 1.2 (to a maximum concentration of 128 µmol L^{-1}), the range of which corresponds to the turbidity maximum downstream of Hamburg (Fig. 4.3). While this increase in concentration did not affect δ^{15}N-NO_3^- to any significant extent, δ^{18}O-NO_3^- decreased abruptly by 2‰. At intermediate salinities from 4 to 12, the nitrate concentration was slightly elevated over conservative mixing; in the salinity range from 12 to 26, δ^{15}N was ~1‰ below and δ^{18}O was slightly enriched above the theoretical conservative mixing line.

The gradient sampled in October 2006 (Fig. 4.2E) differed from the others, because the marine end-member was isotopically more depleted than the riverine end-member. The freshwater nitrate concentrations rose slightly from an initial value of 169 µmol L^{-1}in the port of Hamburg to a mean value of 189 µmol L^{-1} downstream of the city, the increase again coinciding with the turbidity maximum. The δ^{15}N values in the upper estuary ranged from 11 to 12‰, but there was no significant correlation between delta values and nitrate concentration (r^2 = 0.27). No data were available for the intermediate salinity range from 1 to 10, and thus we could not exclude possible biological processing in this salinity interval. However, both nitrate concentration and isotope values that are available for salinities from 10 to 28 showed no significant deviations from conservative mixing (Fig. 4.2E).

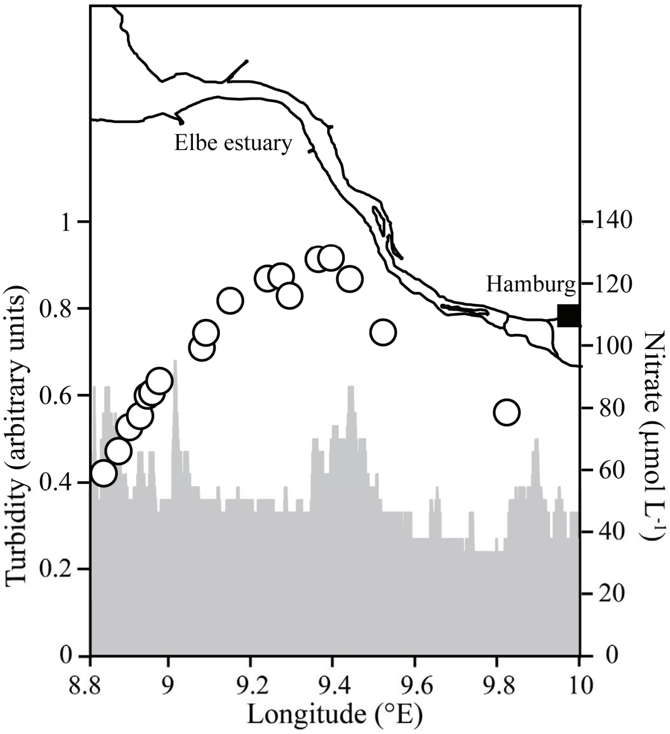

Figure 4.3: Turbidity (grey) and associated nitrate concentrations (µmol L^{-1}) in the Elbe downstream of Hamburg in August 2006. Note the co-occurrence of high turbidity and maximum nitrate concentrations at 9.45°E.

In summary, the data sets showed clear differences in terms of riverine and marine nitrate end-member concentrations and isotope composition depending on the season of sampling. Unexpectedly, no indication of nitrate loss was found in the estuarine mixing gradient between freshwater and marine end-members regardless of the season of sampling. Instead, we found a significant addition of nitrate to the water phase in the salinity range from 0 to 2 at times of biological activity, especially in spring and early summer. This local nitrate source was active in May, June, and August 2006, was not stationary, coincided with the estuarine turbidity maximum, and added between 40 µmol L^{-1} and 130 µmol L^{-1} of nitrate to the river load. This added nitrate had the same N-isotope composition as the riverborne load, but was significantly depleted in δ^{18}O. With the possible exception of August 2006, when a slight increase in nitrate was noted, conservative behaviour of nitrate is always indicated in the higher salinity range of the Elbe estuary out to the German Bight.

4.5. Discussion

4.5.1. Nitrate sources and sinks in estuaries

Net sources and sinks of nitrate in estuaries have been traditionally detected and quantified by mixing lines of fresh and marine waters with different salinities (as the conservative property) and nitrate concentrations. However, balanced sources and sinks of nitrate that have no concentration effects cannot be assessed with this approach. Here, the isotope signature of nitrate offers a powerful tool to identify turnover processes, sources and sinks (Middelburg and Nieuwenhuize 2001): Most biological processes discriminate against the heavier isotope in favor of the light one, so a source of nitrate (supplying nitrate from another pool of reactive nitrogen like ammonia) will add light nitrate to the estuary, whereas removal usually leads to isotopic enrichment of the remainder.

The degree of fractionation depends on the specific biological process. Nitrate assimilation, an important estuarine nitrate sink, leads to an enrichment of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- on a slope of 1 to 1 (Granger et al. 2004). Another nitrate sink is denitrification, which takes place in the water column under conditions of oxygen depletion, or in suboxic or anoxic sediments. While denitrification in sediments does not result in any apparent fractionation because the rate-limiting step is diffusion of nitrate into the reactive sediment zones (Brandes and Devol 1997; Lehmann et al. 2004), denitrification in the water column in marine environments has a large fractionation factor of approximately 20‰ and, in open water, also leads to isotopic enrichment of the remaining nitrate in the ratio 1 : 1 for δ^{15}N and δ^{18}O, respectively (Wankel et al. 2006). Nitrification, the largest potential internal nitrate source in the estuary, adds isotopically depleted nitrate to the nitrate pool. It is characterized by significant isotope fractionation: To our knowledge, there are no studies addressing the isotope effects of nitrite oxidation, the second step in the nitrification process, but the oxidation of ammonia has an isotope fractionation factor between 14 and 38‰, depending on the bacterial species involved (Casciotti et al. 2003).

These different fractionation factors associated with nitrate sources and sinks would result in deviations from the conservative mixing line of isotopes (Fry 2002). This holds true especially for a combined approach of δ^{15}N and δ^{18}O analysis, because ^{18}O has been shown to be an even more sensitive tracer of biological processing than ^{15}N (Wankel et al. 2006).

4.5.2. No nitrate sink in the contemporaneous Elbe estuary

With these general characteristics of reactive N turnover in estuaries in mind, the data from the Elbe estuary were in stark contrast to the concept of estuarine sinks for river-borne nitrate.

The salinity gradient sampled in December 2006 showed strictly conservative behaviour in both concentration and isotopic data throughout the entire salinity gradient. In winter, the marine end-member $\delta^{15}N\text{-}NO_3^-$ was lower than that of the riverine contribution, and was in agreement with the isotope data of Middelburg and Nieuwenhuize (2001) for the outer Thames estuary. The nitrate oxygen values in the outer Elbe estuary also agreed with typical values of marine nitrate (Lehmann et al. 2003). This winter situation, with water temperatures <10°C, ruled out most biological activity and conservative mixing between riverine and North Sea nitrate was not overly surprising. Although the slopes of the mixing lines for different seasons differ due to differing origins in terms of riverine and marine end-member concentrations and compositions, the Elbe nitrate load appeared to pass the estuary without significant loss and instead, nitrate was added to the estuary from an internal source.

4.5.3. A significant nitrate source in the low-salinity Elbe estuary

The nitrate increase in the low salinity (0.4 – 2) upper estuary was most pronounced in June 2006. This nitrate maximum was tied to a geographically shifting salinity range that is associated with a maximum in turbidity, as exemplified by August 2007 data (Fig. 4.3). The peak moved along the estuary, clearly demonstrating that the added nitrate was not provided by a stationary source such as a water treatment plant or a minor nitrate-rich river discharging into the Elbe. Judging from the decrease in $\delta^{18}O$ in nitrate, the source of the added nitrate is nitrification of ammonia: The increase in nitrate concentrations was not associated with substantial changes in $\delta^{15}N$, but with a pronounced drop in $\delta^{18}O$. Because ammonia levels in the Elbe estuary were too low to account for an input of this magnitude, our observation was in accord with nitrification of ammonia derived from the degradation of organic matter and its subsequent rapid oxidation by particle-associated nitrifying bacteria within the turbidity maximum. A comparably intense nitrification has been observed in the Scheldt estuary (De Wilde and De Bie 2000) and, via complete conversion of organic matter-derived ammonia, in the upper Seine estuary (Sebilo et al. 2006). In our case, however, the internal nitrate input must have been even higher than the net addition: Nitrate from nitrification had an oxygen value deriving partly from dissolved oxygen and partly from oxygen atoms from water. We note that there are some arguments about the ratio of oxygen atoms deriving from these different sources. While incubation experiments indicated that no more than two out of three oxygen atoms derive from ambient water, other studies suggest that the $\delta^{18}O\text{-}NO_3^-$ signature of nitrate from nitrification is dominated by the water signal, with one out of six or less oxygen atoms derived from O_2 (Casciotti et al. 2002; Sigman et al. 2005). Apparently, the fraction of oxygen atoms originating from ambient water was influenced by environmental conditions. Therefore, we applied the equation suggested by Casciotti et al. (2003) to calculate the total amount of estuarine nitrate stemming from nitrification:

$$\delta^{18}O\text{-}NO_3^- = {}^5/_6\, \delta^{18}O\text{-}H_2O + {}^1/_6\, \delta^{18}O\text{-}O_2 \qquad (4.5)$$

Using a value of -9‰ for $\delta^{18}O$ for Elbe river water (own data) and of 23.5‰ for atmospheric O_2 (Kroopnick and Craig 1972), the calculated $\delta^{18}O$ of nitrate from nitrification in the particle-rich turbidity maximum is -3.6‰. Calculating the $\delta^{18}O\text{-}NO_3^-$- value of the resulting mixture of original river nitrate and new nitrate from nitrification resulted in an expected value of 5.5‰ for May 2006 and contrasts with the 1.4‰ we found. For August and December, we saw no additional input.

The portion of nitrate added with the depleted nitrification signature thus must have exceeded the observed net input. Some of the nitrified ammonia was removed via coupled nitrification-denitrification processes within the maximum turbidity zone. For May and June, 67 and 11 percent, respectively, of the newly produced nitrate were apparently removed by this pathway. The relevance of this coupling has been observed in other rivers (Dong et al. 2000), although in our case the effect cannot make up for the massive nitrate production. Due to the higher range of oxygen isotope values in comparison to nitrogen, the additional information provided by oxygen isotope composition of nitrate highlights processes that can not be inferred from the signature of $\delta^{15}N$ alone.

4.5.4. Comparison with historical data from the Elbe estuary

Denitrification is thought to be a prominent process of net nitrate removal in estuaries (Dong et al. 2006; Ogilvie et al. 1997; Van Beusekom and De Jonge 1998). Our data do not support this view and beg the question whether this is due to changes in the biogeochemical functioning of the Elbe estuary. Although nutrient data in the estuarine part of the Elbe are scarce before 1979, even the available concentration data alone indicate substantial nitrate removal in the estuary in archive data from the 1970s and early 1980s (Fig. 4.4). This may have been due to higher primary production than today, but phytoplankton primary production in turbid estuaries is limited by light rather than nutrients (Goosen et al. 1999; Kromkamp and Peene 1995). The primary nitrate sink in the historical Elbe has been denitrification in sediments (Schröder et al. 1996). That clear pattern of nitrate loss in the estuary changed in the mid-1980s and was replaced by seemingly conservative nitrate mixing patterns in the present estuary, which in other studies has been attributed to a balance of sources and sinks (Sebilo et al. 2006). Accordingly, Schröder et al. (1996) found pseudo-conservative nitrate behaviour in the

Elbe estuary, but measured significant denitrification rates in sediments of the Elbe that had the potential to remove up to 40% of the riverine nitrate load. The seemingly conservative mixing behaviour in their study was attributed to a balancing nitrate addition by nitrification. By the time of our study, the pseudo-conservative mixing was replaced by truly conservative mixing, and the estuary has turned from a nitrate sink into a nitrate source.

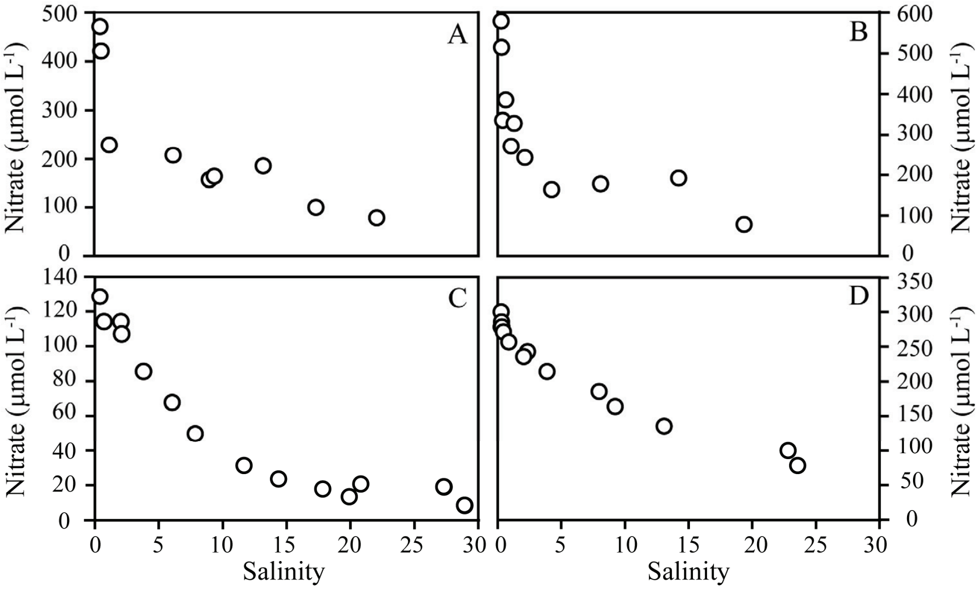

Figure 4.4: Historical records of nitrate concentrations in summer along the salinity gradient in the Elbe estuary from (A) 1977, (B) 1978, (C) 1979, and (D) 1980, determined by the ARGE Elbe.

An obvious first explanation for the lack of nitrate turnover is that ammonia is instead used as a nitrogen source by heterotrophic organisms and phytoplankton (Dortch et al. 1991; Middelburg and Nieuwenhuize 1998). However, ammonia concentrations in the Elbe were much higher in the late 1970s, when nitrate processing in the estuary was indicated by non-conservative mixing (Fig. 4.4). Second, a major sink for nitrate is nitrate assimilation, and that assimilation may have decreased due to imbalanced nutrient ratios: The riverine phosphate loads of the Elbe have decreased significantly over the past decades, leading to N:P ratios that increasingly deviate from the Redfield Ratio of 16:1 and are now ~60:1 in the upper estuary in summer (ARGE Elbe, pers. comm. 2007; Radach and Paetsch 2007). But contrasting with the German Bight, primary production in the estuary is usually light limited, so that the role of phytoplankton assimilation as a significant nitrate sink along the salinity gradient may be overestimated (Goosen et al. 1999). Furthermore, a comparison of DIP and DIN loads in the estuary reveals that the Elbe estuary was by no means exclusively nitrate-limited in the past, making a change in primary production patterns and rates an unlikely reason for the lack of nitrate processing.

What can be learned from other estuaries? Soetaert et al. (2006) found that improved oxygen saturation led to decreased water column denitrification rates in the Scheldt estuary over the past decades. In the Elbe, those parts of the estuary that appear to have been sites of nitrate removal in the data from the late 1970s (salinity range 2 - 12) have not experienced a significant change in the oxygen saturation in comparison to the present situation (ARGE Elbe pers. comm. 2007) and decreased water column denitrification rates can be discounted.

Water residence time in the estuary in the late 1970s was long enough to remove a significant part of riverine nitrogen loads - in agreement with the high sediment denitrification rates calculated by Schröder et al. (1996). But since these data were collected, dredging and diking works in the Elbe River have on average excavated 4.4 million m^3 per year in addition to deepening the ship channel from 12 m to 14.2 m water depth, filling up shallow-water marshes and protecting tributary streams with flood gates. All these measures effectively decreased the sediment area that is in contact with the overlying water column. Alexander et al. (2000) found that the nitrogen retention capacity of rivers decreases with increasing water depth. It appears that the relevance of the port of Hamburg for the regional and national economy has been developed at the expense of a fundamental and highly valuable ecosystem service (Costanza et al. 1997) of the Elbe estuary. Removal of sediments apparently has reached a point where the Elbe estuary has lost its natural denitrification capacity.

We examined the estuarine mixing behaviour and the isotopic signal of nitrate in the Elbe estuary to assess the estuarine nitrogen retention capacity. We found that, regardless of the season of sampling, the estuarine mixing behaviour is mostly conservative and there is no net uptake of nitrate along the estuary. In contrast, a significant net source of nitrate is present in the upper estuary, downstream the city of Hamburg.

Comparing our findings with historical data, we conclude that a change in the estuarine function must have occurred gradually within the last 25 years, when the Elbe still was a sink for reactive nitrogen. From our data we cannot decide whether this is due to a lack of nitrate assimilation or to a decreased denitrification rate in the sediments.

Regardless of which of these two processes eventually is responsible for the drastic changes, our data indicate that the Elbe estuary has lost its natural function as a place of active nitrogen turnover and efficient removal and instead has developed into a significant source of nitrate for the adjacent North Sea

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5. Conclusions and Outlook

5.1. Conclusions

In this thesis I have examined different perspectives of the nitrogen cycle in coastal environments using stable isotopes as a valuable tool to assess sources, sinks and processing of reactive nitrogen or nitrate. It could be shown that nitrogen isotope ratios do indeed shed light on nutrient processing and transport.

In rivers, nitrate isotopes are dominated by an annual cycle that is characterized by elevated isotope values in summer due to biological fractionation as compared to winter months. Despite this fluctuation, the overall isotopic value is strongly enriched in ^{15}N. Considering the winter signal, it becomes clear that biological activity in the river is not the only source of heavy nitrate: leaching of soil nitrate from nitrification contributes nitrate to the river water throughout the entire year. The δ^{15}N value is significantly coupled to the percentage of agricultural land-use in the catchment area, which shows the relevance of anthropogenic inputs of sewage and/or manure. δ^{18}O values suggest that anthropogenic nitrogen is nitrified in the soils of the catchment area.

This riverine nitrate is often thought to be denitrified in estuaries, so that the actual effect of anthropogenic nitrogen is minor. The close examination of the Elbe estuary, however, revealed that the net removal of riverine nitrate in the estuary is negligible. It appears that the main reason for this lack of nitrogen retention is not a balance of nitrification and denitrification, but very little biological processing in total. When coupled nitrification-denitrification takes place, as it does in the maximum turbidity zone in the upper estuary, which can be deduced especially from oxygen isotopes of nitrate, this even leads to a net nitrate input, presumably from organic nitrogen in suspended sediments. Given this nitrate release, in the past decades the estuary has developed into a significant nitrate source, by no means fulfilling its presumed function as a nitrogen filter. It may be possible that the removal of sediments is responsible, or it may be related to construction measures that cut off important sites of denitrification like the Mühlenberger Loch, which was filled up in 2001. Whatever the exact mechanism is, the nitrogen from the rivers is not processed in the estuaries, which is supported by the findings described in Chapter 4.

A large amount of anthropogenic nitrogen from the river-mouths finally reaches the German Bight, which is reflected by high nitrate concentrations in the water column and elevated isotope signatures in surface sediments. The main transport pathway of these sediments is northwards, following the Jutland Current to the main sedimentary depositional centre, the Skagerrak. The isotope signature of sediments in this area should thus be enriched over the pre-anthropogenic signal as inferred from sediment cores. That this approach is indeed valuable to trace anthropogenic inputs can be derived from data in the Kattegat, where such enrichment over time is visible and probably stems from terrestrial runoff. In the Skagerrak, however, there is no evidence of increasing isotope values. Either sediment transport pathways differ from the presumed pattern – which is unlikely because other substances such as heavy metals from the German Bight can be detected in the Skagerrak – or the enriched nitrogen from the river mouths is quantitatively removed before it even reaches the Skagerrak.

5.2. Outlook

While it was possible to resolve many questions related to nitrogen cycling in the German Bight, the conclusions outlined above pose a number of new questions. One, of course, is the regime shift in the Elbe estuary. Further investigations should be carried out to address the reasons of the missing denitrification beyond speculation, which may also involve the measurement of potential and natural denitrification rates in sediment cores from the Elbe River and its estuary.

Another question regards the fate of the anthropogenic nitrogen entrained to the German Bight by major rivers. As the data from the Elbe suggest, it reaches the German Bight and should consequently be found in the main depositional centres. This, however, is not the case: It seems that in the German Bight itself nitrogen removal takes place and leads to the lack of isotopic enrichment in recent Skagerrak sediments. This highlights the importance of sedimentary processes, and shows that studies addressing the water column only just offer a very limited view of nitrogen turnover. Important pathways like denitrification and anammox, need to be assessed for a more complete picture.

In a detailed approach, both the potential and in situ reaction rates and the fractionation factors of sedimentary processes should be investigated. The rates of nitrification, denitrification and anammox in the German Bight can be determined in sediment incubation experiments (An and Joye 2001; Cook et al. 2006; Engstrom et al. 2005). Especially anammox is still poorly constrained, it was discovered only a few years ago and has now been found to occur in wide ranges of shelf sediment types (Thamdrup and Dalsgaard 2002). Still, little is known about its spatial and temporal variability: It is known that anammox activity depends on benthic O_2 consumption, remineralisation of soluble components (Engstrom et al. 2005) and the amount of microphytobenthos (Risgaard-Petersen et al. 2005), but up-scaling these results to a larger area like the German Bight is difficult (McClain et al. 2003). Investigating the balance and control of denitrification, and anammox, which depends on different sediment characteristics such as organic matter content, reactivity and oxygen penetration depth (Davidson and Seitzinger 2006), may be helpful to better assess nitrogen turnover in the German Bight.

It may also be worthwhile to question the fractionation factor assigned to sedimentary turnover. The current view is that this fractionation is low (Lehmann et al. 2004, Brandes and Devol 2002), but recent studies suggest it might have to be revised upwards (Lehmann et al. 2007).

These more accurate estimates are necessary if a coupled mass flux/isotope model shall be set up to better estimate the impact of atmospheric deposition and answer the question on the isotopic signature of exported nitrogen on a mathematical level. At present, there are only few data to evaluate such models with in the North Sea. Given that sedimentary denitrification or anammox may remove very large portions of nitrogen (close to 50%, cf. Seitzinger et al. 2006), a model that contains both mass and isotope fluxes is prone to large uncertainties where isotope effects are poorly constrained.

Another input pathway that should be addressed to better constrain such a model is atmospheric deposition. Oxidised, isotopically light nitrate species are transported over long distances, but near the coast, isotopically heavier ammonia may also play a significant role and may have to be treated separately in such a modelling approach.

To conclude, both the measurement of reaction rates and their implementation in a mass flux/isotope model appear like very promising approaches to further evaluate the fate of anthropogenic nitrogen in the German Bight/Southern North Sea.

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Figure Captions

Figure 1.1: Natural and anthropogenic N fluxes to terrestrial and oceanic ecosystems. Source: Gruber and Galloway 2008.

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Table captions

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List of Abbreviations

AMS	Accelerator Mass Spectrometry
ARGE	Arbeitsgemeinschaft zur Reinhaltung der Elbe
DIN	dissolved inorganic nitrogen
DIP	dissolved inorganic phosphorous
ε	fractionation factor
GC	gravity core
HCl	hydrochloric acid
ICP-OES	inductively coupled plasma optical emission spectrometry
MUC	multicore
R	isotope ratio
rN	reactive nitrogen
RV	research vessel
TN	total nitrogen
VSMOW	Vienna Standard Mean Ocean Water
WSA Lauenburg	Wasser- und Schifffahrtsamt Lauenburg

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A. Data Appendix

In the following appendix, the basic data used in the three publications this thesis is based on are listed.

A.1 River data from Eider, Elbe, Ems, Rhine and Weser

Table A.1: Sampling dates, nitrate concentration and isotope values from five German rivers sampled over the course of one year. Samples were taken at the surface in the freshwater part of the rivers Eider, Ems, Rhine and Weser were sampled by the respective monitoring authorities.

	Elbe				**Eider**		
Date	**Nitrate (μmol L^{-1})**	**δ^{15}N-nitrate**	**δ^{18}O-nitrate**	**Date**	**Nitrate (μmol L^{-1})**	**δ^{15}N-nitrate**	**δ^{18}O-nitrate**
16.01.06	292.8	9.3	0.2	24.03.06	225.1	10.4	2.7
20.02.06	304.3	8.5	2.0	15.05.06	197.6	11.6	2.6
07.03.06	309.8	8.7	1.2	12.06.06	123.2	13.3	4.1
20.03.06	315.3	8.2	n.a.	11.07.06	25.2	11.9	n.a.
31.03.06	343.1	8.3	0.6	09.08.06	4.4	2.1	n.a.
31.03.06	345.9	8.3	0.7	06.09.06	3.8	n.a.	n.a.
10.04.06	364.2	6.4	0.6	09.10.06	37.9	11.4	n.a.
03.05.06	223.9	8.8	1.9	23.10.06	101.5	10.9	n.a.
22.06.06	113.0	16.5	7.6	22.11.06	171.3	11.7	n.a.
04.07.06	77.5	19.3	8.4	11.12.06	270	11.8	n.a.
24.07.06	92.0	17.0	7.2	08.01.07	298	12.2	4.2
03.08.06	32.0	22.5	12.1	05.02.07	352	11.2	3.8
24.08.06	144.4	11.8	3.0	06.03.07	288	11.8	4.5
12.09.06	98.4	16.6	7.9				
10.10.06	104.7	16.9	7.5				
03.11.06	134.1	13.2	3.5				
28.01.01	204.0	9.8	0.8				
21.12.06	246.0	10.1	0.4				

Table A.1, continued.

	Rhine				Ems				Weser		
Date	**Nitrate (µmol L^{-1})**	**δ^{15}N-nitrate**	**δ^{18}O-nitrate**	**Date**	**Nitrate (µmol L^{-1})**	**δ^{15}N-nitrate**	**δ^{18}O-nitrate**	**Date**	**Nitrate (µmol L^{-1})**	**δ^{15}N-nitrate**	**δ^{18}O-nitrate**
22.03.06	262.5	7.3	0.8	23.03.06	429.7	12.5	3.0	17.03.06	342.5	7.5	n.a.
05.04.06	215.3	6.5	n.a.	26.04.06	336.3	13.2	4.6	25.04.06	235.6	7.7	3.4
19.04.06	181.9	8.2	1.0	10.05.06	200.9	17.5	n.a.	09.05.06	196.2	10.8	n.a.
03.05.06	173.6	8.7	n.a.	22.05.06	152.8	15.1	4.9	23.05.06	150.5	11.0	3.6
17.05.06	136.8	9.5	1.4	07.06.06	255.1	14.0	n.a.	06.06.06	218.2	8.1	n.a.
31.05.06	182.4	8.2	n.a.	20.06.06	272.9	15.9	6.8	20.06.06	174.3	11.2	4.1
14.06.06	135.7	9.6	1.7	05.07.06	181.1	18.1	n.a.	04.07.06	125.9	13.0	n.a.
12.07.06	157.8	10.9	1.1	18.07.06	149.8	19.9	7.6	15.08.06	199.9	10.9	1.8
26.07.06	154.2	10.0	n.a.	31.07.06	68.4	20.9	n.a.	29.08.06	182.1	10.6	n.a.
09.08.06	139.1	10.1	0.1	15.08.06	151.5	15.9	5.2	12.09.06	217.4	10.2	1.4
23.08.06	150.0	9.9	0.6	30.08.06	266.7	14.5	n.a.	26.09.06	146.8	11.2	n.a.
06.09.06	138.9	9.2	-0.1	21.09.06	206.5	18.6	5.1	10.10.06	193.4	10.7	n.a.
20.09.06	160.3	10.6	n.a.	10.10.06	227.5	18.1	5.1	24.10.06	213.1	10.4	1.3
04.10.06	223.3	9.6	0.7	03.11.06	217.2	17.9	n.a.	07.11.06	202.7	10.2	1.5
18.10.06	154.0	10.1	n.a.	23.11.06	333.9	13.3	2.9	21.11.06	248.1	9.9	1.4
02.11.06	179.1	10.1	0.1	06.12.06	338.6	14.2	3.2	19.12.06	297.4	9.5	1.2
15.11.06	235.4	8.9	n.a.	21.12.06	497.5	11.9	2.4	03.01.07	284.0	9.5	1.4
29.11.06	188.6	10.4	n.a.	17.01.07	671.7	10.7	1.7	16.01.07	384.7	7.5	0.5
14.12.06	221.7	8.3	-0.2	31.01.07	525.9	10.5	2.3	30.01.07	328.7	7.5	0.8
11.01.07	259.7	7.8	-0.2	14.02.07	639.3	9.5	1.3	06.02.07	343.3	8.0	1.1
24.01.07	261.9	7.1	0.6	28.02.07	547.0	10.2	2.0	27.02.07	321.0	7.9	1.0
07.02.07	253.3	8.2	0.8	14.12.07	474.4	11.7	2.7	13.03.07	275.5	7.6	1.3
21.02.07	242.1	7.4	0.3	28.03.07	420.3	12.2	3.6	27.03.07	362.7	6.9	1.3
07.03.07	210.7	6.9	0.5								
28.03.07	252.8	7.5	1.2								

A.2 Sediment data from Skagerrak and Kattegat

A.2.1 Surface sediments

Table A.2.1: Surface sediment δ^{15}N data and sampling locations. Data east of 10°E have been published by Voss et al. (2005) and are not listed.

Lon (°E)	Lat (°N)	δ^{15}N (‰)	Lon (°E)	Lat (°N)	δ^{15}N (‰)	Lon (°E)	Lat (°N)	δ^{15}N (‰)
5.248	58.251	6.5	6.500	54.750	8.8	8.8475	54.042	10.5
7.392	57.767	6.7	6.736	55.679	8.9	8.8435	54.046	11.7
7.950	57.915	7.4	5.499	53.719	7.7	8.8455	54.042	11.8
8.305	57.870	6.8	6.161	53.835	9.3	8.8485	54.040	10.7
8.725	57.925	6.7	5.370	54.293	7.8	8.9452	53.886	9.4
9.412	58.233	6.9	5.340	54.776	8.0	8.935	53.899	11.4
9.851	58.435	6.8	5.493	55.250	8.0	8.9267	53.880	9.3
9.867	57.833	7.1	5.584	55.608	7.9	8.928	53.880	8.3
9.750	57.917	6.8	6.156	55.215	8.2	8.9642	53.893	9.2
9.666	58.017	6.2	6.472	54.760	9.0	8.3015	54.815	12.1
9.567	58.118	6.3	7.218	54.351	9.1	8.3118	54.853	12.6
5.999	56.999	6.7	8.128	54.067	8.9	8.574	54.791	13.7
6.004	56.2525	7.4	8.352	54.100	8.5	8.692	53.990	10.0
6.000	56.000	6.5	8.615	54.102	7.1	6.500	56.000	8.5
5.523	56.000	6.6	6.000	55.000	8.6	6.000	54.500	8.9
5.511	56.247	6.8	5.998	54.498	8.0	10.000	58.067	7.1
5.502	56.500	7.6	6.695	53.543	9.1	5.939	54.653	7.4
5.498	56.749	6.5	6.805	53.485	9.4	8.983	58.000	6.6
9.252	53.879	11.6	8.077	53.677	9.2	7.000	57.667	6.0
9.172	53.877	9.0	8.140	53.782	12.6	5.683	55.333	6.4
9.048	53.872	9.3	8.1278	54.067	8.8	8.001	57.334	6.8
8.635	53.967	8.6	5.001	55.168	7.0	6.502	54.499	7.9
8.348	54.000	10.3	5.330	55.082	7.3	5.996	55.083	7.1
6.433	54.834	10.2	5.000	55.002	7.3	6.497	54.998	7.3
6.718	53.834	8.8	5.000	55.097	8.1	8.848	54.040	11.1
7.282	53.833	8.3	5.000	54.751	7.8	8.642	54.029	9.1
7.983	54.001	8.0	5.247	54.751	7.8	8.710	54.049	7.5
7.852	54.000	7.1	5.625	54.818	7.6	8.771	54.014	8.7
7.287	54.000	6.3	6.003	54.750	7.6	8.298	53.960	10.1
6.718	54.167	8.4	6.504	54.752	7.3	8.438	53.885	11.9

Table A.2.1, continued.

Lon (°E)	Lat (°N)	$\delta^{15}N$ (‰)	Lon (°E)	Lat (°N)	$\delta^{15}N$ (‰)	Lon (°E)	Lat (°N)	$\delta^{15}N$ (‰)
8.340	54.114	9.4	6.897	54.677	8.1	8.575	54.003	11.5
7.114	56.254	8.6	7.616	54.375	9.0	6.797	54.583	8.3
7.091	57.667	6.0	5.807	54.488	7.1	7.499	54.169	8.5
8.711	57.774	5.3	5.679	54.408	11.9	8.001	54.053	8.8
8.697	57.837	5.8	5.656	54.339	7.7	9.197	53.874	8.0
8.697	57.837	5.8	5.603	54.2756	7.3	9.395	53.822	7.9
9.620	58.032	6.2	5.658	54.481	7.5	9.283	53.857	8.2
9.619	58.034	6.2	5.502	54.500	7.0	9.014	53.872	8.6
8.208	54.033	9.2	7.814	54.017	9.4	8.770	53.891	8.2
8.125	54.067	9.1	7.245	54.001	8.8	8.751	53.924	8.1
8.383	54.135	9.4	6.750	54.000	8.3	8.733	53.950	9.6
7.800	54.250	9.2	6.000	54.000	8.5	8.683	53.977	9.2
7.500	54.233	8.6	6.090	53.869	8.4	5.500	55.500	6.4
7.400	53.940	7.6	6.202	53.826	9.1	6.585	54.833	7.9
7.400	54.108	7.7	6.748	53.719	7.6	8.083	54.050	8.8
7.000	55.833	9.0	6.997	54.667	8.6	5.833	55.417	7.2
6.333	55.067	8.2						

A.2.2 Sediment cores from Skagerrak and Kattegat

Tab. A.2.2 Sediment cores from the Skagerrak and Kattegat, 0-200 cm depth. Note that two gravity cores (225514 and 225521) overpenetrated, sample depths thus do not represent original depth in sediments.

225517 MUC		**225517 GC**		**225512 MUC**		**225514 GC**		**225521 MUC**		**225521 GC**	
depth (cm)	**$\delta^{15}N$ (‰)**	**depth (cm)**	**$\delta^{15}N$ (‰)**	**depth (cm)**	**$\delta^{15}N$ (‰)**	**depth (cm)**	**$\delta^{15}N$ (‰)**	**depth (cm)**	**$\delta^{15}N$ (‰)**	**depth (cm)**	**$\delta^{15}N$ (‰)**
0.5	6.0	0.5	6.3	0.5	5.8	0.5	6.1	0.5	7.2	0.5	6.0
2.5	6.3	10.5	5.8	2.5	6.3	10.5	5.7	2.5	7.1	10.5	6.0
4.5	6.1	20.5	5.5	4.5	6.0	16.5	6.1	4.5	7.1	20.5	4.9
6.5	5.9	30.5	5.2	6.5	6.1	25.5	5.7	6.5	7.1	30.5	5.8
8.5	6.4	40.5	5.1	8.5	6.1	35.5	5.4	8.5	7.1	40.5	5.8
10.5	6.0	50.5	5.5	10.5	6.1	45.5	5.8	10.5	7.0	50.5	5.1
12.5	5.9	55.5	5.5	12.5	6.3	55.5	5.7	12.5	7.0	60.5	5.8
14.5	5.6	65.5	4.9	14.5	6.2	65.5	6.1	14.5	6.9	70.5	5.7
16.5	5.9	75.5	5.4	16.5	6.1	75.5	5.7	16.5	6.9	80.5	5.8
18.5	6.1	85.5	5.3	18.5	6.2	85.5	5.7	18.5	7.0	90.5	5.6
20.5	5.3	95.5	5.9	20.5	6.2	95.5	5.7	20.5	6.8	100.5	5.5
22.5	5.9	105.5	4.7	22.5	6.2	105.5	5.6	22.5	6.7	110.5	5.7
24.5	5.7	115.5	4.8	24.5	6.2	110.5	6.1	24.5	6.8	120.5	5.6
26.5	5.6	125.5	5.3	26.5	6.1	120.5	5.8	26.5	6.9	130.5	5.8
28.5	5.9	135.5	5.1	28.5	6.1	130.5	5.3	28.5	7.1	140.5	5.6
30.5	5.6	145.5	6.0	30.5	6.0	140.5	5.7	30.5	6.3	150.5	5.6
32.5	5.1	154.5	5.7	32.5	6.1	150.5	5.5	32.5	6.5	160.5	5.2
34.5	5.4	160.5	4.5	34.5	6.1	160.5	5.8	34.5	6.6	170.5	5.5
36.5	5.7	170.5	5.3			170.5	5.8	36.5	6.8	180.5	5.7
38.5	5.8	180.5	5.3			180.5	5.7	38.5	6.6	190.5	5.7
40.5	5.8	190.5	5.8			190.5	5.4	40.5	6.6		
		200.5	5.4					42.5	6.8		
								44.5	6.7		

Tab. A.2.2, continued.

225510 MUC		225510 GC		242970 MUC		242970 GC	
depth (cm)	δ^{15}N (‰)	depth (cm)	δ^{15}N (‰)	depth (cm)	δ^{15}N (‰)	depth (cm)	δ^{15}N (‰)
0.5	6.2	0.5	6.2	0.5	5.3	0.5	5.6
2.5	6.3	10.5	5.6	1.5	6.2	5.5	5.8
4.5	6.2	20.5	6.0	2.5	6.1	15.5	5.2
6.5	5.9	30.5	6.1	3.5	5.8	20.5	4.7
8.5	6.1	40.5	5.2	4.5	6.4	25.5	4.4
10.5	6.1	50.5	5.9	5.5	6.5	30.5	5.2
12.5	6.2	60.5	5.8	6.5	6.2	35.5	5.0
14.5	6.0	70.5	5.9	7.5	5.4	40.5	5.0
16.5	6.1	80.5	6.2	8.5	5.7	45.5	4.8
18.5	6.1	90.5	5.8	9.5	5.6	55.5	5.0
20.5	6.0	100.5	6.3	10.5	5.6	60.5	4.9
22.5	5.8	110.5	6.2	11.5	5.7	65.5	4.8
24.5	6.0	120.5	6.1	12.5	5.8	70.5	4.6
26.5	5.8	130.5	6.2	13.5	5.1	75.5	5.0
28.5	6.0	140.5	6.0	14.5	5.6	80.5	4.9
30.5	5.6	150.5	6.5	15.5	5.4	85.5	4.9
32.5	5.7	160.5	6.2	16.5	5.4	90.5	5.0
34.5	5.9	172.5	6.2	17.5	5.4	95.5	4.8
36.5	6.2	180.5	6.3	18.5	5.0	100.5	4.7
38.5	6.0	192.5	5.5			105.5	4.9
40.5	6.1					110.5	4.7
						115.5	4.7
						120.5	6.5
						125.5	4.4
						130.5	4.9
						135.5	5.1
						140.5	4.7
						145.5	4.8
						150.5	4.8
						155.5	5.3
						160.5	4.6
						165.5	4.8
						170.5	4.5
						175.5	5.0
						180.5	4.8
						185.5	5.1
						190.5	4.8
						195.5	5.1

A.3 Elbe estuary

Table A.3.1: Salinity gradient in the Elbe estuary, October 2005 (cf. Chapter 4), sampled with RV *Ludwig Prandtl*.

Station	No.	Lat (°N)	Lon (°E)	Salinity (psu)	Nitrate (µmol L^{-1})	δ^{15}N (‰)	t (°C)	Depth (m)	Time (UTC)	Date
Tesperhude	1-1	53°24.014'	10°25.507'	0.46	185.8	11.2	11.3	1.5	9:32	24.10.05
	1-2	53°24.014'	10°25.507'	0.46	184.6	11.2	11.3	3.0	9:26	24.10.05
	2-1	53°24.025'	10°25.510'	0.46	184.4	11.2	11.3	2.0	9:23	24.10.05
	2-2	53°24.025'	10°25.510'	0.46	184.8	11.3	11.3	4.0	9:19	24.10.05
	3-1	53°24.059'	10°25.507'	0.46	181.0	11.4	11.1	2.0	9:10	24.10.05
	3-2	53°24.059'	10°25.507'	0.46	178.6	11.5	11.1	4.0	9:09	24.10.05
Zollenspieker	1-1	53°23.753'	10°10.747'	0.46	181.6	11.5	12.5	1.5	11:39	24.10.05
	1-2	53°23.753'	10°10.747'	0.46	183.4	11.5	12.5	5.0	11:38	24.10.05
	2-1	53°23.781'	10°10.716'	0.46	184.2	11.4	12.5	1.5	11:52	24.10.05
	2-2	53°23.781'	10°10.716'	0.46	185.9	11.6	12.5	3.0	11:49	24.10.05
	2-3	53°23.781'	10°10.716'	0.46	185.1	11.5	12.5	5.0	11:48	24.10.05
	3-1	53°23.832'	10°10.698'	0.46	184.5	11.4	12.5	1.5	11:56	24.10.05
	3-2	53°23.832'	10°10.698'	0.46	185.6	11.4	12.5	4.5	11:55	24.10.05
Köhlbrandhöft, Norderelbe	1-1	53°32.432'	9°56.244'	0.42	173.8	11.2	12.4	1.5	13:33	24.10.05
	1-2	53°32.432'	9°56.244'	0.42	173.0	11.3	12.4	13	13:31	24.10.05
	2-1	53°32.469'	9°56.184'	0.43	169.9	11.4	12.3	1.5	13:56	24.10.05
	2-2	53°32.469'	9°56.184'	0.43	168.8	11.1	12.3	7	13:53	24.10.05
	2-3	53°32.469'	9°56.184'	0.43	161.3	11.2	12.3	15	13:52	24.10.05
	3-1	53°32.567'	9°56.257'	0.42	168.7	11.6	12.3	1.5	13:26	24.10.05
	3-2	53°32.567'	9°56.257'	0.42	170.1	n.a.	12.3	8.0	13:25	24.10.05
Köhlbrandhöft, Süderelbe	1-1	53°32.214'	9°56.007'	0.43	181.7	n.a.	12.3	1.5	14:04	24.10.05
	1-2	53°32.214'	9°56.007'	0.43	173.9	11.4	12.3	14.0	14:03	24.10.05
	2-1	53°32.234'	9°56.075'	0.43	170.6	11.4	12.3	1.5	14:14	24.10.05
	2-2	53°32.234'	9°56.075'	0.43	170.1	11.4	12.3	7.0	14:11	24.10.05
	2-3	53°32.234'	9°56.075'	0.43	170.5	11.3	12.3	14	14:10	24.10.05
	3-1	53°32.292'	9°56.148'	0.43	172.0	11.2	12.4	1.5	14:23	24.10.05
	3-2	53°32.292'	9°56.148'	0.43	172.9	11.1	12.4	7.0	14:22	24.10.05
Seemannshöft	1-1	53°32.429'	9°53.039'	0.42	176.1	11.4	12.5	1.5	14:43	24.10.05
	1-2	53°32.429'	9°53.039'	0.42	176.1	11.3	12.5	11.0	14:39	24.10.05
	2-1	53°32.528'	9°53.974'	0.43	172.4	11.6	12.5	1.5	14:55	24.10.05

Table A.3.1, continued.

Station	No.	Lat (°N)	Lon (°E)	Salinity (psu)	Nitrate (µmol L^{-1})	δ^{15}N (‰)	t (°C)	Depth (m)	Time (UTC)	Date
Seemannshöft	2-2	53°32.528'	9°53.974'	0.43	170.4	11.4	12.4	7.0	14:52	24.10.05
	2-3	53°32.528'	9°53.974'	0.43	172.7	11.3	12.4	15.0	14:51	24.10.05
	3-1	53°32.645'	9°53.536'	0.43	171.8	n.a.	12.4	1.5	15:01	24.10.05
	3-2	53°32.645'	9°53.536'	0.43	170.5	11.3	12.4	11.5	15:00	24.10.05
Grauerort	1-1	53°40.440'	9°30.015'	0.51	188.5	11.7	12.8	1.5	10:49	25.10.05
	1-2	53°40.440'	9°30.015'	0.51	187.9	11.3	12.8	10.0	10:48	25.10.05
	2-1	53°40.510'	9°30.552'	0.63	190.0	11.4	12.8	1.5	11:10	25.10.05
	2-2	53°40.510'	9°30.552'	0.51	189.8	11.4	12.8	7.5	10:57	25.10.05
	2-3	53°40.510'	9°30.552'	0.51	188.4	11.4	12.8	15.0	10:56	25.10.05
	3-1	53°40.779'	9°30.655'	0.51	189.3	11.5	12.8	1.5	11:06	25.10.05
	3-2	53°40.779'	9°30.655'	0.51	190.6	11.3	12.8	5.0	11:04	25.10.05
Pagensander Nebenelbe	1-1	53°41.992'	9°31.373'	0.56	184.6	11.4	12.6	1.5	10:00	25.10.05
	1-2	53°41.992'	9°31.373'	0.56	184.8	11.5	12.6	4.5	10:00	25.10.05
	2-1	53°42.002'	9°31.467'	0.56	185.3	11.4	12.6	1.5	10:10	25.10.05
	2-2	53°42.002'	9°31.467'	0.56	184.4	11.4	12.6	3.5	10:07	25.10.05
	2-3	53°42.002'	9°31.467'	0.56	184.4	11.6	12.6	6.0	10:06	25.10.05
	3-1	53°42.045'	9°31.500'	0.55	186.1	11.5	12.5	1.5	10:15	25.10.05
	3-2	53°42.045'	9°31.500'	0.55	184.9	11.5	12.5	4.0	10:14	25.10.05
Glückstadt	1-1	53°47.101'	9°22.603'	0.77	180.5	11.7	12.8	1.5	12:14	25.10.05
	1-2	53°47.101'	9°22.603'	0.81	180.3	11.7	12.8	7.0	12:13	25.10.05
	2-1	53°47.170'	9°23.088'	0.77	181.5	11.8	12.9	1.5	12:25	25.10.05
	2-2	53°47.170'	9°23.088'	0.77	183.3	11.6	12.9	7.5	12:22	25.10.05
	2-3	53°47.170'	9°23.088'	0.85	184.0	11.7	12.9	15.0	12:21	25.10.05
	3-1	53°47.349'	9°23.526'	0.70	184.4	11.8	12.8	1.5	12:00	25.10.05
	3-2	53°47.349'	9°23.526'	0.70	185.8	11.5	12.8	6.5	11:59	25.10.05
Brunsbüttel	1-1	53°52.457'	9°10.064'	11.2	108.9	12.2	12.7	1.5	10:45	26.10.05
	1-2	53°52.457'	9°10.064'	13.4	n.a.	12.3	12.6	7.0	10:45	26.10.05
	2-1	53°52.928'	9°10.832'	12.2	101.2	12.0	12.6	1.5	10:34	26.10.05
	2-2	53°52.928'	9°10.832'	12.4	98.4	n.a.	12.6	7.5	10:31	26.10.05
	2-3	53°52.928'	9°10.832'	13.5	95.0	n.a.	12.6	15.0	10:30	26.10.05
	3-1	53°53.260'	9°11.092'	11.2	105.8	n.a.	12.6	1.5	10:22	26.10.05
	3-2	53°53.260'	9°11.092'	13.2	96.8	n.a.	12.6	12.0	10:21	26.10.05

Table A.3.1, continued.

Station	No.	Lat (°N)	Lon (°E)	Salinity (psu)	Nitrate (µmol L^{-1})	$\delta^{15}N$ (‰)	t (°C)	Depth (m)	Time (UTC)	Date
Cux-haven	1-1	53°53.392'	8°41.560'	23.4	36.6	11.7	12.4	1.5	12:49	26.10.05
	1-2	53°53.392'	8°41.560'	27.5	22.1	10.9	12.3	15.0	12:45	26.10.05
Elbe, Tonne 53	1-1	53°51.394'	9°01.664'	15.5	81.7	11.9	12.4	1.5	11:23	26.10.05
	1-2	53°51.394'	9°01.664'	18.5	68.9	12.1	12.4	15.0	11:19	26.10.05
Elbe, Tonne 47	1-1	53°50.524'	8°56.071'	17.2	72.8	12.1	12.4	1.5	11:49	26.10.05
	1-2	53°50.524'	8°56.071'	21.1	60.1	11.8	12.4	13.0	11:47	26.10.05
Elbe, Tonne 33	01-1	53°51.440'	8°44.381'	21.2	50.8	12.0	12.4	1.5	12:30	26.10.05
	1-2	53°51.440'	8°44.381'	25.8	30.2	11.4	12.4	15.0	12:28	26.10.05

Table A.3.2: Salinity gradient in the Elbe estuary, May 2006, sampled with the RV *Uthörn*. Note that samples are always taken at the surface, therefore depths are not given.

Sample No.	Lat (°N)	Lon (°E)	Con-ductivity (mS)	Nitrate (µmol L^{-1})	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	t (°C)	Time	Date
11	53° 34.1	09° 99.0	0.4	LOST	LOST	LOST	14.3	15.35	03.05.06
10	53° 41.3	09° 29.7	0.4	261	8.2	7.5	13.7	14.30	03.05.06
9	53° 45.4	09° 23.8	0.4	276	8.3	6.3	13.7	13.45	03.05.06
8	53° 49.4	09° 21.3	0.4	282	8.0	1.3	13.5	13.00	03.05.06
7	53° 50.9	08° 59.2	1.1	319	7.7	1.4	12.2	11:05	03.05.06
6	53° 50.5	08° 56.1	1.7	314	7.8	0.7	12	10:40	03.05.06
5	53° 50.1	08° 50.8	2.6	307	7.6	0.5	11.9	10.00	03.05.06
4	53° 50.6	08° 45.8	5.0	289	7.6	0.6	11.5	9:20	03.05.06
1	53° 52.8	08° 42.0	9.5	239	8.4	0.6	11	8:10	03.05.06
12	53° 53.8	08° 41.9	11.4	228	8.3	n.a.	11.3	8:15	04.05.06
2	53° 52.8	08° 42.1	13.0	203	8.4	0.5	10.4	8:30	03.05.06
3	53° 52.6	08° 42.5	14.3	188	8.4	1.2	10.4	8:40	03.05.06
13	53° 56.5	08° 39.8	14.9	183	8.3	n.a.	10.9	8:30	04.05.06
14	53° 59.5	08° 33.4	18.3	148	8.4	n.a.	10.6	9.00	04.05.06
15	53° 59.5	08° 31.2	20.4	121	8.5	n.a.	10.4	9:09	04.05.06
16	54° 00.0	08° 22.2	22.1	103	7.9	n.a.	10.2	9:39	04.05.06
17	54° 02.1	08° 13.7	25.4	65	8.1	1.4	9.6	10:08	04.05.06
18	5°4 04.7	08° 07.1	29.6	17	9.6	2	8.6	10:37	04.05.06
19	54° 09.6	07° 49.8	31.2	7	11.8	5.6	8.1	12:06	04.05.06
20	54° 15.6	07° 35.4	31.2	9	11.4	9.5	7.7	13.15	04.05.06

Table A.3.3: Salinity gradient in the Elbe estuary, June 2006. Sampled with RV *Ludwig Prandtl.*

Station	Lat (°N)	Lon (°E)	Conductivity (mS)	Nitrate (µmol L^{-1})	δ^{15}N (‰)	δ^{18}O (‰)	t (°C)	depth (m)	time (UTC)	Date
Tesperhude	53°40.06	10°42.5	0.4	111	n.a.	n.a.	21.9	1	10:21	22.06.06
	53°40.06	10°42.5	0.4	115	16.2	7.3	21.9	3	10:18	22.06.06
Zollenspieker	53°39.58	10°17.99	0.4	114	16.8	7.5	22.6	0.5	08:06	22.06.06
	53°39.58	10°17.99	0.4	114	n.a.	n.a.	22.6	1.5	08:03	22.06.06
Köhbrandhöft, Norderelbe	53°54.02	9°93.57	0.4	155	12.3	3.8	22	1	14:46	21.06.06
	53°54.02	9°93.57	0.4	148	n.a.	n.a.	22	11	14:43	21.06.06
Köhbrandhöft, Süderelbe	53°53.69	9°93.72	0.4	148	n.a.	n.a.	22.2	1	14:35	21.06.06
	53°53.69	9°93.72	0.4	151	n.a.	n.a.	22.2	5	14:32	21.06.06
Seemannshöft	53°54.04	9°88.26	0.4	169	12	3	21.9	1	14:15	21.06.06
	53°54.04	9°88.26	0.4	170	n.a.	n.a.	21.9	8.5	14:12	21.06.06
Grauerort	53°67.21	9°50.31	0.5	221	10.0	n.a.	20.3	1	12:06	21.06.06
	53°67.21	9°50.31	0.5	228	9.8	n.a.	20.3	9.5	12:03	21.06.06
Glückstadt	53°78.51	9°38.06	0.8	243	9.4	1.0	19.5	1	11:04	21.06.06
	53°78.51	9°38.06	0.8	242	9.8	n.a.	19.5	11	11:00	21.06.06
Brunsbüttel	53°87.7	9°17.43	2.6	202	10.8	n.a.	19.2	1	09:55	21.06.06
	53°87.7	9°17.43	4.3	179	11.1	n.a.	19.2	13	09:51	21.06.06
Cuxhaven	53°86.39	8°70.97	17.2	52	10.9	n.a.	17.6	1	06:57	20.06.06
	53°86.39	8°70.97	22.5	49	n.a.	n.a.	17	18	07:01	20.06.06
Tonne 53	53°85.51	9°02.02	8.1	147	n.a.	n.a.	18.7	1	09:13	21.06.06
	53°85.51	9°02.02	8.7	145	10.9	n.a.	18.6	17	09:09	21.06.06
Tonne 47	53°84.3	8°94.21	10.0	135	11.4	n.a.	18.5	1	08:48	21.06.06
	53°84.3	8°94.21	12.8	117	11.1	2.0	18.4	16	08:44	21.06.06
Tonne 33	53°85.11	8°75.47	19.1	70	11.3	n.a.	17.7	1	08:01	21.06.06
	53°85.11	8°75.47	20.2	58	11.4	n.a.	17.6	18	07:57	21.06.06
Tonne 22	53°97.96	8°60.91	23.6	37	11.4	3.6	17.1	1	07:52	21.06.06
	53°97.96	8°60.91	25.7	29	11.2	4.0	16.6	10	07:54	21.06.06
Tonne 12	53°99.22	8°43.84	26.1	30	11.4	4.4	16.5	1	08:34	20.06.06
	53°99.22	8°43.84	29.9	14	11.3	n.a.	14.9	9	08:41	20.06.06
Tonne 2	54°02.81	8°22.44	27.8	23	11.5	5.4	16.4	1	09:42	20.06.06
	54°02.81	8°22.44	31.3	8	11.4	n.a.	13.3	14	09:35	20.06.06
Elbe 1	54°03.18	8°11.63	30.7	8	12.0	10.3	14.3	1	10:17	20.06.06
	54°03.18	8°11.63	31.6	6	12.2	n.a.	12.2	18	10:12	20.06.06
north of Elbe 1	54°07.43	8°00.78	30.0	6	13.9	17.3	15.7	1	10:56	20.06.06
	54°07.43	8°00.78	31.2	6	13.0	n.a.	13.1	15.5	10:52	20.06.06

Table A.3.4: Salinity gradient in the Elbe estuary, August 2006. Sampled with RV *Ludwig Prandtl*. Water samples taken from the surface (1 m depth) with the ship's membrane pump.

Sample No.	Lat (°N)	Lon (°E)	Salinity (psu)	Nitrate (µmol L^{-1})	δ^{15}N	δ^{18}O	t (°C)	Time (UTC)	Date
19	53°54.88	9°82.51	0.5	78.5	13.4	3.2	20.5	10:36	17.08.06
18	53°63.67	9°52.33	0.6	104.3	13.5	n.a.	21.4	09:11	17.08.06
17	53°73.12	9°44.25	0.8	121.4	13.3	0.66	21.0	08:32	17.08.06
16	53°79.47	9°39.59	1.2	128.3	13.3	n.a.	21.3	08:05	17.08.06
15	53°82.73	9°36.57	1.9	127.8	13.1	n.a.	21.4	07:50	17.08.06
14	53°85.74	9°29.57	3.2	116.1	13.2	n.a.	20.9	07:32	17.08.06
13	53°86.5	9°27.42	4.3	122.2	13.3	0.55	20.9	07:27	17.08.06
12	53°87.41	9°24.2	5.4	121.6	13.1	n.a.	20.8	07:20	17.08.06
11	53°87.79	9°15.01	6.7	114.5	13	0.34	20.6	07:01	17.08.06
10	53°87.28	9°09.13	9.7	104.2	12.8	0.72	20.2	06:49	17.08.06
9	53°87.07	9°08.15	10.7	99.3	12.7	n.a.	20.0	06:47	17.08.06
8	53°84.79	8°97.73	12.2	88.7	12.8	n.a.	19.7	06:26	17.08.06
6	53°84.47	8°94.89	12.9	83.9	12.5	1.28	19.6	06:20	17.08.06
7	53°84.61	8°95.98	13.5	85.0	12.4	n.a.	19.7	06:22	17.08.06
5	53°84.29	8°92.99	14.5	77.5	12.4	0.86	19.5	06:16	17.08.06
4	53°84.08	8°90.34	15.9	73.8	12.4	1.03	19.4	06:11	17.08.06
3	53°83.81	8°87.73	16.4	66.1	12.4	1.35	19.4	06:06	17.08.06
2	53°83.71	8°84.18	17.8	59.0	12.2	1.2	19.2	05:59	17.08.06
30	53°88.59	8°70.04	20.4	49.0	12.4	1.24	19.3	14:33	16.08.06
1	53°85.84	8°73.82	21.0	33.8	12.4	1.51	19.3	05:38	17.08.06
29	53°89.5	8°69.16	21.1	42.5	n.a.	n.a.	19.2	14:30	16.08.06
28	53°91.24	8°67.45	22.0	27.4	12.2	1.7	19.1	14:25	16.08.06
27	53°92.72	8°66.09	23.0	35.6	12.2	1.8	19.2	14:20	16.08.06
26	53°94.28	8°63.89	23.5	32.9	12.1	1.5	19.5	14:15	16.08.06
25	53°95.41	8°61.25	25.2	24.9	12.3	2.1	19.4	14:10	16.08.06
23	54°02.55	8°27.85	30.4	2.1	12.4	5.2	19.2	13:08	16.08.06
24	53°98.12	8°40.13	30.7	5.4	12.4	5.1	19.1	13:36	16.08.06
20	54°15.23	8°01.67	31.2	2.5	10.2	5.9	19.7	11:30	16.08.06
21	54°11.48	8°04.62	31.4	2.2	n.a.	n.a.	19.6	12:16	16.08.06
22	--no data--	--no data--	-no data-	4.5	n.a.	n.a.	-no data-	13:08	16.08.06

Table A.3.5: Salinity gradient in the Elbe estuary, December 2006. Sampled with RV *Ludwig Prandtl.* Water samples taken from the surface (1 m depth) with the ship's membrane pump.

Lat (° N)	Lon (° E)	Salinity (psu)	Nitrate (µMol L^{-1})	δ^{15}N	δ^{18}O	t (°C)	Time (UTC)	Date
53°56.58	9°65.78	0.5	231.7	10.5	-0.1	7.45	13:33	20.12.06
53°77.91	9°38.25	0.8	228.7	10.4	-0.1	7.56	11:59	20.12.06
53°81.12	9°36.69	1.1	228.9	10.3	-0.1	7.63	11:49	20.12.06
53°84.73	9°31.42	2.1	218.9	10.4	-0.1	7.95	11:35	20.12.06
53°86.62	9°27.04	2.8	241.8	9.0	2.3	8.05	11:26	20.12.06
53°87.71	9°20.25	4.0	204.5	10.3	-0.1	8.09	11:13	20.12.06
53°87.8	9°15.24	5.1	194.7	10.5	0.2	8.03	11:05	20.12.06
53°87.6	9°10.94	6.6	184.3	10.8	0.6	7.94	10:58	20.12.06
53°86.4	9°05.76	7.5	161.1	10.7	0.5	7.78	10:49	20.12.06
53°85.37	9°01.45	8.6	162.4	10.6	0.4	7.73	10:41	20.12.06
53°84.7	8°96.94	9.5	154.5	10.6	0.5	7.66	10:33	20.12.06
53°84.3	8°93.96	10.6	147.8	10.9	0.7	7.63	10:28	20.12.06
53°84.02	8°90.15	12.0	133.4	10.5	0.4	7.58	10:22	20.12.06
53°83.65	8°82.3	13.7	124.1	10.7	0.5	7.51	10:09	20.12.06
53°84.38	8°76.85	16.5	103.4	10.0	0.2	7.43	09:59	20.12.06
---no data---	---no data---	16.9	98.9	10.1	0.9	7.45	07:40	20.12.06
---no data---	---no data---	18.1	89.6	10.3	0.5	7.45	07:44	20.12.06
---no data---	---no data---	21.1	73.5	9.7	0.6	7.43	07:52	20.12.06
---no data---	---no data---	22.3	65.5	9.7	0.5	7.46	08:00	20.12.06
53°96.2	8°56.61	23.6	57.1	9.1	0.2	7.48	08:07	20.12.06
53°96.36	8°55.13	25.0	50.3	9.1	0.7	7.52	08:11	20.12.06
53°96.3	8°55.75	27.2	33.9	8.0	0.3	7.54	09:03	20.12.06

6. Curriculum Vitae

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June 1998	Abitur at Gymnasium Glinde
April 1999 –October 1999	Study of Chemistry at the University of Hamburg
October1999 – December. 2004	Study of Biology at the University of Hamburg, Major: Applied Botany, Minors: Microbiology, Zoology
Dec. 2003 – Sept. 2004	Diploma thesis in the Institute of Applied Botany at the University of Hamburg: β-Glucosidase in leaves of the cyanogenic plant *Phaseolus lunatus* L. (in German)
Since February 2005:	PhD-thesis at the University of Hamburg in Cooperation with the GKSS Research Centre, Institute for Coastal research: Nitrogen Cycling in the Southern North Sea – Assessment by stable isotopes

List of Publications:

- Dähnke, K., Bahlmann, E., Emeis, K. 2008. A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary. *Limnology and Oceanography* **43:** 1504-1511.
- Dähnke, K., Blanz, T., Emeis, K. 2008. Tracing changes in the nitrogen cycle of the North Sea and Kattegat (northwest Europe) by nitrogen isotopes in marine sediments. *Marine Geology,* doi: 10.1016/j.margeo2008.04.017.
- Johannsen, A., Dähnke, K., Emeis, K. 2008. Isotopic composition of nitrate in five German rivers discharging into the North Sea. *Organic Geochemistry,* doi: 10.1016/j.orggeochem.2008.03.004.

- Tim Schlarbaum, T., Dähnke, K., Bahlmann, E., Emeis, K.: Dissolved organic nitrogen turnover in the Elbe estuary: results of nitrogen isotope investigations (*in preparation*).
- Mara, V., Mihalopoulos, N., Gogou, A., Daehnke, K., Schlarbaum, T., Emeis K., and J. Krom: Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete/ Eastern Mediterranean Sea, submitted to *Global Biogeochemical Cycles*.
- Dähnke, K., Paetsch J., and K. Emeis: Nitrogen budget of the southern North Sea: A stable isotope approach (*in preparation).*