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Organic matter degradation in the German Bight/SE North Sea: Implications from stable nitrogen isotopes and amino acids

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ABSTRACT

Rising stable nitrogen isotope ratios ($\delta^{15}N$) in dated sediment records of the German Bight/SE North Sea track river-induced coastal eutrophication over the last 2 centuries. Fully exploiting their potential for reconstructions of pristine conditions and quantitative analysis of historical changes in the nitrogen cycle from these sediment records requires knowledge on processes that alter the isotopic signal in non-living organic matter (OM) of sinking particles and sediments. In this study, we analyze the isotopic composition of particulate nitrogen (PN) in the water column during different seasons, in surface sediments, and in sediment cores to assess diagenetic influences on the isotopic composition of OM. Amino acid (AA) compositions of suspended matter, surface sediments, and dated cores at selected sites of the German Bight serve as indicators for quality and degradation state of PN. The $\delta^{15}N$ of PN in suspended matter had seasonal variances caused by two main nitrate sources (oceanic and river) and different stages of nitrate availability during phytoplankton assimilation. Elevated $\delta^{15}N$ values (>20‰) in suspended matter near river mouths and the coast coincide with a coastal water mass receiving nitrate with elevated isotope signal ($\delta^{15}N > 10$‰) derived from anthropogenic input. Particulate nitrogen at offshore sites fed by oceanic nitrate having a $\delta^{15}N$ between 5 and 6‰ had low $\delta^{15}N$ values (<2‰), indicative of an incipient phytoplankton bloom. Surface sediments along an offshore–onshore transect also reflect the gradient of low $\delta^{15}N$ of nitrate in offshore sites to high values near river mouths, but the range of values is smaller than between the end members listed above and integrates the annual $\delta^{15}N$ of detritus. Sediment cores from the coastal sector of the gradient show an increasing $\delta^{15}N$ trend (increase of 2.5‰) over the last 150 years. This is not related to any change in AA composition and thus reflects eutrophication. The $\delta^{15}N$ signals from before AD 1860 represent a good estimation of pre-industrial isotopic compositions with minimal diagenetic overprinting. Rising $\delta^{13}C$ in step with rising $\delta^{15}N$ in these cores is best explained by increasing productivity caused by eutrophication.

1. Introduction

The ratios of stable nitrogen isotopes expressed as $\delta^{15}N$ in sedimentary N have recently been used to detect imprints of nitrate eutrophication in sediment records of several estuaries in NW Europe (Clarke et al., 2003, 2006), in the Baltic Sea (Voß and Struck, 1997; Struck et al., 2000; Emeis et al., 2002), in the northern North Sea and Kattegat as well as in the German Bight/SE North Sea (Dähnke et al., 2008; Serna et al., 2010). Rivers draining cultivated catchments, such as the Elbe, have elevated $\delta^{15}N$ values (>8‰) in their annual nitrate and suspended matter load (Voß and Struck, 1997; Johannsen et al., 2008; Schlarbaum et al., 2010). These high values are distinct from the marine end member nitrate in the North Sea which is close to the deep water oceanic nitrate reservoir having a $\delta^{15}N$ of 5‰ (Sigman et al., 2009) due to its provenance from the North Atlantic subthermocline nitrate pool (Dähnke et al., 2010). Terrestrial plants have a $\delta^{15}N$ range of −5‰ to 18‰ (with an average around 3‰; Müller and Voss, 1999) and marine organisms of 3‰ to 10‰ (with an average around 6‰; Peters et al., 1978; Müller and Voss, 1999). Therefore, their utility, as indicators of OM sources in near coastal areas, is limited by a wide variability in ^{15}N signatures.

Measurements of $\delta^{15}N$ in dated sediment cores from the German Bight showed an increase from approximately 6‰ at AD 1860 to 8.5‰ at AD 2000 (Serna et al., 2010). The increase in sedimentary $\delta^{15}N$ over time has been attributed to increased $\delta^{15}N$ of riverborne nitrate loads reflecting anthropogenic activities in rivers discharging into the SE North Sea (Johannsen et al., 2008; Schlarbaum et al., 2010). The

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lower-than-present $\delta^{15}N$ of pre-1860 sediments were the target levels set for hindcast modeling of pristine loads of N in rivers discharging a good part of catchments in continental Europe. Using a numerical ecosystem model (Pätsch et al., 2010), the $\delta^{15}N$ of surface sediments in the German Bight for pristine conditions with reduced N loads were modeled and displayed values up to 2‰ lower than those modeled and observed for recent N load conditions (Serna et al., 2010). The approach was based on the assumption that the N-isotope composition in sediments integrates N-inputs, assimilation, and cycling in the German Bight over time, and that sediment values delineate the averaged mixing gradient of riverborne with marine nitrate (Pätsch et al., 2010). The model results in comparison to data indeed showed that the surface sediment signal reflects the integration of the variable isotopic compositions of nitrate over the seasons. The model approach also assumed that the $\delta^{15}N$ signal in sediment cores is not affected by post-depositional alteration during protein degradation (Gaye-Haake et al., 2005; Pätsch et al., 2010; Möbius et al., 2011). Sensitivity experiments with the model indicated that the isotopic fractionation effect associated with burial and degradation of detritus in the sediment is a crucial step in modeling $\delta^{15}N$ patterns (Pätsch et al., 2010). The validity of that assumption can be put to test by analyzing amino acid composition of OM to establish and track degradation state during sinking and burial of particulate N, in conjunction with $\delta^{15}N$ measurements. Amino acids comprise a large fraction of the organic N in phytoplankton, zooplankton and sedimenting matter (Cowie and Hedges, 1992; Carstens et al., 2013). Typically, the abundance of amino acids (AAs) decreases with increasing depth in the water column or with the aging of OM (Lee and Cronin, 1984; Cowie and Hedges, 1992). But motivated by contrasting results produced in studies related to changes of the isotopic composition of OM with microbial degradation (Libes and Deuser, 1988; Freudenthal et al., 2001; Lehmann et al., 2002; Möbius et al., 2010), we here combine information of several digenetic indicators, including the concentration of AA, two degradation indices, and the ratios of the precursors aspartic acid (Asp) and glutamic acid (Glu) to their decompositional products β-alanine (β-Ala) and γ-aminobuteric acid (γ-Aba), respectively (Lee and Cronin, 1982; Cowie and Hedges, 1994). Negative values of the AA based degradation index (DI) indicate more degradation and positive values indicate less degradation of the OM (Dauwe and Middelburg, 1998). Poorest OM preservation is indicated by values of the reactivity index (RI) close to 0, whereas fresh marine plankton ranges between 4 and 6 (Jennerjahn and Ittekkot, 1997).

The goal of this study is to elucidate the effect of OM degradation on the isotopic composition of N in suspended particulate matter in the water column, in surface sediments, and in sediment cores along a land-sea gradient of distinct nitrate sources in the SE North Sea. If a significant effect on $\delta^{15}N$ of sediments can be excluded, then the values may be used to reconstruct the anthropogenic history of the German Bight due to ^{15}N-enriched riverborne nitrate loads.

2. Materials and methods

2.1. Study area

The shallow German Bight/SE North Sea receives nitrogen from a net influx of water masses from the west, partly from the English Channel, partly from the Rhine River and other rivers, and from atmospheric deposition. A significant export to the north occurs as a consequence of the counter-clockwise circulation pattern of the North Sea (Pätsch et al., 2010), and a significant amount of reactive nitrogen (Nr) is eliminated by denitrification in the sediments and nitrate assimilation followed by sedimentation of detritus (Lohse et al., 1993). Suspended matter concentrations in the German Bight vary between 0.3 mg L^{-1}, in calm weather conditions, and 35 mg L^{-1}, during stormy weather (König et al., 1994; Puls et al., 1997). A prominent depositional area in the North Sea is the Helgoland mud area, where sediments accumulate due to a small-scale eddy driven by the interaction of the longshore coastal current, tidal dynamics, and the discharge from the Elbe and Weser rivers (Hertweck, 1983). River inputs of nutrients have increased drastically, especially during the second half of the 20th century (Howarth et al., 1996; Radach and Pätsch, 2007; Johannsen et al., 2008; Pätsch and Kühn, 2008; Pätsch and Radach, 1997). This raised the primary production rates of the North Sea coastal waters, among other clear indications of eutrophication (Pätsch and Radach, 1997; Radach, 1998).

We determined $\delta^{15}N$ and AA compositions in suspended matter ($\delta^{15}N_{SM}$) and the underlying surface sediments ($\delta^{15}N_{SS}$) in a transect from the Elbe estuary to the open NW North Sea, and in dated sediment cores from the Helgoland mud area in the German Bight (Fig. 1). Data of C/N molar ratios and the $\delta^{13}C$ composition of organic carbon aid in the interpretation of spatial and temporal variability detected.

2.2. Surface sediments and suspended matter sampling

Surface sediments were obtained from gravity cores or van Veen grab sampler during cruises Aldebaran ALD (July, 2005) and Heincke HE267 (May, 2007) in the German Bight/SE North Sea, and on a transect from the Elbe estuary to the NE North Sea during cruise Valdivia VAL157 (March, 1996) (Fig. 1) that sampled the entire gradient from river to oceanic sourced nitrate. Each sampling occurred during different seasons in the German Bight and North Sea. Samples were dried, sieved and homogenized for analyses of elemental, AA and isotopic composition. To sample suspended particles, GF/F pre-combusted filters were used to filter different volumes of water obtained with Niskin bottles. Filters were dried at 40–50 °C for at least 24 h prior to chemical and isotopic analyses. Zooplankton material was removed from the filtered material to exclude any contribution to the analyses. Salinity and nutrient data of water samples taken during VAL157 are from Ittekkot (1999). Salinity was obtained from CTD data and nitrate, nitrite and ammonium concentrations were determined with an auto-analyzer II (Technicon, Bad Vilbel), summed as dissolved inorganic nitrogen (DIN).

2.3. Multicores and gravity cores

We analyzed three short (<40 cm) cores from the Helgoland depositional area (Table 1 and Fig. 1). Multicore (MUC) HE267/327 was collected on expedition RV Heincke HE267 (2007) and sampled in 1 cm intervals. Samples were dried and treated the same way as surface sediments. Gravity core (GC) HE 215/4-2 was collected on expedition Heincke-215 (2004) and treated the same way as MUCs (Serna et al., 2010). GC GeoB/4801 was collected on expedition RV Meteor M40/0 (1997) and sub-sampled at 5 cm intervals throughout the core with an increased resolution of 1 cm intervals in the upper 135 cm (Hebbeln et al., 2003).

2.4. Carbon and nitrogen

Concentrations of TC and TN in dried and homogenized samples of sediments from GC GeoB/4801 were measured by a Heraeus-CHN-analyzer; all other homogenized samples were measured by a Carlo Erba 1500 elemental analyzer. The precision of this method is 0.05% for carbon and 0.005% for nitrogen. For TOC analysis the samples were acidified with 2 N hydrochloric acid and/or 2 N phosphoric acid and then dried overnight on a 40 °C hot plate. Sediments from GC GeoB/4801 were acidified with 6 N hydrochloric acid and dried on an 80 °C hot plate. TOC was calculated as the difference between total carbon and carbonate carbon. Organic matter was calculated as 1.8 × TOC (Anderson and Sarmiento, 1994; Francois et al., 2002). TOC and TN concentrations by weight were used to compute C/N molar ratios.