Biogeosciences Discuss., 7, 7543–7574, 2010
www.biogeosciences-discuss.net/7/7543/2010/
doi:10.5194/bgd-7-7543-2010

Biogeosciences Discussions

Dissolved and particulate reactive nitrogen in the Elbe River/NW Europe: a 2-year N-isotope study

T. Schlarbaum[1,2], K. Dähnke[1,2,3], and K. Emeis[2]

[1]GKSS Research Centre, Institute of Coastal Research, Max-Planck-Str. 1, 21502 Geesthacht, Germany
[2]IfBM, University of Hamburg, Bundesstr. 55, 20146 Hamburg, Germany
[3]present address: Institute of Biology, University of Southern Denmark, 5230 Odense M, Denmark

Received: 17 September 2010 – Accepted: 21 September 2010 – Published: 19 October 2010

Correspondence to: K. Emeis (kay.emeis@zmaw.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Rivers collect and transport reactive nitrogen to coastal seas as nitrate, ammonium, dissolved organic nitrogen (DON), or particulate nitrogen. DON is an important component of reactive nitrogen in rivers and is suspected to contribute to coastal eutrophication, but little is known about seasonality of DON loads and turnover within rivers. We measured the concentrations and the isotope ratios $^{15}N/^{14}N$ of combined DON+NH_4^+ (δ^{15}DON+NH_4^+), nitrate ($\delta^{15}N-NO_3^-$) and particulate nitrogen (δ^{15}PN) in the non-tidal Elbe River (SE North Sea, NW Europe) over a period of 2 years (June 2005 to December 2007) at monthly resolution. Combined DON+NH_4^+ concentrations ranged from 22 to 75 µM and comprised nearly 23% of total dissolved nitrogen in the Elbe River in annual mean; PN and nitrate concentrations ranged from 11 to 127 µM, and 33 to 422 µM, respectively. Combined PN and DON+NH_4^+ concentrations were, to a first approximation, inversely correlated to nitrate concentrations. δ^{15}DON+NH_4^+, which varied between from 0.8‰ to 11.5‰, changed in parallel to δ^{15}PN (range 6 to 10‰), and both were anti-correlated to $\delta^{15}N-NO_3^-$ (range 6 to 23‰). Seasonal patterns of DON+NH_4^+ concentrations and δ^{15}DON+NH_4^+ diverge from those expected from biological DON+NH_4^+ production in the river alone and suggest that the elution of organic fertilisers significantly affects the DON+NH_4^+ pool in the Elbe River.

1 Introduction

Dissolved organic nitrogen (DON) is a major contributor to total dissolved nitrogen (TDN, the sum of nitrate, nitrite, ammonium and DON) discharged from land to the coastal ocean. Meybeck (1993) estimated that nearly 70% of the nitrogen entering coastal regions via rivers is in the form of DON, and highest relative DON contributions characterize TDN loads of unpolluted rivers (Wiegner et al., 2006). But although DON comprises a smaller fraction than nitrate of the total N load in many eutrophied rivers, anthropogenic sources may significantly increase the natural DON background (Agedah et al., 2009; Howarth, 2004) up to a point where anthropogenic sources exceed wetland-derived DON in low-N streams (Stanley and Maxted, 2008). DON is thought to be an inert pool of heterogeneous composition that is not a relevant N-source for freshwater and estuarine ecosystems (Williams and Druffel, 1987), but recent work suggests that labile fractions of DON are selectively turned over in estuaries (Schlarbaum et al., 2010). When discharged to coastal seas, DON may substitute for dissolved inorganic nitrogen (DIN) as a substrate for phytoplankton assimilation. A substantially larger fraction of DON is assimilated by marine than by freshwater bacterioplankton; the susceptibility of DON to mineralization by bacteria appears to increase with increasing salinity during transport from fresh to marine water (Stepanauskas et al., 1999a, b). In seasons when the inorganic N pools are exhausted DON may in particular promote harmful algal blooms (Bronk, 2002; Bronk et al., 2007).

The lack of knowledge on DON sources and turnover in rivers, as well as the potential influence of coastal ecosystems near river discharge areas motivated our investigation into DON dynamics in the Elbe river, possible seasonality of DON discharge into the adjacent estuary and coastal sea, and use of isotopic indicators for origin, as well as for possible sources and sinks of DON in the river.

As a sequel to a study on combined DON and ammonium dynamics in the Elbe estuary (Schlarbaum et al., 2010), we here present a data set on concentrations and the $^{15}N/^{14}N$ composition of combined DON and ammonium (DON+NH_4^+), particulate nitrogen (PN), and nitrate (expressed as the δ value in ‰ $= [(R_{sample}/R_{standard})-1] \cdot 1000$, $R = {}^{15}N/{}^{14}N$ in DON+NH_4^+, nitrate, or PN, and in the international standard atmospheric dinitrogen) of the Elbe River. The first objective of this study is to investigate the seasonal pattern of combined DON and ammonium in the river that drains an intensely farmed (70% agriculture) catchment of 148 268 km^2 in central Europe, and in which policy measures, such as a ban on organic fertilizers from beginning of November to the end of January (DüV, 2009), potentially impose an external rhythm on possible external DON and ammonium sources. Secondly, we were interested in links between

BGD
7, 7543–7574, 2010

the DON and PN pools, which both may be products of phytoplankton assimilation of the dissolved inorganic nitrogen (DIN) load, or – in the case of DON – may originate from dissimilation of PN within the river. The data set is of monthly resolution and permits us to assess seasonal variations depending on internal cycling or external inputs, and turnover of reactive N between different pools.

2 Materials and methods

2.1 Study site

The Elbe River is 1094 km long and one of the largest rivers in Germany discharging into the North Sea. The weir at Geesthacht (built 1957–1959 AD) at stream kilometre 585 is the only barrage along the Elbe River and separates a tidal estuary from the upstream river system (Fig. 1). The average fresh water discharge at the weir Geesthacht is 700 m^3/s, and can rise to 4000 m^3/s during floods; nearly 25 million people live in the entire catchment area of 148 268 km^2 (Behrendt et al., 2004). The Elbe River is the largest nutrient source of the German Bight (Brockmann and Pfeiffer, 1990), which is severely affected by eutrophication (Osparcom, 2008). In 2007, the Elbe discharged 87 kt reactive N (85% nitrate, 15% DON+NH_4^+ + PN) into the estuary (Arge, 2008).

2.2 Sampling

From June 2005 to December 2007, monthly water samples were collected at the weir using a Ruttner sampler. Initially, samples were collected at two different water depths (0.5 m and 3 m), which was reduced to only 1 sample from 1–2 m after initial analyses showed no significant difference between the two depths. The river water was immediately filtered through precombusted GF/F filters and stored in PE bottles that had been soaked in acid overnight and rinsed with deionised water (DIW). Each bottle was rinsed with sample water before being filled. Water samples were frozen at −18 °C until analysis. Filters were dried at 60–70 °C and stored at 4 °C before analyses.

BGD
7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

2.3 Methods

Glassware was washed with deionised water (DIW), soaked in soap and 10% HCl baths and washed again with DIW after each single step. All non-volumetric glassware was combusted at 450 °C for at least 4 h, volumetric glassware and PE-bottles were washed with DIW, soaked in 10% HCl bath overnight, washed again with DIW and dried at 50 °C.

Concentration of total dissolved nitrogen (TDN) in DIW was determined using the "persulfate oxidation method" (Solórzano and Sharp, 1980; Koroleff, 1976; Knapp et al., 2005) (see below) with a blank of <1 µmol/l.

2.3.1 Concentrations and δ^{15}N analysis of nitrate and nitrite

Concentrations of nitrate and nitrite were measured with standard colorimetric techniques (Grasshoff and Anderson, 1999) on an AutoAnalyzer3 by Bran and Luebbe. Concentration of nitrite in the water samples was negligible (below 2% of the nitrate concentration) at a detection limit of 0.05 µM. $\delta^{15}N-NO_3^-$ of nitrate was analysed by using the "denitrifier method" (Sigman et al., 2001; Casciotti et al., 2002). Nitrate was quantitatively reduced to nitrous oxide (N_2O) by using a strain of denitrifier bacteria that lacks N_2O reductase activity. N_2O was automatically extracted, purified in a Gasbench (ThermoFinnigan) and analysed on a Finnigan Delta plus XP mass spectrometer. The sample size was adjusted to 20 nmol nitrate in each sample. The samples were referenced to injections of N_2O from a pure N_2O gas cylinder and then standardised using an internationally accepted nitrate isotopic reference material (IAEA-N3, $\delta^{15}N = 4.7‰$). We used an internal potassium nitrate standard for further validation of our results, which we measured with each batch of samples. The standard deviation for replicate analyses ($n = 4$) was ±0.2‰. The method also permits determination of $\delta^{18}O-NO_3^-$ (Sigman et al., 2001; Casciotti et al., 2002; Dähnke et al., 2008), which is referenced to IAEA-N3 with a $\delta^{18}O-NO_3^-$ of 22.7‰ versus Vienna Standard Mean Ocean Water (VSMOW) (Böhlke et al., 2003). We note that this value has recently been corrected

BGD
7, 7543–7574, 2010
Dissolved and particulate reactive nitrogen
T. Schlarbaum et al.

and is now reported as 25.6‰, but decided to use the formerly assigned value for a better comparison with previous studies (Johannsen et al., 2008; Schlarbaum et al., 2010).

2.3.2 Concentration and δ^{15}N analysis of TDN

To determine the TDN concentration and δ^{15}TDN we used the method of Knapp et al. (2005), with small modifications as described in Schlarbaum et al. (2010). In brief, total dissolved nitrogen is oxidized to nitrate using the "persulfate oxidation method" (Solórzano and Sharp, 1980; Koroleff, 1976; Knapp et al., 2005). Concentration of TDN was determined as nitrate after oxidation by the method described above.

For the determination of δ^{15}TDN nitrate in oxidised samples and reagent blanks was converted to N_2O using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002) as described above.

2.3.3 Concentration and δ^{15}N analysis of combined DON+NH $_4^+$

Concentration of combined DON+NH_4^+ was calculated by the difference between TDN and nitrate, because concentration of nitrite was consistently negligible.

For the δ^{15}DON+NH_4^+ mass balance calculations were made using the measured nitrate concentrations and δ^{15}N values of the oxidised sample, the reagent blank and the unoxidised sample:

$$\delta^{15}\mathrm{DON}+\mathrm{NH}_4^+ = \delta^{15}\mathrm{TDN}\cdot c(\mathrm{TDN})/c(\mathrm{DON}+\mathrm{NH}_4^+) - [\delta^{15}\mathrm{N}-\mathrm{NO}_3^-\cdot c(\mathrm{NO}_3^-)+ \delta^{15}\mathrm{N}_{\mathrm{Blank}}\cdot c(\mathrm{Blank})]/c(\mathrm{DON}+\mathrm{NH}_4^+) \quad (1)$$

The combination of persulfate digestion and denitrifier method to measure δ^{15}DON+NH_4^+ has been tested by oxidation of urea standard solutions with a concentration range of 10 to 400 µM. The δ^{15}N of solid urea was measured by using a Flash EA 1112 elemental analyzer coupled to a Finnigan Delta plus XP mass spectrometer,

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

yielding a δ^{15}N value of 0.5‰ ± 0.2‰. Measurements of the urea solutions after preparation as above yielded in δ^{15}N values of 0.4‰ ± 0.2‰ after blank correction.

Repeated measurements of the same water sample demonstrated the reproducibility of the δ^{15}N method for δ^{15}DON+NH_4^+ analyses. The mean measured standard deviation of δ^{15}TDN and δ^{15}N–NO_3^- was 0.2‰ (3 to 4 repetitions). The mean standard deviation for TDN and nitrate concentration was 1 µM. Because of error propagation, the calculated standard deviation of δ^{15}DON+NH_4^+ ranged from 0.1 to 2.8‰ with a mean value of 1.2‰ , and the calculated mean standard deviation for combined DON+NH_4^+ concentration was 2.2 µM.

The method does not separate DON and ammonium. However, in comparison with DON concentration, ammonium concentrations were near to or below detection limit (<2.9 µM) except for samples taken during winter seasons and in June 2007. During winter seasons, ammonium concentrations occasionally increased up to 34 µM (February 2006), equalling 50% of the combined DON+NH_4^+ loads; in June 2007, ammonium accounted for approximately 10% of combined DON+NH_4^+.

2.3.4 Concentration and δ^{15}N analysis of PN

Particulate nitrogen was sampled by filtering the water samples through precombusted (6 h, 450 °C) and tared GF/F filters. After filtration the filters were dried at 60 °C and stored dark at 4 °C until analysed. The weight of particulate matter on the filters was determined, and C and N weight % were analysed by using a Flash EA 1112 elemental analyzer. The δ^{15}PN was analysed with a Flash EA 1112 elemental analyzer coupled to a Finnigan Delta plus XP mass spectrometer. Results were standardised using the internationally accepted isotopic reference materials "High organic sediment standard OAS" (Cat.no. B2151, Batch no. 2824, δ^{15}N = + 4.4‰ ± 0.19‰), "Low Organic Content Soil Standard OAS" (Cat.no. B2153, Batch no. 2822, δ^{15}N = + 6.7‰ ± 0.15‰) and IAEA-N1 (δ^{15}N = + 0.4‰). The standard deviation for replicate analysis was 0.2‰ (3 replicates).

BGD
7, 7543–7574, 2010

2.4 Annual and seasonal loads and load-weighted isotopic values

For an estimate of the mass loads of DON+NH_4^+, TDN, PN, and nitrate and the average N-isotope composition of these compounds, we used our analytical data and the discharge rates of the sampling dates to calculate annual loads as:

$$L = \sum |J_i| \cdot c_i \cdot \text{flow}_i \tag{2}$$

The entire time interval J of 12 months for annual calculations (6 months for seasonal calculations) was divided in n sampling intervals with the duration $|J_i|$, the concentration c_i and the discharge flow$_i$. The annual load L is the sum of the single loads in the sampling intervals J_i (Hebbel and Steuer, 2006; Johannsen et al., 2008).

For the calculation of the load-weighted annual average isotope composition, the isotope values were multiplied with the respective concentration and weighted with the loads according to the formulas:

$$\delta^{15}\text{N}_{\text{wml}} = \sum \delta^{15}\text{N}_i \cdot c_i \cdot \text{flow}_i / \sum c_i \cdot \text{flow}_i \tag{3}$$

$$\delta^{18}\text{O}_{\text{wml}} = \sum \delta^{18}\text{O}_i \cdot c_i \cdot \text{flow}_i / \sum c_i \cdot \text{flow}_i \tag{4}$$

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 measured isotope values of individual samples, c_i is the respective concentration, and flow$_i$ the discharge flow.

3 Results

The analytical results from sampling in the period June 2005 to December 2007 are plotted in Fig. 2. Water discharge for the sampling dates were plotted as bars and show an exceptional spring flood in April 2006. In the first 6 months of sampling, we determined only concentrations and δ^{15}N of nitrate and DON+NH_4^+; the last two years,

BGD

7, 7543–7574, 2010

measurements included also $\delta^{18}O-NO_3^-$, and concentrations and $\delta^{15}PN$ (from July 2006 to December 2007).

3.1 Nitrate concentrations and isotopic compositions

Throughout the entire sampling period covered in our current study, nitrate displays a clear seasonal trend in concentrations and isotopic composition. $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ were both enriched during summer months (maxima 23‰ and 12‰, respectively) and were both depleted during winter times (minima 6‰ and <1‰, respectively) (Fig. 2a) and are anti-correlated ($r^2 = 0.84$, $r = -0.92$, $\alpha \leq 0.01$) (Table 1) to nitrate concentrations (min. 30 µM in summer seasons, max. 420 µM in winter seasons). $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ varied almost parallel and are strongly correlated ($r^2 = 0.96$, $r = 0.98$, $\alpha \leq 0.01$, Table 1) to each other. A plot of $\delta^{18}O$ vs. $\delta^{15}N$ shows that the isotope values plot a slope of 0.81:1, which is close to a 1:1 slope (Fig. 3). Nitrate concentration and isotopic composition from January 2006 to December 2006 are also published in Johannsen et al. (2008).

3.2 DON+NH_4^+ concentrations and isotopic compositions

DON+NH_4^+ concentrations also showed a distinct seasonality: Concentrations varied between 22 µM and 76 µM, δ^{15}DON+NH_4^+ ranged from 1‰ in November 2006 to 12‰ in March 2006 (Fig. 2b). We found two distinct maxima in both concentration and δ^{15}DON+NH_4^+ per year. The first maximum with higher values in both concentration and δ^{15}DON+NH_4^+ appeared in winter months (from December to March), the second in summer; minima occurred during spring and autumn seasons. Unlike nitrate, δ^{15}DON+NH_4^+ and DON+NH_4^+ concentration are only loosely correlated ($r^2 = 0.35$, $r = 0.59$, $\alpha \leq 0.01$, Table 1).

BGD
7, 7543–7574, 2010

3.3 DON+NH_4^+/TDN ratios

The DON+NH_4^+ contribution to TDN differs through the seasons, with an annual average of DON+NH_4^+/TDN of 23%. The highest DON+NH_4^+/TDN ratio occurred in August 2006 (57%), the lowest in March 2006 (8%) (Table 2). On average, the DON+NH_4^+/TDN ratio in summer is about twice as high as in seasons with less biologic activity (33% versus 15% in winter, 18% in spring and 17% in autumn).

3.4 Particulate nitrogen

Concentrations of PN had no clear seasonal trend, and δ^{15}PN fluctuated in a small range of 6 to 10‰ (Fig. 2c). In general, higher concentrations and lower δ^{15}PN values were measured in spring and summer seasons (55.0–65.6 µM, 7.2–7.5‰), while lower concentrations (20.2–41.4 µM) and higher δ^{15}PN values (7.9–9.1‰) were detected in samples from winter and autumn seasons. PN thus shows a similar seasonal cycle as nitrate, but varies in a considerably smaller range. In contrast to nitrate, no significant anti-correlation between δ^{15}PN and PN concentration was evident ($r^2 = 0.14$, $r = -0.30$, $\alpha > 0.05$, Table 1). δ^{15}PN is higher than but closely tracks δ^{15}DON+NH_4^+ (Fig. 4), with a correlation of $r^2 = 0.53$ ($r = 0.73$, $\alpha \leq 0.01$) between these two parameters (Fig. 5).

3.5 Loads and annual isotopic values

The annual loads transported in the Elbe River and discharged into the downstream estuary at the weir of Geesthacht are listed in Table 3. The annual TDN loads were 107 kt in 2006 and 72 kt in 2007. An unusual flood in April 2006 caused high discharge at high concentrations, and created the nearly 50% difference in total dissolved nitrogen loads between the two years.

Excluding the anomalous flood data, a clear seasonal pattern of higher loads in winter seasons (October to March) emerges: In the case of nitrate, the winter load is

BGD
7, 7543–7574, 2010

more than three times the summer load, and for DON+NH_4^+ the winter load is twice as high. In contrast, the PN load is relatively constant throughout the year.

Table 4 lists the results of load-weighted annual isotope values for DON+NH_4^+, TDN, nitrate and PN in addition to seasonal load-weighted isotope values. In the case of nitrate, δ^{15}N–NO_3^- and δ^{18}O–NO_3^- values were higher in summer (δ^{15}N–NO_3^-: 11.7‰–18.7‰; δ^{18}O–NO_3^-: 1.6‰–5.6‰) than in winter (δ^{15}N–NO_3^-: 8.8‰– 9.5‰; δ^{18}O–NO_3^-: 0.7‰–1.1‰). For the particulate loads, δ^{15}PN also showed lower values in summer seasons (4.8‰–7.1‰) than in winter seasons (8.2‰–8.4‰).

Combined DON+NH_4^+ showed an opposite trend with lower δ^{15}DON+NH_4^+ values in summer (5.0‰–5.9‰) than in winter (6.3‰–7.5‰), so that isotopic differences between summer and winter seasons were much smaller than for nitrate and PN. Because of the greater share of nitrate in TDN, δ^{15}TDN followed the same trend as δ^{15}N–NO_3^- with the higher values in summer seasons (10.3‰–14.5‰) compared to winter seasons (8.6‰–9.1‰).

4 Discussion

Our results show the composition of total nitrogen and the isotopic composition of different reactive N sources in the Elbe River over a time period of more than 2 years from June 2005 to December 2007. In the next section we will discuss the data for nitrate, combined DON+NH_4^+ and PN under the aspects of seasonality and correlations between the measured parameters. We were interested if not only biological processes but also external factors affect seasonal patterns. Furthermore we wanted investigate the correlations of the different N pools like nitrate, DON+NH_4^+ and PN, since both DON and PN may be products of phytoplankton assimilation of the nitrate load; DON+NH_4^+ may also originate from dissimilation of PN within the river.

4.1 Nitrate

Nitrate concentrations were high in winter seasons and low in summer seasons and the isotopic composition of δ^{15}N–NO_3^- and δ^{18}O–NO_3^-, had maxima during summer seasons and minima during winter seasons (Fig. 2a). The seasonal variability is essentially due to seasonal changes in biological activity, which causes isotopic fractionation (Kendall, 1998). The first process is assimilation of nitrate: Phytoplankton preferentially incorporates light isotopes (^{14}N, ^{16}O) and discriminates slightly against nitrate with heavy isotopes. At higher temperatures in summer, increased phytoplankton productivity leads to an enrichment of heavy isotopes (^{15}N, respectively ^{18}O) in the residual nitrate (Johannsen et al., 2008; Kendall, 1998). A second process potentially raising δ^{15}N–NO_3^- and δ^{18}O–NO_3^- is water column denitrification, which strongly discriminates against the heavy isotopes. Available field and experimental data in seawater suggest equal permil fractionation factors $^{15}\varepsilon$ and $^{18}\varepsilon$ ($^{15}\varepsilon = (^{14}k/^{15}k - 1)^{*}$ 1000, where ^{14}k and ^{15}k are the rate coefficients of the reactions for the ^{14}N- and ^{15}N-bearing forms of nitrate, respectively $^{18}\varepsilon$ for oxygen) for nitrate assimilation (Casciotti et al., 2002; Granger et al., 2004) and denitrification (Granger et al., 2004; Sigman et al., 2003), but little is known about the fractionation factors associated with nitrate assimilation in fresh water; in the case of denitrification, $^{18}\varepsilon$:$^{5}\varepsilon$ ratios of ~0.5–0.6 have been reported (Bottcher et al., 1990; Lehmann et al., 2003; Mengis et al., 1999). However, water column denitrification is unlikely given the oxygen concentrations in the study area, so we expect that coupled enrichment of oxygen and nitrogen isotopes will be mainly associated to assimilation. In Fig. 3 we plotted δ^{15}N–NO_3^- versus δ^{18}O–NO_3^- and obtain a slope of 0.81. This slope represents the ratio of the fractionation factors $^{15}\varepsilon$ and $^{8}\varepsilon$ as described by Granger et al. (2004) in their experiments of coupled nitrogen and oxygen isotope fractionation and indicates a major influence of nitrate assimilation, because both isotopes have almost the same fractionation factor (Granger et al., 2004). In July 2005 Deutsch et al. (2009) measured a ratio of 1.12 in the Elbe River. In combination with increased concentrations of chlorophyll-*a* and particulate organic carbon they demonstrated that nitrate assimilation by phytoplankton plays a major role in nitrogen transformation processes in the Elbe River (Deutsch et al., 2009).

4.2 Particulate nitrogen

Because of the relative short sampling period and the lack of seasonality in both concentration and δ^{15}PN, it is difficult to establish the role of PN in the nitrogen cycle in the Elbe River, which is further complicated by its heterogeneous composition: PN consists both of detritus and newly produced phytoplankton, with presumably large differences in δ^{15}PN.

The higher mean concentrations in spring and summer (65.6 µM and 55.0 µM, Table 2) are accompanied by low δ^{15}PN values (7.5‰ in spring, 7.2‰ in summer) and decreasing DIN concentration. This pattern is consistent with PN originating from internal phytoplankton production (Raabe et al., 2004), and fits well with data from July 2005, when a PN concentration of 61 µM and a δ^{15}PN value of ~7‰ was determined (Deutsch et al., 2009). Assimilation of low-δ^{15}N ammonium in the beginning of the phytoplankton bloom in spring could be the reason for the decreasing δ^{15}PN, since ammonium is the preferred N source when abundant (Hadas et al., 2009). After ammonium is exhausted, ^{15}N-enriched DON and nitrate were assimilated, leading to increasing δ^{15}PN. Resuspension of particulate matter from surface sediments should result in an increase in both concentration and δ^{15}PN, thus explaining our observations in summer 2006, when both δ^{15}PN and PN concentration reach a maximum value.

The increase in δ^{15}PN and decrease in concentration in autumn and winter indicates consumption during this period, coupled to resuspension of low-N sedimentary organic matter due to increased flow rates. This suspended matter can be degraded due to biological activity in the sediments and have low N content, but high δ^{15}PN values. The similar curve progression of δ^{15}PN and δ^{15}DON+NH_4^+ indicates a relationship between the dissolved and the particulate matter fraction (Fig. 4), mirrored in the correlation coefficient of $r^2 = 0.53$ ($\alpha \leq 0.01$) (Fig. 5). The lower δ^{15}DON+NH_4^+ compared to δ^{15}PN suggest that particulate matter is, at any time of year, a significant source for DON

BGD
7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

and/or ammonium, so DON and/or ammonium are produced by release of small soluble fractions of PN (see next section).

4.3 DON+NH_4^+

The combined DON+NH_4^+ load of the Elbe River at the weir of Geesthacht apparently is fed by both external and internal sources. The abiotic external sources of DON+NH_4^+ include terrestrial runoff, such as DON and/or ammonium input by surface runoff, tributaries, groundwater (Valiela et al., 1990; Tobias et al., 2001) and from the atmosphere (Cornell et al., 1995). These external sources are often dominated by discharge of sewage treatment plants, and elution of slurry and liquid manure from farmland.

During our observation period, we found seasonal differences in both DON+NH_4^+ concentration and δ^{15}DON+NH_4^+ (Fig. 2b). In contrast to nitrate dynamics, the annual DON+NH_4^+ cycle appears to be more differentiated and can be separated into four seasonal phases: DON+NH_4^++ concentrations and δ^{15}DON+NH_4^+ decreasing in concert (spring), a coupled increase of both parameters (summer), decreasing DON+NH_4^+ concentration and isotope values in autumn and then another increase of both in winter.

4.3.1 Spring

During spring, decreasing DON+NH_4^+ concentration may be explained by heterotrophic and autotrophic uptake of reactive low-molecular-weight DON (LMW DON) (Bronk et al., 2007) and ammonium. Only small fractions of the heterogeneous DON pool in river water are bioavailable (Bronk et al., 2007; Seitzinger and Sanders, 1997; Seitzinger et al., 2002). The proportion of DON that is utilizable by phytoplankton varies by source and land use pattern in the catchment: up to 59% of DON from urban/suburban stormwater runoff and 30% from agriculture sources can be bioavailable (Seitzinger et al., 2002). Incubation experiments by Berman et al. (1999) showed that LMW DON, composed mainly urea, is easily degraded by indigenous bacteria and/or free dissolved enzymes. The portion of this labile fraction is variable: In a study about

BGD
7, 7543–7574, 2010
Dissolved and particulate reactive nitrogen
T. Schlarbaum et al.

fifty rivers draining a major part of the Baltic Sea watershed (Stepanauskas et al., 2002) total nitrogen was composed by 48% dissolved inorganic nitrogen (DIN), 41% DON and 11% particulate nitrogen (PN). The labile fraction of DON was composed of urea and dissolved combined amino acids (DCAA) with 4–20% of DON each, and <3% dissolved free amino acids (DFAA).

Besides land use pattern, the bioavailability of DON appears to depend also on seasonal influences that may determine the type of DON. Highest uptake rates of DON originating from urban/suburban stormwater runoffs and agriculture sources were observed in spring times (Seitzinger et al., 2002). The decreasing δ^{15}DON+NH_4^+ values observed in spring apparently reflect that uptake of the bioavailable fraction is complete to the point that we have no apparent isotope effect, and the low δ^{15}DON+NH_4^+ value measured in the remaining pool is due to recalcitrant DON that remains in the water column.

4.3.2 Summer

In the second distinct phase in DON+NH_4^+ seasonal cycling (June to August) both concentration and δ^{15}DON+NH_4^+ increase. In 2005 Deutsch et al. (2009) measured low δ^{15}N–NH_4^+ values of 2–3‰ in the Elbe River, so this increase in δ^{15}DON+NH_4^+ should mainly be due to increasing δ^{15}DON. In summer, elution of organic fertilisers in the form of slurry and liquid manure dispersed on farmland during the first main fertilisation period in spring leads to an increase in DON concentration and δ^{15}DON (Heaton, 1996), in accord with our data.

The data from monitoring at the weir also indicate a limitation of biological production in the river by ammonium and phosphate during summer (Table 5). This seasonal lack of nutrients apparently leads to high rates of DON release by phytoplankton: When phytoplankton cells are stressed by nutrient limitation, they react by high release rates of organic matter (Carlson et al., 1994; Larsson and Hagström, 1979). Furthermore, such nutrient limitation induces an uptake of DON as an alternative N-source

BGD
7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

(Jackson and Williams, 1985). Kaushal and Lewis Jr. (2005) examined two streams in Colorado and found highest uptake rates of bioavailable DON, when concentration of DIN in stream water was lowest. In incubation experiments they showed that 40% of the DON could be consumed by microbes in stream sediment. This suggested that DON has the potential to be used biotical at a high rate in nitrogen poor rivers, and may be generated by heterotrophic bacteria when DIN concentration dropped and labile DOM with low relative nitrogen content prevails. We assume that if ammonium is limited, the uptake of DON is an almost effective alternative to the uptake of nitrate. Stepanauskas et al. (1999b) postulate that DON may be even the dominant input of bioavailable nitrogen to coastal seas during summer, when nitrate concentrations in rivers decrease.

We interpret our data from summer, when both concentration and δ^{15}DON+NH_4^+ decrease, as a reflection of a dynamic equilibrium of uptake and release of DON: the elution of organic fertilisers and the uptake of DON by phytoplankton cause an increase in δ^{15}DON+NH_4^+, while the DON released due to nutrient limitation should cause a decrease in δ^{15}DON+NH_4^+. This is supported by the close correlation of δ^{15}DON+NH_4^+ and δ^{15}PN (Fig. 5), which suggests that ^{15}N depleted DON is released from particulate N. Phytoplankton, which is highly abundant at this time of year, is a likely source of this DON, as has been observed in Lake Kinneret, Israel, where Hadas et al. (2009) found a similar relation between particulate organic matter (POM) and DON, and conclude that algal production is a major source for DON.

4.3.3 Autumn

In autumn, from September to October, we again observed a decrease in DON+NH_4^+ concentration and δ^{15}DON+NH_4^+, followed by parallel increases in winter months to higher values in both concentration and δ^{15}DON+NH_4^+ than in summer.

In autumn, at the end of the biological production period, there is still a lack of phosphate in the river water, so that the release of ^{15}N-depleted DON is still in progress.

BGD
7, 7543–7574, 2010

However, due to sinking algal production, DON+NH_4^+ concentration is decreasing. The remaining DON is isotopically depleted. We infer that sedimentation is also a major sink of DON as an explanation for decreasing DON+NH_4^+ concentration and δ^{15}DON+NH_4^+. In the Colne River (which has a TDN composition comparable to the Elbe River), Agedah et al. (2009) observed a similar decrease when ^{15}N enriched DON is removed from the water column. The low PN concentrations further support this assumption.

4.3.4 Winter

The increase of DON+NH_4^+ concentration and δ^{15}DON+NH_4^+ in winter is due to the elution of organic fertilisers of the second main fertilisation period in autumn after the last harvest in October before the blocking period starts (from beginning of November until the end of January, DüV, 2009). Recent measurements of δ^{15}N–NH_4^+ in January 2010 showed low values of 0–1‰ at concentrations of ~13 µM (Schlarbaum et al., unpublished data), so DON must be highly enriched in ^{15}N to obtain measured δ^{15}DON+NH_4^+ values. The elevated concentration in comparison to summer is due to high ammonium concentrations in winter (10–30 µM, Table 5).

5 Summary and conclusions

In our study about different forms of nitrogen in the Elbe River at the weir of Geesthacht we measured both concentration and stable isotope signatures of nitrate, combined DON+NH_4^+ and PN. On an annual basis, nearly 23% of TDN is in the form of DON+NH_4^+.

For nitrate the seasonal pattern has two periods with a contrasting development of concentration and dual nitrate isotopes, due to biological processes. We attribute this to nitrate assimilation during biological activity, as is supported by the co-variance of δ^{15}N–NO_3^- and δ^{18}O–NO_3^-.

In contrast, the seasonal cycling of combined DON+NH_4^+ is more complex and is influenced by many different factors, both biotic and abiotic. The annual DON+NH_4^+

BGD
7, 7543–7574, 2010
Dissolved and particulate reactive nitrogen
T. Schlarbaum et al.

cycle can be separated into four periods, with an increase in both concentration and δ^{15}DON+NH_4^+ in summer and winter, and a decrease in spring and autumn. As the main abiotic source, we assume the elution of ^{15}N-enriched organic fertiliser, after the main fertilisation periods in spring and after the harvest in autumn, to have an important influence on DON in the Elbe River. In summer, this is accompanied by DON release by phytoplankton due to nutrient limitation, indicated by the similar, almost parallel progression of δ^{15}DON+NH_4^+ and δ^{15}PN. The decrease in spring and autumn is on the one hand due to autotrophic and heterotrophic uptake (springtime) and on the other hand due to lower biological production in autumn. Our measurements suggest that the recalcitrant high-molecular-weight DON fraction in the Elbe River is isotopically depleted in ^{15}N, compared to the reactive low-molecular-weight DON.

References

Agedah, E. C., Binalaiyifa, H. E., Ball, A. S., and Nedwell, D. B.: Sources, turnover and bioavailability of dissolved organic nitrogen (DON) in the Colne estuary, UK, Mar. Ecol. Prog. Ser., 382, 23–33, 2009.

ARGE: Wassergütedaten der Elbe – Zahlentafel 2004, Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg, 2005.

ARGE: Wassergütedaten der Elbe – Zahlentafel 2005, Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg, 2007a.

ARGE: Wassergütedaten der Elbe – Zahlentafel 2006, Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg, 2007b.

ARGE: Gewässergütebericht der Elbe 2006, Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg, 2008.

Behrendt, H., Bach, M., Opitz, D., and Pagenkopf, W. G.: Maßgebliche anthropogene Einflüsse auf die Gewässerqualität, in: Wasser- und Nährstoffhaushalt im Elbegebiet und Möglichkeiten zur Stoffeintragsminderung, edited by: Becker, A. and Lahmer, W., Weissensee Verlag, Berlin, 42–58, 2004.

Berman, T., Béchemin, C., and Maestrini, S. Y.: Release of ammonium and urea from dissolved organic nitrogen in aquatic ecosystems, Aquat. Microb. Ecl., 16, 295–302, 1999.

BGD

7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

Böhlke, J. K., Mroczkowski, S. J., and Coplen, T. B.: Oxygen isotopes in nitrate: new reference materials for 18O:17O:16O measurements and observations on nitrate-water equilibration, Rapid Commun. Mass Spectrom., 17, 1835–1846, 2003.

Bottcher, J., Strebel, O., Voerkerlius, S., and Schmidt, H. L.: Using isotope fractionation of nitrate nitrogen and nitrate oxygen for evaluation of microbial denitrification in a sandy aquifer, J.Hydrol., 114, 413–424, 1990.

Brockmann, U. H. and Pfeiffer, A.: Seasonal changes of dissolved and particulate material in the turbidity zone of the River Elbe, in: Estuarine Water Quality Management, edited by: Michaelis, W., Springer, Heidelberg, 327–334, 1990.

Bronk, D. A.: Dynamics of DON, in: Biogeochemistry of Marine Dissolved Organic Matter, edited by: Hansell, D. A. and Carlson, C. A., Academic Press, New York, 153–247, 2002.

Bronk, D. A., See, J. H., Bradley, P., and Killberg, L.: DON as a source of bioavailable nitrogen for phytoplankton, Biogeosciences, 4, 283–296, doi:10.5194/bg-4-283-2007, 2007.

Carlson, C. A., Ducklow, H. W., and Michaels, A. F.: Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea, Nature, 371, 405–408, 1994.

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Bohlke, J. K., and Hilkert, A.: Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74(19), 4905–4912, 2002.

Cornell, S., Rendell, A., and Jickells, T.: Atmospheric inputs of dissolved organic nitrogen to the oceans, Nature, 376, 243–246, 1995.

Dähnke, K., Bahlmann, E., and Emeis, K.-C.: A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary, Limnol. Ocean., 53(4), 1504–1511, 2008.

Deutsch, B., Voss, M., and Fischer, H.: Nitrogen transformation processes in the Elbe River: distinguishing between assimilation and denitrification by means of stable isotope ratios in nitrate, Aquat. Sci., 71, 228–237, 2009.

Düngeverordnung (DüV) in der Fassung der Bekanntmachung vom 27. Februar 2007 (BGBl. I S. 22), geändert durch Artikel 1 der Verordnung vom 6. Februar 2009 (BGBl. I S.153).

Granger, J., Sigman, D. M., Needoba, J. A., and Harrison, P. J.: Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton, Limnol. Ocean., 49(5), 1763–1773, 2004.

Grasshoff, K., Ehrhardt, M., Kremling, K., and Anderson, L. G.: Methods of Seawater Analysis, Verlag Chemie, Weinheim, 632 pp., 1999.

Hadas, O., Altabet, M. A., and Agnihotri, R.: Seasonally varying nitrogen isotope biogeochemistry of prticulate organic matter in Lake Kinneret, Israel, Limnol. Oceanogr., 54(1), 75–85, 2009.

Heaton, T. H. E.: Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review, Chemical Geology: Isotope Geoscience section, 59, 87–102, 1986.

Hebbel, H. and Steuer, D.: Empirische Untersuchungen zur Berechnung von Frachten in Fließgewässern, in: Discussion Papers in Statistics and Quantitative Economics, edited by: Bauptmann, H. and Krumbholz, W., Hamburg, 2006.

Howarth, R. W.: Human acceleration of the nitrogen cycle: drivers, consequences, and steps toward solutions, Water Sci. Technol., 49, 7–13, 2004.

Johannsen, A., Dähnke, K., and Emeis, K.: Isotopic composition of nitrate in five German rivers discharging into the North Sea, Org. Geochem., 39, 1678–1689, 2008.

Kaushal, S. S. and Lewis Jr., W. M.: Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA, Biogeochemistry, 74, 303–321, 2005.

Kendall, C.: Tracing nitrogen sources and cycling in catchments, in: Isotope Tracers in Catchment Hydrology, edited by: Kendall, C. and McDonnell, J. J., Elsevier, 521–576, 1998.

Knapp, A. N., Sigman, D., and Lipschultz, F.: N-isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-Series study site, Global Biogeochem. Cy., 19, GB1018, doi:10.1029/2004GBC002320, 2005.

Koroleff, F.: Total and organic nitrogen, in: Methods of Seawater Analysis, edited by: Grasshoff, K., Ehrhard, M., and Kremling, K., Verlag Chemie, Weinheim, 125–139, 1976.

Lara, R. J., Rachold, V., Kattner, G., Hubberten, H. W., Guggenberger, G., Skoog, A., and Thomas, D. N.: Dissolved organic matter and nutrients in the Lena River, Siberia Arctic: Characteristics and distribution, Mar. Chem., 59, 301–309, 1998.

Lehmann, M. F., Reichert, P., Bernasconi, S. M., Barbieri, A., and McKenzie, J. A.: Modelling nitrogen and oxygen isotope fractionation during nitrate reduction in a hypolimnetic redox transition zone, Geochim. Cosmochim. Ac., 67, 2529–2542, 2003.

Larsson, U. and Hagström, Å.: Phytoplankton exudate release as an energy source for the growth of pelagic bacteria, Mar. Biol., 52, 199–206, 1979.

Mengis, M., Schiff, S. L., Harris, M., English, M. C., Aravena, R., Elgood, R. J., and MacLean, A.: Multiple geochemical and isotopic approaches for assessing ground water NO_3^- elimination in a riparian zone, Ground Water, 37, 448–457, 1999.

Meybeck, M.: C, N, P and S in rivers: From sources to global inputs, in: Interactions of C, N, P,

BGD

7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

and S Biogeochemical Cycles and Global Change, edited by: Wollast, R., Mackenzie, F. T., and Chou, L., Springer Verlag Berlin, 163–193, 1993.

OSPAR: Second OSPAR Integrated Report on the Eutrophication Status of the OSPAR Maritime Area, OSPAR Commission, 2008.

Raabe, T., Yu, Z., Zhang, J., Sun, J., Starke, A., Brockmann, U., and Hainbucher, D.: Phase-transfer of nitrogen species in the water column of the Bohai Sea, J. Marine Syst., 44, 213–232, 2004.

Schlarbaum, T., Dähnke, K., and Emeis, K.: Dissolved organic nitrogen turnover in the Elbe estuary/NW Europe: results of nitrogen isotope investigations, Mar. Chem., 119, 91–107, 2010.

Seitzinger, S. P. and Sanders, R. W.: Contributions of dissolved organic nitrogen from rivers to estuarine eutrophication, Mar. Ecol. Prog. Ser., 159, 1–12, 1997.

Seitzinger, S. P., Sanders, R. W., and Styles, R.: Bioavailability of DON from natural and anthropogenic sources to estuarine plankton, Limnol. Oceanogr., 47(2), 353–366, 2002.

Sigman, D. N., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., and Böhlke, J. K.: A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal. Chem., 73(17), 4145–4153, 2001.

Sigman, D. N., Robinson, R., Knapp, A. N., van Geen, A., McCorkle, D. C., Brandes, J. A., and Thunell, R. C.: Distinguishing between water column and sedimentary denitrification in the Santa Barbara Basin using stable isotopes of nitrate, Geochem. Geophys. Geosyst., 4, 1040–1059, 2003.

Solórzano, L. and Sharp, J. H.: Determination of total dissolved nitrogen in natural waters, Limnol. Oceanogr., 25(4), 751–754, 1980.

Stanley, E. H. and Maxted, J. T.: Changes in the dissolved nitrogen pool across land cover gradients in Wisconsin streams, Ecol. Appl., 18(7), 1579–1590, 2008.

Stepanauskas, R., Edling, H., and Tranvik, L. J: Differential dissolved organic nitrogen availability and bacterial aminopeptidase activity in limnic and marine waters, Microbiol. Ecology, 38, 264–272, 1999a.

Stepanausjkas, R. Leonardson, L., and Tranvik, T. J.: Bioavailabilty of wetland-derived DON to freshwater and marine bacterioplankton, Limnol. Oceanogr., 44(6), 1477–1485, 1999b.

Stepanauskas, R., Jørgensen, N. O. G., Eigaard, O. R., Žvikas, A., Tranvik, L. J., and Leonardsen, L.: Summer inputs of riverine nutrients to the Baltic Sea: bioavailability & eutrophication relevance, Ecol. Monogr., 72(4), 579–597, 2002.

Tobias, C. R., Harvey, J. W., and Anderson, I. C.: Quantifying groundwater discharge through fringing wetlands to estuaries: Seasonal variability, methods comparison, and implications for wetland-estuary exchange, Limnol. Oceanogr., 46, 604–615, 2001.

Valiela, I., Costa, J. Foreman, K., Teal, J. M., Howes, B., and Aubrey, D.: Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters, Biogeochemistry, 10, 177–197, 1990.

Wiegner, T. N., Seitzinger, S. P., Glibert, P. M., and Bronk, D. A.: Bioavailability of dissolved organic nitrogen and carbon from nine rivers in the eastern United States, Aquat. Microb. Ecol., 53, 277–287, 2006.

Williams, P. M. and Druffel, E. R. M.: Radiocarbon in dissolved organic matter in the central North Pacific Ocean, Nature, 330, 246–248, 1987.

BGD

7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

BGD

7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

Table 1. Correlation coefficients of all measured parameters in the Elbe River at the weir of Geesthacht, June 2005–December 2007. r^2 in bold, italic coefficients present a level of significance $\alpha \leq 0.01$.

r^2\ r	$c(NO_3^-)$	c(TDN)	$c(DON+NH_4^+)$	c(PN)	$\delta^{15}N-NO_3^-$	$\delta^{18}O-NO_3^-$	$\delta^{15}TDN$	$\delta^{15}DON+NH_4^+$	$\delta^{15}PN$
$c(NO_3^-)$		*0.995*	*0.462*	*−0.674*	*−0.918*	*−0.897*	*−0.902*	0.369	*0.584*
c(TDN)	***0.991***		*0.547*	*−0.656*	*−0.907*	*−0.868*	*−0.898*	0.414	*0.579*
$c(DON+NH_4^+)$	***0.214***	***0.299***		−0.104	−0.359	−0.278	−0.424	*0.592*	0.193
c(PN)	***0.454***	***0.431***	**0.011**		*0.745*	*0.770*	*0.655*	−0.296	−0.375
$\delta^{15}N-NO_3^-$	***0.843***	***0.822***	**0.129**	***0.555***		*0.977*	*0.964*	−0.287	−0.487
$\delta^{18}O-NO_3^-$	***0.805***	***0.754***	**0.077**	***0.593***	***0.955***		*0.916*	−0.380	−0.496
$\delta^{15}TDN$	***0.813***	***0.807***	**0.179**	***0.429***	***0.930***	***0.840***		−0.275	−0.552
$\delta^{15}DON+NH_4^+$	**0.136**	**0.171**	***0.351***	**0.088**	**0.082**	**0.144**	**0.076**		*0.726*
$\delta^{15}PN$	***0.341***	***0.336***	**0.037**	**0.141**	**0.237**	**0.246**	**0.305**	***0.528***	

Table 2. Annual and seasonal mean concentrations and mean isotope values of nitrate, TDN, DON+NH_4^+ and PN, and annual and seasonal mean DON+NH_4^+ ratio in the Elbe River at the weir of Geesthacht, June 2005–December 2007.

	c(NO_3^-) [µM]	c(TDN) [µM]	c(DON+NH_4^+) [µM]	c(PN) [µM]	ratio [%]	δ^{15}N–NO_3^- [‰]	δ^{18}O–NO_3^- [‰]	δ^{15}TDN [‰]	δ^{15}DON+NH_4^+ [‰]	δ^{15}PN [‰]
summer half-year (Apr–Sep)	112±76	150±78	38±9	57±32	29.1±11.4	16.5±4.1	6.5±3.3	12.8±2.3	4.8±1.7	7.2±0.9
winter half-year (Oct–Mar)	258±82	303±91	45±15	33±25	15.1±3.6	10.1±2.2	1.6±1.9	9.5±1.5	6.2±2.8	8.5±1.1
winter (Dec–Feb)	295±48	346±56	51±14	20±6	14.7±2.9	9.3±0.7	0.8±0.6	9.0±0.7	7.4±0.9	9.1±0.7
spring (Mar–May)	261±119	308±125	47±17	66±32	18.0±10.3	10.3±4.1	3.0±3.4	9.3±2.4	5.9±3.2	7.5±1.4
summer (Jun–Aug)	84±28	122±28	38±7	55±33	32.6±9.8	18.0±2.7	7.6±2.7	13.7±1.3	4.9±1.6	7.2±0.8
autumn (Sep–Nov)	168±50	200±51	32±3	41±30	16.9±5.0	12.5±2.9	3.5±3.0	11.0±1.8	4.3±2.6	7.9±1.3
annual mean	177±107	218±113	41±12	46±30	22.9±11.2	13.6±4.6	4.1±3.7	11.3±2.6	5.4±2.4	7.8±1.2
Max	422	458	75	127	56.6	22.5	12.1	15.8	11.5	10.0
Min	33	75	22	11	7.9	6.4	0.2	6.5	0.8	5.9

BGD
7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

Table 3. Annual and seasonal loads (in kt) of nitrate, TDN, DON+NH_4^+ and PN in the Elbe River at the weir of Geesthacht, June 2005–December 2007 (n.d. = not determined).

Load	summer '05 (Jun–Sep)	winter '05/'06 (Oct–Mar)	summer '06 (Apr–Sep)	winter '06/'07 (Oct–Mar)	summer '07 (Apr–Sep)	winter '07 (Oct–Dec)	annual load '06	annual load '07
TDN Load [kt]	12.02	58.73	63.26	39.59	14.84	52.18	107.11	72.03
NO_3^- Load [kt]	8.67	50.35	53.55	32.97	10.97	45.44	91.19	59.16
DON+NH_4^+ Load [kt]	3.35	8.38	9.71	6.62	3.87	6.74	15.92	12.87
PN Load [kt]	n.d.	n.d.	5.27	4.09	5.00	5.01	8.20	10.09

BGD
7, 7543–7574, 2010

BGD

7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

Table 4. Load weighted annual and seasonal mean isotope values of nitrate, TDN, DON+NH_4^+ and PN in the Elbe River at the weir of Geesthacht, June 2005–December 2007 (n.d. = not determined).

	summer '05 (Jun–Sep)	winter '05/'06 (Oct–Mar)	summer '06 (Apr–Sep)	winter '06/'07 (Oct–Mar)	summer '07 (Apr–Sep)	winter '07 (Oct–Dec)	annual load '06	annual load '07
δ^{15}TDN wml	14.5	8.6	7.7	8.8	12.4	9.1	8.3	9.4
$\delta^{15}N-NO_3^-$ wml	18.7	8.8	8.1	9.3	15.0	9.5	8.6	10.2
$\delta^{18}O-NO_3^-$ wml	n.d.	0.7	1.6	1.1	5.6	1.0	1.3	1.8
δ^{15}DON+NH_4^+ wml	5.6	7.5	5.9	6.5	5.0	6.3	6.5	6.0
δ^{15}PN wml	n.d.	n.d.	4.8	8.2	7.1	8.4	6.0	7.1

Table 5. Selected nutrient concentrations in the Elbe River at the weir of Geesthacht in the years 2005–2007, measured by the ARGE-Elbe (ARGE 2005, 2007a, b) (d.l. = detection limit).

		ammonium [µM]	o-phosphate [µM]	nitrite [µM]
2005	Feb	10.7	1.9	1.4
	May	<d.l.	<d.l.	<d.l.
	Jun	<d.l.	<d.l.	1.4
	Jul	<d.l.	0.6	<d.l.
	Aug	<d.l.	<d.l.	0.7
	Nov	<d.l.	2.3	<d.l.
2006	Feb	33.6	1.6	1.4
	May	<d.l.	0.6	0.7
	Jun	<d.l.	0.3	0.7
	Jul	<d.l.	0.6	<d.l.
	Aug	<d.l.	1.6	<d.l.
	Nov	2.9	2.6	<d.l.
2007	Feb	2.9	1.9	0.7
	May	<d.l.	<d.l.	0.7
	Jun	4.3	<d.l.	1.4
	Jul	<d.l.	<d.l.	0.7
	Aug	2.9	<d.l.	0.7
	Nov	4.3	2.9	0.7

BGD
7, 7543–7574, 2010

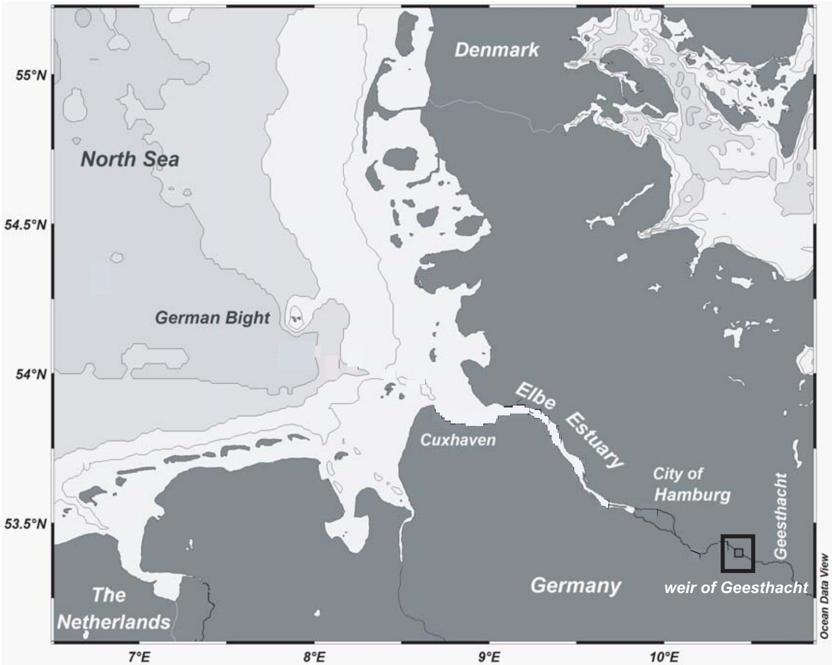

Fig. 1. Sample station weir of Geesthacht, Northern Germany, NW Europe.

BGD
7, 7543–7574, 2010

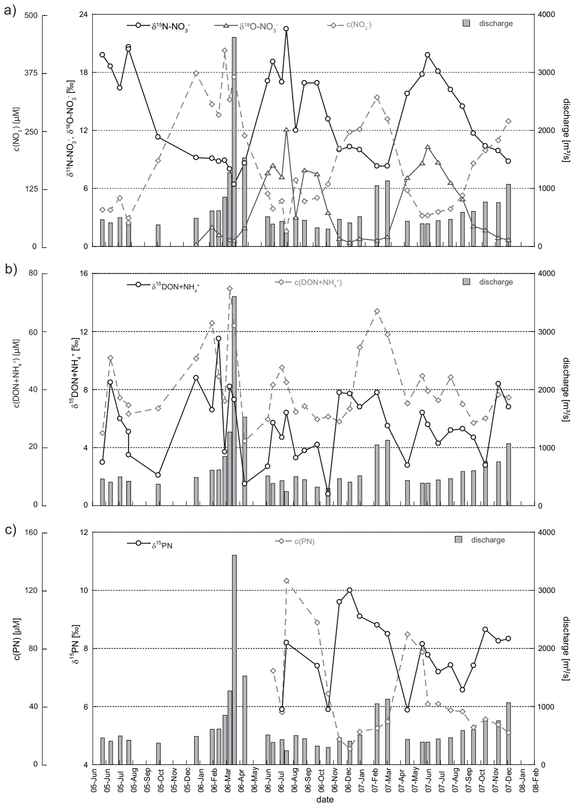

Fig. 2. Concentration and isotopic values in the Elbe River at the weir of Geesthacht, June 2005–December 2007, bars represent the river discharge. Note the different scales of the y-axes. **(a)** Nitrate concentration, δ^{15}N$-NO_3^-$ and δ^{18}O$-NO_3^-$ in the Elbe River. Data from 2006 have been published in Johannsen et al. (2008). **(b)** combined DON+NH_4^+ concentration and δ^{15}DON+NH_4^+. **(c)** PN concentration and δ^{15}PN.

BGD

7, 7543–7574, 2010

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀I | ▶I
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

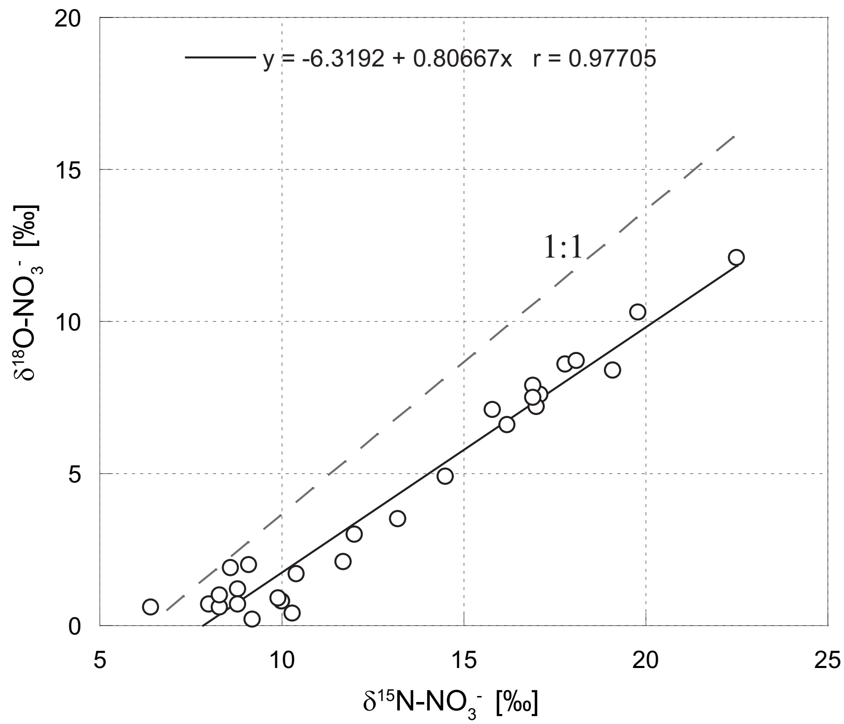

Fig. 3. Relationship between $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ to examine the fractionation factor ratio $\varepsilon^{15}/\varepsilon^{18}$, dashed line represents a 1:1 ratio.

BGD
7, 7543–7574, 2010

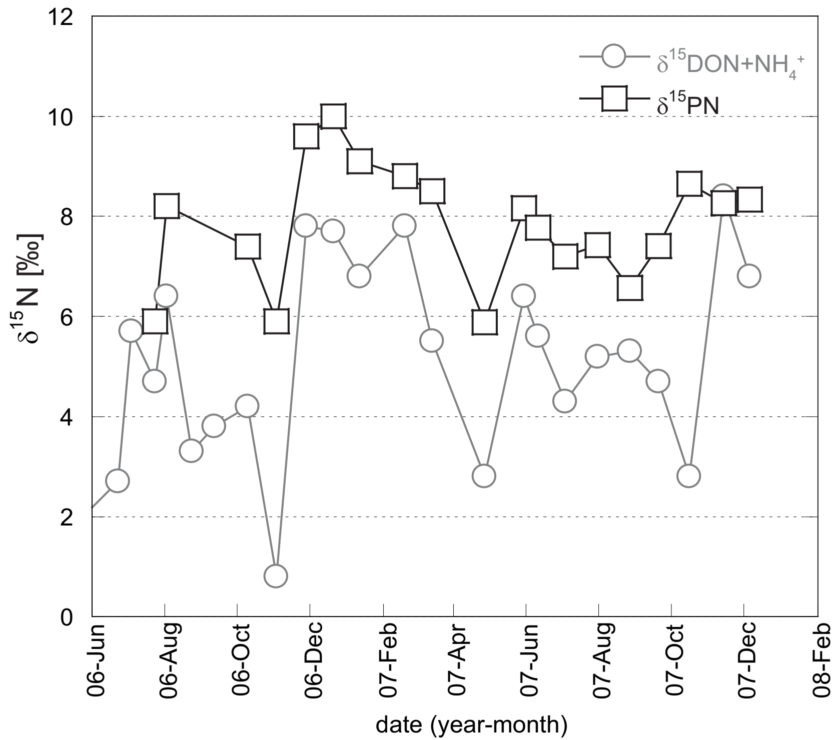

Fig. 4. δ^{15}DON+NH$_4^+$and δ^{15}PN in the Elbe River at the weir of Geesthacht, June 2006–December 2007.

BGD
7, 7543–7574, 2010

Dissolved and particulate reactive nitrogen

T. Schlarbaum et al.

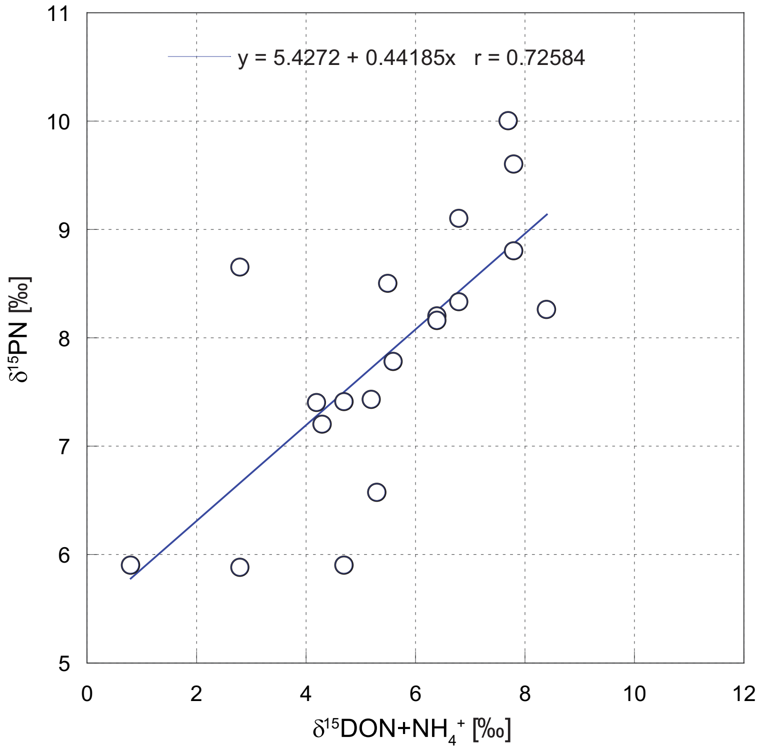

Fig. 5. Relationship between δ^{15}DON+NH_4^+ and δ^{15}PN in the Elbe River at the weir of Geesthacht, June 2006–December 2007.

BGD
7, 7543–7574, 2010