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Nitrate consumption in sediments of the German Bight (North Sea)

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ABSTRACT

Denitrification on continental margins and in coastal sediments is a major sink of reactive N in the present nitrogen cycle and a major ecosystem service of eutrophied coastal waters. We analyzed the nitrate removal in surface sediments of the Elbe estuary, Wadden Sea, and adjacent German Bight (SE North Sea) during two seasons (spring and summer) along a eutrophication gradient ranging from a high riverine nitrate concentrations at the Elbe Estuary to offshore areas with low nitrate concentrations. The gradient encompassed the full range of sediment types and organic carbon concentrations of the southern North Sea. Based on nitrate penetration depth and concentration gradient in the porewater we estimated benthic nitrate consumption rates assuming either diffusive transport in cohesive sediments or advective transport in permeable sediments. For the latter we derived a mechanistic model of porewater flow. During the peak nitrate discharge of the river Elbe in March, the highest rates of diffusive nitrate uptake were observed in muddy sediments (up to 2.8 mmol m^{-2} d^{-1}). The highest advective uptake rate in that period was observed in permeable sediment and was tenfold higher (up to 32 mmol m^{-2} d^{-1}). The intensity of both diffusive and advective nitrate consumption dropped with the nitrate availability and thus decreased from the Elbe estuary towards offshore stations, and were further decreased during late summer (minimum nitrate discharge) compared to late winter (maximum nitrate discharge). In summary, our rate measurements indicate that the permeable sediment accounts for up to 90% of the total benthic reactive nitrogen consumption in the study area due to the high efficiency of advective nitrate transport into permeable sediment. Extrapolating the averaged nitrate consumption of different sediment classes to the areas of Elbe Estuary, Wadden Sea and eastern German Bight amounts to an N-loss of $3.1 * 10^6$ mol N d^{-1} from impermeable, diffusion-controlled sediment, and $5.2 * 10^7$ mol N d^{-1} from permeable sediment with porewater advection.

1. Introduction

The German Bight is part of the southern North Sea and is semi-enclosed by a densely populated and industrialized hinterland from which major continental European rivers (Rhine, Maas, Elbe, Weser, and Ems) transport significant amounts of nutrients to the coastal waters (Los et al., 2014). Riverine nitrogen loads into the German Bight reached a maximum in the 1980s (e.g. Radach and Patsch, 2007). Stratification from high freshwater discharge in combination with high riverine nutrient loads led to large phytoplankton blooms and oxygen deficiencies during the 1980′s (Westernhagen von et al., 1986; Hickel et al., 1993). Eutrophication promoted blooms of phytoplankton, spread of green macroalgae and a decrease in seegrass, especially in the Wadden Sea, one of the largest intertidal ecosystems on earth (Cadée and Hegeman, 2002; Reise and Siebert, 1994; van Dolch et al., 2013; van Katwijk et al., 1997). Although various mitigation efforts constantly reduced the nutrient load since then (Amann et al., 2012), the entire SE North Sea is still flagged as an eutrophication problem area (OSPAR, 2010).

Natural attenuation mechanisms such as denitrification and anammox in sediments counteract eutrophication by converting reactive nitrogen in suboxic sediment layers to inert N_2. These processes are a significant global sink for nitrate (Middelburg et al., 1996; Seitzinger et al., 2006), and are particularly effective in sediments of continental margins, shelf seas, and coastal permeable sediments with elevated concentrations of organic matter (e.g., Cornwell et al., 1999). In the face of increasing developments and modifications of sea floors in offshore North Sea areas such as bottom trawling, dredging, removal of

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sand and gravel, and offshore construction (Emeis et al., 2015), there is a need to assess the role of sediments and different sediment types in the turn-over of organic matter and nutrients. Of particular interest is their capacity to sequester or eliminate potentially problematic substances such as reactive nitrogen - a natural environmental service of considerable value to society (e.g., Costanza et al., 1997).

In spite of its acknowledged importance as an ecosystem function, benthic denitrification rate measurements on continental shelves and in coastal seas are scarce and have rarely been investigated in terms of sediment texture, organic matter loading and seasonality. The available data base for North Sea sediments is highly local and sporadic, and model attempts to estimate the elimination of reactive nitrogen in German Bight sediments have no recent data basis (e.g., Pätsch et al., 2010). Exploitation of the available data sets for a systematic assessment is also hampered by the heterogeneity of methods used. Schroeder et al. (1996) measured nitrate consumption rates in the Elbe estuary in the late 1980s with benthic chambers. Lohse et al. (1993, 1996) investigated several stations encompassing different sediment types in the outer German Bight in the early 1990s applying the acetylene blocking method, core flux incubations and isotope pairing to determine denitrification rates. More recently, Deek et al. (2012) measured N-turnover in Wadden Sea sediment using core flux incubations and isotope pairing. Gao et al. (2012) and Marchant et al. (2014, 2016) reported denitrification rates in intertidal and subtidal permeable sediments obtained from slurry incubations and percolated sediment cores. However, these measurements cover a limited area, especially in subtidal waters, and do not trace the N-loss along major river runoff characterized by constantly changing environmental conditions with respect to nutrient loads (Amann et al., 2012) and primary production (e.g. Cadée and Hegeman, 2002; Philippart et al., 2007; van Beusekom et al., 2009), both of which are among the most important determinants of denitrification rates.

In this paper we report pore water concentration profiles of nitrate for a wide range of North Sea sediment types and for various bottom water concentrations of nitrate. Assuming steady state conditions, the nitrate profiles reflect the balance of transport intensity (either by diffusive or advective processes) and sediment reactivity. If the nitrate transport is high in comparison with reactivity, then nitrate penetrates deeply into the sediment until it is eventually consumed by denitrifying bacteria and archaea. Conversely, all nitrate is consumed in the uppermost sediment layer in cases where the nitrate import from the bottom water is low compared to the sediment reactivity. It is thus possible to estimate nitrate turnover rates on the basis of transport intensity and the depth of nitrate penetration into the sediment. Assuming steady-state conditions such interpretation of porewater profiles is a standard procedure to calculate diffusive solute fluxes (e.g. Berg et al., 1998). Based on the concentration gradient, the calculation of the diffusive flux requires only the diffusivity of the solute in water, corrected for effects of temperature and porosity. As implemented in the one-dimensional transport-reaction model of Berg et al. (1998), this method interprets the first and second derivative of the nitrate concentration profile to calculate the diffusive nitrate flux and associated reaction rates. If influx and efflux are not balanced then the model assumes either production or consumption of nitrate to balance fluxes and turnover.

However, mass transport by molecular diffusion is slow compared to porewater advection along pressure gradients in permeable sediments. Coarse grained permeable sediments are found predominantly in shallow coastal waters with strong tidal currents that usually form a rippled seabed topography. Across the ripples, the water current induces pressure gradients that pump bottom water into the sediment where reactive compounds such as nitrate are consumed. Although this form of porewater advection has been well described (e.g. Elliott and Brooks, 1997; Precht and Huettel, 2003; Precht et al., 2004, and Huettel et al., 2014) it was often neglected in field measurements and biogeochemical modelling. Here, we interpret measured nitrate profiles in two ways. First, we employ the method of Berg et al. (1998) for a conservative estimate of the diffusive nitrate flux by assuming steady-state diffusion as the dominant benthic transport mode. Second, we expand the analytical model for porewater flow by Elliott and Brooks (1997) and Ahmerkamp et al. (2015) to derive an estimate of sediment nitrate consumption for advective pore water regimes. Finally, we use the rates determined by both methods and apply them to areas with specific permeability properties to estimate total nitrate consumption in the SE German Bight.

Table T1
Overview of sampling campaigns in the Elbe Estuary, German Bight and North-Frisian (NF) Wadden Sea.

Cruise	Vessel	Date (month/year)	area
Pr-0309	RV L. Prandtl	03/2009	Elbe Estuary, NF Wadden Sea
HE-304	RV Heincke	05/2009	German Bight
Pr-0909	RV L. Prandtl	09/2009	Elbe Estuary, NF Wadden Sea
HE-318	RV Heincke	02/2010	German Bight, Dogger Bank

2. Material and methods

2.1. Study site and sampling

The sampling campaign in Elbe estuary, German Bight and North-Frisian Wadden Sea was carried out between March 2009 and February 2010 during 4 cruises with RV Ludwig Prandtl and RV Heincke (Table T1). The sampled stations are depicted in Fig. F1. Temperature, salinity and oxygen saturation of the bottom water were measured with an OTS 1500 multiprobe (Meerestechnik-Elektronik) during the cruises *Pr*-0309 and *Pr*-0909, and with a SBE911plus (Seabird) during the cruises HE-304 and HE-318.

Sediment cores were retrieved with a multicorer equipped with acrylic glass tubes (PMMA, 60 cm long and 10 cm wide). A subset of these tubes was prepared for pore water sampling by drilling holes in 1 cm intervals and sealing them with a septum prior to deployment. Directly after retrieval, the supernatant of the cores was carefully removed and the pore water was extracted with rhizon core solution samplers (Rhizosphere Research) connected to disposable syringes (Meijboom and van Noordwijk, 1992; Seeberg-Elverfeldt et al., 2005). The first few hundred microliters of pore water were discarded to remove air bubbles and oxygenated pore water. The porewater samples were then transferred to evacuated Exetainers (Labco) and stored frozen until nutrient analysis. One core of each station was sliced in 1 cm intervals and stored frozen for further analysis of sediment characteristics.

2.2. Sediment characteristics

The frozen sediment slices were freeze-dried, and the resulting weight loss was used to calculate the water content and porosity based on the assumed mean grain density of 2.65 g cm^{-3}. The dried sediment was then sieved through mesh sizes of 1000 µm, 500 µm, 250 µm, 125 µm, and 63 µm to establish the grain size distributions using Gradistat (Blott and Pye, 2001). Additional subsamples of the dry sediments were used to determine the concentrations of total nitrogen and organic carbon with an Elemental Analyzer (Thermo Flash EA) calibrated against acetanilide.

2.3. Pore water nutrient analysis

The pore water samples were kept frozen in septum capped Exetainers (Labco). After fast thawing in a water bath at room temperature, the samples were acidified with 6 M hydrochloric acid (1% v/v final concentration) to stabilize any gaseous ammonia as ammonium