

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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $78 \mu\text{mol L}^{-1}$ to $232 \mu\text{mol L}^{-1}$; $\delta^{15}\text{N}$ varied from 8.2‰ to 16.2‰, and the $\delta^{18}\text{O}$ values ranged from -0.1‰ to 3.2‰. The nitrate concentrations in the German Bight were between $2 \mu\text{mol L}^{-1}$ and $34 \mu\text{mol L}^{-1}$, with $\delta^{15}\text{N}$ between 8.0‰ and 12.2‰ and $\delta^{18}\text{O}$ between 0.3‰ and 9.5‰. Both riverine and marine end-member concentrations 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.

Estuaries have a prominent role in regulating material fluxes from land to sea (Crossland et al. 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 50% of reactive nitrogen (OsparCom 2000). In spite of its salient relevance as a 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 $\sim 5\%$ in the Humber estuary (Jickells et al. 2000) to $\sim 20\%$ 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 $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ 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 riverborne 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 data sets of 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.

Materials and Methods

Study site—The Elbe estuary (Fig. 1) is a turbid estuary with suspended matter concentration ranging from

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Acknowledgments

We thank the participants of cruises with RV *Uthörn* for their help with sample collection on the vessel. We also thank M. Bergemann and G. Burghardt from the Arbeitsgemeinschaft für die Reinhaltung der Elbe (ARGE) for providing the archive data sets and for many helpful suggestions. We would like to thank Jay Brandes and one anonymous reviewer, whose comments helped to improve the manuscript significantly.

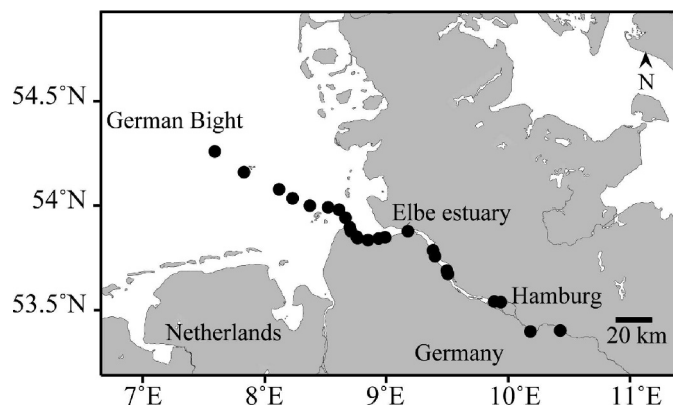


Fig. 1. Sampling area and stations.

~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 m³ s⁻¹ and an annual nitrate load of 79 × 10⁶ kg N yr⁻¹, the Elbe is one of the most important nitrogen sources for 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. in press), complicate the attainment of environmental quality goals.

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 behavior within the water column, both surface and bottom samples were taken. Further sampling campaigns were carried out in May, June, August, and December 2006 (Table 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 are from a marine end-member station only few miles offshore (Fig. 1). Sampling of summer cruises also covered salinities up to 31, representing typical German Bight coastal water (BSH 2006).

The river water samples were either taken with a colloidal organic carbon (COC) Limnos sampler (Hydro-Bios) attached to the multiprobe or with the ship's membrane pump. The inlet of the membrane pump was situated below the ship's bow at a depth of 1 m. Water samples were filtered through precombusted glass fiber filters (GF/F) 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):

$$\text{salinity} = 1.805 \times \text{chlorinity}(\text{‰}) + 3 \times 10^{-2}$$

Analytical Methods

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-naphthyl)-ethylenediamine, which was then determined photometrically at a wavelength of 540 nm with an auto-analyzer 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.

Isotopic analysis of water samples—δ¹⁵N and δ¹⁸O of nitrate were determined with the denitrifier method (Sigman et al. 2001; Casciotti et al. 2002). In brief, the water samples were injected into a suspension of *Pseudomonas aureofaciens* (ATCC#13985) for combined analysis of δ¹⁵N and δ¹⁸O, or *P. chlororaphis* for δ¹⁵N analysis only. Both bacterial strains denitrify nitrate under anoxic conditions but lack nitrous-oxide reductase activity. The resulting N₂O 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

Table 1. Overview of sampling campaigns in the Elbe estuary.

Date	Vessel	No. of stations	Maximum salinity	Temperature range (°C)
October 2005	RV <i>Ludwig Prandtl</i>	13	27.5	11.1–12.9
May 2006	RV <i>Uthörn</i>	20	31.2	7.7–14.3
June 2006	RV <i>Ludwig Prandtl</i>	17	31.3	22.2–13.1
August 2006	RV <i>Ludwig Prandtl</i>	30	31.4	19.1–21.7
December 2006	RV <i>Ludwig Prandtl</i>	22	27.2	7.4–8.1

(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 $\delta^{18}\text{O}$ values was negligible (Casciotti and McIlvin 2007).

The standard deviation for IAEA- NO_3 was >0.2‰ ($n = 5$) for $\delta^{15}\text{N}$ and >0.4‰ for $\delta^{18}\text{O}$. 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ as in IAEA-N3.

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

$$\delta^{15}\text{N} \left(\frac{^{15}\text{N}/^{14}\text{N}_{\text{sample}}}{^{15}\text{N}/^{14}\text{N}_{\text{std}}} - 1 \right) \times 1,000 \quad (1)$$

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‰.

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

$$C_{\text{MIX}} = f \times C_{\text{R}} + (1 - f)C_{\text{M}} \quad (2)$$

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:

$$f = (31 - \text{measured salinity})/31 \quad (3)$$

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):

$$\delta_{\text{MIX}} = [f \times C_{\text{R}} \times \delta_{\text{R}} + (1 - f)C_{\text{M}} \times \delta_{\text{M}}]/C_{\text{MIX}} \quad (4)$$

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).

Results

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. The lowest nitrate concentrations were found in late summer and were followed by an

increase over the course of the year with maximum nitrate concentrations of $260 \mu\text{mol L}^{-1}$ 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. 2A) represents a situation of low biological activity in river, estuary, and German Bight. Nitrate concentrations in the river end-member were $230 \mu\text{mol L}^{-1}$, decreasing to a value of $34 \mu\text{mol L}^{-1}$ in the coastal waters. The $\delta^{18}\text{O}$ values did not change along the salinity gradient and remained stable around 0‰, whereas $\delta^{15}\text{N}$ 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 $260 \mu\text{mol L}^{-1}$ and indicated only limited nitrate consumption upstream at this time of the year. A clear increase in nitrate concentration by about $60 \mu\text{mol L}^{-1}$, 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 $\delta^{15}\text{N}$ and a very pronounced decrease in $\delta^{18}\text{O}$ 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. 2B). $\delta^{15}\text{N-NO}_3^-$ values remained stable at $8.1 \pm 0.3\%$ 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 behavior.

The gradient sampled in June 2006 (Fig. 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 $150 \mu\text{mol L}^{-1}$ to $240 \mu\text{mol L}^{-1}$, while the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$, but concentration data suggest a slight nitrate sink within the estuary may have removed ~5–10% of the total nitrate load. $\delta^{15}\text{N-NO}_3^-$ 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 $\leq 1\%$ for $\delta^{18}\text{O}$ and no apparent fractionation for $\delta^{15}\text{N}$. 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. 2D), the initial nitrate concentration determined landward of the weir was $104 \mu\text{mol L}^{-1}$, decreasing to $78 \mu\text{mol L}^{-1}$ 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 $128 \mu\text{mol L}^{-1}$), the range of which corresponds to the turbidity maximum downstream of Hamburg (Fig. 3). While this increase in concentrations did

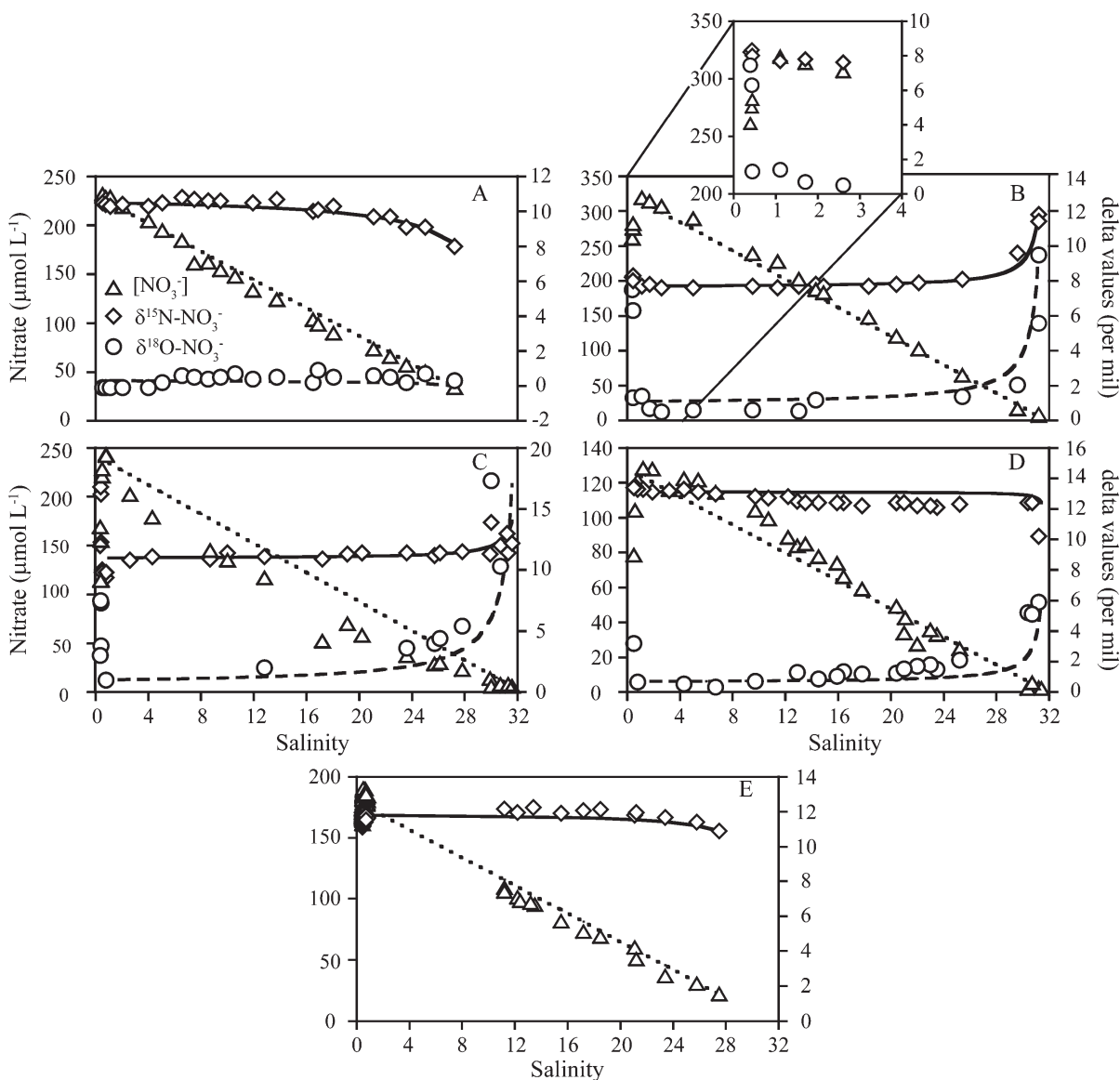


Fig. 2. Nitrate concentrations and isotopic values of nitrate along the salinity gradient in the Elbe estuary. (A) December, (B) May (insert shows the increase in nitrate concentrations in the upper estuary), (C) June, (D) August, (E) October.

not affect $\delta^{15}\text{N-NO}_3^-$ to any significant extent, $\delta^{18}\text{O-NO}_3^-$ 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, $\delta^{15}\text{N}$ was $\sim 1\%$ below and $\delta^{18}\text{O}$ was slightly enriched above the theoretical conservative mixing line.

The gradient sampled in October 2006 (Fig. 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 $169 \mu\text{mol L}^{-1}$ in the port of Hamburg to a mean value of $189 \mu\text{mol L}^{-1}$ downstream of the city, the increase again coinciding with the turbidity maximum. The $\delta^{15}\text{N}$ 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 were available for salinities from 10 to 28 showed no significant deviations from conservative mixing (Fig. 2E).

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

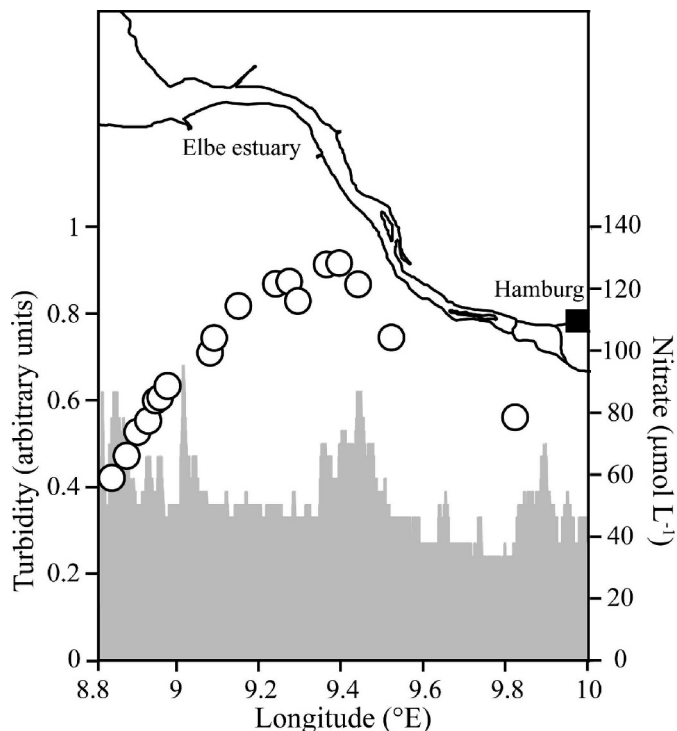


Fig. 3. Turbidity (grey) and associated nitrate concentrations ($\mu\text{mol L}^{-1}$) in the Elbe downstream of Hamburg in August 2006. Note the co-occurrence of high turbidity and maximum nitrate concentrations at 9.45°E .

added between $40 \mu\text{mol L}^{-1}$ and $130 \mu\text{mol L}^{-1}$ of nitrate to the river load. This added nitrate had the same N-isotope composition as the riverborne load, but it was significantly depleted in $\delta^{18}\text{O}$. With the possible exception of August 2006, when a slight increase in nitrate was noted, conservative behavior of nitrate is always indicated in the higher salinity range of the Elbe estuary out to the German Bight.

Discussion

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 offered 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 $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ 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 $\sim 20\%$ and, in open water, also leads to isotopic enrichment of the remaining nitrate in the ratio 1:1 for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, 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 no studies have addressed 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analysis, because ^{18}O has been shown to be an even more sensitive tracer of biological processing than ^{15}N (Wankel et al. 2006).

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 riverborne nitrate.

The salinity gradient sampled in December 2006 showed strictly conservative behavior in both concentration and isotopic data throughout the entire salinity gradient. In winter, the marine end-member $\delta^{15}\text{N}-\text{NO}_3^-$ 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 wintertime situation, with water temperatures $<10^\circ\text{C}$, 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.

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. 3). The peak moved along the estuary, clearly demonstrating that the added nitrate was not provided by a stationary

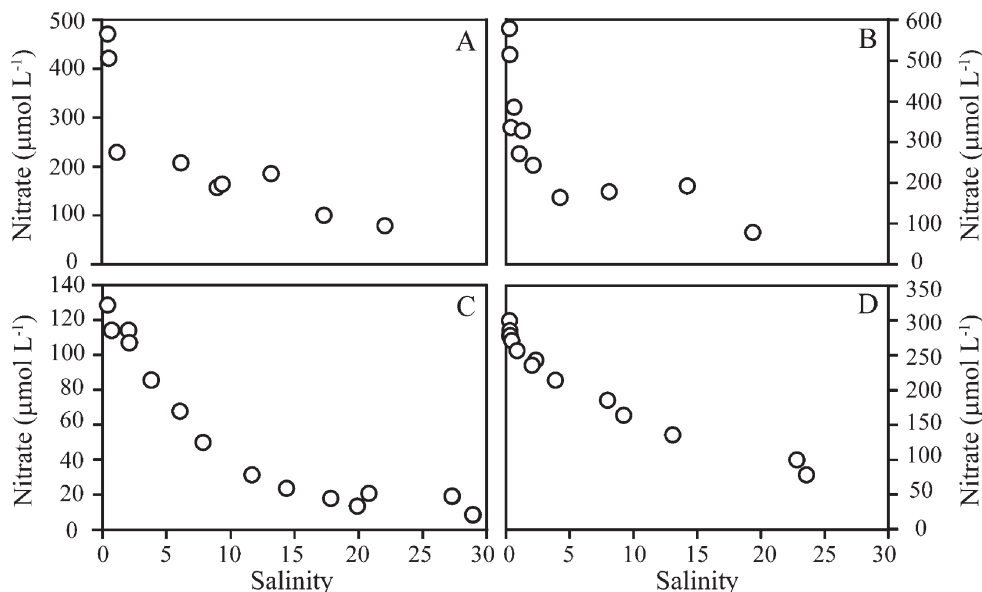


Fig. 4. Historical records of nitrate concentrations in summer along the salinity gradient in the Elbe estuary from (A) 1977, (B) 1978, (C) 1979, and (D) 1980, determined by the ARGE Elbe.

source such as a water treatment plant or a minor nitrate-rich river discharging into the Elbe. Judging from the decrease in $\delta^{18}\text{O}$ in nitrate, the source of the added nitrate is nitrification of ammonia: The increase in nitrate concentrations was not associated with substantial changes in $\delta^{15}\text{N}$, but with a pronounced drop in $\delta^{18}\text{O}$. 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 $\delta^{18}\text{O}\text{-NO}_3^-$ 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. (2002) to calculate the total amount of estuarine nitrate stemming from nitrification:

$$\delta^{18}\text{O}\text{-NO}_3^- = \frac{5}{6}\delta^{18}\text{O}\text{-H}_2\text{O} + \frac{1}{6}\delta^{18}\text{O}\text{-O}_2 \quad (5)$$

Using a value of -9‰ for $\delta^{18}\text{O}$ for Elbe river water (our data) and of 23.5‰ for atmospheric O_2 (Kroopnick and Craig 1972), the calculated $\delta^{18}\text{O}$ of nitrate from nitrification in the particle-rich turbidity maximum is -3.6‰ . Calculating the $\delta^{18}\text{O}\text{-NO}_3^-$ 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%, 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 cannot be inferred from the signature of $\delta^{15}\text{N}$ alone.

*Comparison with historical data from the Elbe estuary—*Denitrification is thought to be a prominent process of net nitrate removal in estuaries (Ogilvie et al. 1997; Van Beusekom and De Jonge 1998; Dong et al. 2006). 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). This may have been due to higher primary production than today, but phytoplankton prima-

ry 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 pseudoconservative nitrate behavior 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 behavior 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.

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 1970's, when nitrate processing in the estuary was indicated by non-conservative mixing (Fig. 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 Patsch 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 from 2 to 12) have not experienced a significant change in the oxygen saturation in comparison to the present situation (ARGE Elbe pers. comm.) 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 $4.4 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ in addition to deepening the ship channel from a 12-m depth to a 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 behavior 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 behavior 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 to historical data, we conclude that a change in the estuarine function must have occurred gradually within the last 25 yr, 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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Received: 19 November 2007

Accepted: 23 March 2008

Amended: 6 March 2008