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Turnover of combined dissolved organic nitrogen and ammonium in the Elbe estuary/NW Europe: Results of nitrogen isotope investigations

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ABSTRACT

Dissolved organic nitrogen (DON) is often the dominant form of reactive nitrogen transported from land to sea by rivers, but is considered to be largely recalcitrant and behaves conservatively in many estuaries. We measured the concentration and the isotope ratio $\delta^{15}N$ of combined DON and ammonium ($\delta^{15}DON + NH_4^+$) in the Elbe River estuary (SE North Sea, NW Europe) by a combination of a modified persulfate digestion and the denitrifier method. Measurements were made on samples taken along the salinity gradient from 1 to 32 during different seasons, in order to gauge the effects of internal biological processes and external signatures (such as pollution). Combined DON and ammonium concentrations ranged from 20 to 60 µM, and $\delta^{15}DON + NH_4^+$ from 0 to 11‰. The results show that $DON + NH_4^+$ contributes <20% to total reactive nitrogen in the river end member and rises to 50% in the outer estuary. By comparison with older data, the DON load in the Elbe River did not change since the 1980s, when nitrate and phosphate pollution was maximal. We find evidence that DON and/or ammonium or reactive components in DON are both consumed and produced in the estuary, indicated by changing isotope ratios and non-conservative mixing gradients. The estuarine turbidity maximum zone (TMZ) at salinities <5, which today is a significant source of nitrate from nitrification, coincides with significantly decreased $DON + NH_4^+$ concentrations and $\delta^{15}DON + NH_4^+$ in all seasons sampled. Whether this is due to selective absorption/desorption of ^{15}N enriched moieties onto particle surfaces, or to selective heterotrophic assimilation and nitrification is yet unclear, and the loss of $DON + NH_4^+$ does not balance the added nitrate. Because $DON + NH_4^+$ concentrations and $\delta^{15}DON + NH_4^+$ rise sharply seaward of the TMZ, we consider adsorption/desorption processes most likely. In the salinity gradient 5 to 30, $DON + NH_4^+$ behaves conservatively in both concentration and isotopic composition.

1. Introduction

Dissolved organic nitrogen (DON) is a major (between 15% and 90%) component of total dissolved nitrogen (TDN) transported to the coastal ocean by rivers, with highest DON dominance in unpolluted rivers (Wiegner et al., 2006). DON has until recently been considered to be a largely inert pool of heterogeneous composition that is not a relevant N-source for estuarine and coastal ecosystems. This view is changing: Although only parts of the heterogeneous DON pool in estuarine environments apparently are bioavailable (Bronk et al., 2007; Seitzinger and Sanders, 1997; Seitzinger et al., 2002), labile moieties of DON are now seen as potentially important nitrogen sources for assimilatory and dissimilatory biological processes in coastal environments, and in particular in those situations, when dissolved inorganic nitrogen (DIN) is exhausted (Bronk, 2002). Significantly, there is some evidence that a decrease in the DIN/DON ratio of coastal waters (due to decreasing ratios in river loads or to seasonal depletion of DIN) may be favourable to dinoflagellates and cyanobacteria and may be implicated in the triggering of harmful algal blooms (Bronk et al., 2007).

Our interest here is to investigate the fate of DON in the extended estuarine salinity gradient of the Elbe River/NW Europe between a well-defined riverine (weir at Geesthacht) and marine end member in the German Bight/southeastern North Sea (Fig. 1). The estuary has been monitored continuously over the last decades for changes in water quality (ARGE, 2008), and data are available that offer a long-term view of the estuarine biogeochemistry of DON. The role of DON may have changed as a result of pollution reduction measures in the watershed, and since the mid-1980s, TDN and DIN loads of the river have decreased by 30% (Radach and Paetsch, 2007). The first objective of the present study was to investigate whether the combined concentration of DON and ammonium and the $NO_3^-/DON + NH_4^+$ ratio in this river have changed as well.

Secondly, we present (to our knowledge) a first systematic and seasonally resolved data set on the $^{15}N/^{14}N$ composition of combined

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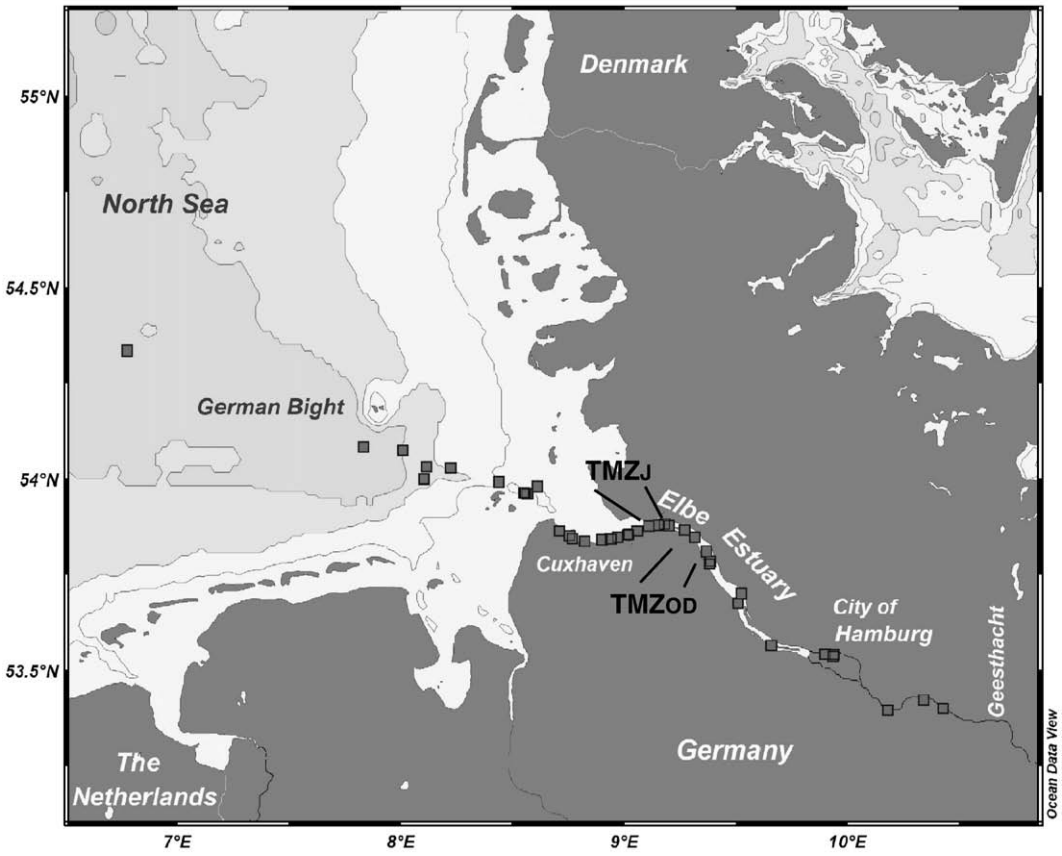

Fig. 1. Sample stations in the Elbe estuary and location of places referred to in the text.

DON and ammonium (expressed as the δ value in ‰ = [(R_{sample}/$R_{standard}$) − 1]*1000, $R = {}^{15}N/{}^{14}N$ in DON + NH_4^+ and in the international standard atmospheric dinitrogen) of an estuary, allowing us to better evaluate whether or not DON + NH_4^+ behaves conservatively in the mixing zone between marine and fresh waters than concentrations alone. This was motivated by the fact that decreased DIN loads were accompanied by significant changes in estuarine nitrate turnover: The estuary changed from being a nitrate sink to being a nitrate source (Dähnke et al., 2008), and the nitrate source was associated with the estuarine turbidity maximum zone (TMZ) that forms at salinities between 0.4 and 2 (Bergemann, 1995). That nitrate increase was most pronounced in June 2006, when the internal addition doubled the original riverine nitrate concentration (Dähnke et al., 2008). Based on a concomitant decrease in $\delta^{18}O$ of nitrate, the source of the added nitrate was most likely nitrification of ammonium: The increase in nitrate concentrations was not associated with substantial changes in $\delta^{15}NO_3^-$, but only by a pronounced drop in $\delta^{18}O$. Because ammonium levels in the Elbe estuary are too low to account for an input of this magnitude, it was suggested that local nitrification of ammonium derived from the degradation of organic matter and its subsequent rapid oxidation by particle-associated nitrifying bacteria within the TMZ caused the nitrate peak. This would involve either DON or particulate nitrogen (PN) and should thus be accompanied by changes in concentrations and/or isotopic composition of DON and PN.

In summary, our objectives here are to 1) test if the NO_3^-/DON + NH_4^+ ratio in the Elbe river changed, and whether this is due to enhanced DON + NH_4^+ production, or decreasing nitrate levels alone over the last decades, 2) to examine concentration and isotopic changes versus salinity in the estuary for evidence of DON + NH_4^+ turnover, and in particular turnover in the TMZ, and 3) to establish whether seasonal differences in DON + NH_4^+ turnover are apparent in the estuary.

2. Materials and methods

Our approach is based on determinations of combined DON and ammonium concentrations and the isotope ratio δ^{15}DON + NH_4^+ along the salinity gradient during different seasons in the Elbe estuary. Mixing diagrams of salinity versus DON + NH_4^+ concentrations, or versus δ^{15}DON + NH_4^+, help to determine whether DON + NH_4^+ behaves conservatively in the estuary or not. The mixing behaviour of dissolved compounds can be assessed by using a mixing model for calculating concentrations (Liss, 1976):

$$c_{mix} = f^*c_r + (1-f)^*c_m. \quad (1)$$

The indexes r and m denote riverine and marine concentrations, and f indicates the fraction of freshwater in each sample calculated from salinity, with 32 as salinity of the marine end member for German Bight water (f = (32-salinity)/32).

For isotopic values a calculation of mixing with concentration-weighted isotopic values is used (Fry, 2002):

$$\delta_{mix} = [f^*c_r^*\delta_r + (1-f)^*c_m^*\delta_m] / c_{mix}. \quad (2)$$

Conservative mixing leads to linear mixing paths in the case of concentrations, whereas salinity-based isotope mixing diagrams usually show curvilinear mixing behaviours, reflecting concentration-based weighting of end member isotopic contributions.

2.1. Study site

The Elbe River is 1094 km long and the second largest river discharging into the North Sea (Fig. 1). The tidal estuary extends over 142 km from the weir at the city of Geesthacht (stream kilometre