

Sub-recent nitrogen-isotope trends in sediments from Skagerrak (North Sea) and Kattegat: Changes in N-budgets and N-sources?

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ABSTRACT

We determined $^{15}\text{N}/^{14}\text{N}$ ratios of total nitrogen in surface sediments and dated sediment cores to reconstruct the history of N-loading of the North Sea. The isotopic N composition in modern surface sediments is equivalent to and reflects the isotopic mixture of oceanic nitrate on the one hand ($\delta^{15}\text{N}=5\text{‰}$) and the imprint of river-borne nitrogen input into the SE North Sea ($\delta^{15}\text{N}$ up to 12‰ in estuaries of the SE North Sea) on the other hand. We compare the results with $\delta^{15}\text{N}$ records from pre-industrial sediment intervals in cores from the Skagerrak and Kattegat areas, which both constitute significant depositional centres for N in the North Sea and the Baltic Sea/North Sea transition. As expected, isotopically enriched anthropogenic nitrogen was found in the two records from the Kattegat area, which is close to eutrophication sources on land. Enrichment of $\delta^{15}\text{N}$ in cores from the Skagerrak – the largest sediment sink for nitrogen in the entire North Sea – was not significant and values were similar to those found in sediment layers representing pre-industrial conditions. We interpret this isotopic uniformity as an indication that most riverine reactive nitrogen with its characteristic isotopic signature is removed by denitrification in shallow shallow-water sediments before reaching the main sedimentary basin of the North Sea.

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1. Introduction

The present-day coastal ocean is loaded with nutrients from continental runoff and from the atmosphere, and both changed nutrient element mass fluxes and inter-element ratios are held responsible for ecological changes observed over the past decades in estuaries, coastal waters, and entire shelf seas (Nixon, 1995; Howarth et al., 1996; Nixon et al., 1996; Rabalais, 2004; Crossland et al., 2005). As in other coastal seas, a tenfold increase in N-loads of rivers and the atmosphere in the North Sea induced eutrophication, the spread of oxygen deficient conditions in bottom waters, the demise of macrophytes in many coastal settings, increases in harmful algal blooms, and changes in the food web structure (Lancelot et al., 1987; Galloway et al., 2003; OSPAR, 2003; van Beusekom, 2005; Smith et al., 2006). An important step to curb the loading of coastal oceans with nutrients originating from river runoff in Europe is the European Water Framework Directive (WFD, 2000), which requires that member states of the EU re-establish good ecological conditions in riverine and coastal environments. In this endeavour the most important challenge is the reduction of reactive nitrogen loads. Whereas the reduction of P loads

in many rivers has been quite successful due to replacement of phosphates in detergents and enhanced waste water treatment, success of nitrate reduction measures has been poor, and removal from runoff by biological treatment is significantly more costly.

A further problem in attaining the environmental goals is the definition of the ecological target conditions, because direct observations on nutrient levels and ratios in rivers and coastal oceans are scarce before the 1960's. Instead, numerical models are commonly used to estimate nutrient runoff from pristine river catchments (Behrendt and Opitz, 1999; Seitzinger et al., 2002). Here, we evaluate the use of stable isotope ratios in nitrogen of sediments to reconstruct reactive nitrogen discharges from land into the North Sea and westernmost Baltic Sea. This approach has previously been employed in tracing eutrophication through time in the Baltic Sea (Voss and Struck, 1997; Struck et al., 2000; Voss et al., 2005) and in individual fjords, estuaries, and embayments of the North Sea (Clarke et al., 2003; Clarke et al., 2006) and elsewhere (Church et al., 2006).

Suitable sediment archives are from sediment accumulations in the Skagerrak and Kattegat sediment basins; they collect material from extended submarine catchments, which in turn received reactive nitrogen that has been produced and cycled in densely populated and industrialised watersheds of NW Europe in the course of industrialisation over the last 150 yr.

Our objectives here thus are to establish the present-day pattern of $\delta^{15}\text{N}$ in surface sediments, and then to trace the history of DIN input

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from anthropogenic sources by analysing N mass accumulation rates and N isotopic composition in dated sediment records of the last 150 yr – the period of industrialization (Galloway et al., 2003) – to obtain an estimate of changes in the N isotopic composition that are coupled to increasing anthropogenic nitrogen input. These data are then compared with those of sediments deposited before the onset of industrialisation and the increasing production of reactive nitrogen. To substantiate results of isotope measurements, we also use the mass accumulation rate of sedimentary nitrogen, and changes in the ratio of nitrogen to aluminosilicate material in the samples that provide information on changing N-mass-fluxes due to eutrophication.

2. Working area

The North Sea catchment is home to 180 million inhabitants and is a large export source for reactive nitrogen (Howarth et al., 1996). Inputs of nitrogen vary from year to year, but have increased significantly since the 1950's (Paetsch and Radach, 1997; Behrendt et al., 2002). This reactive nitrogen is completely assimilated by organisms, but only a small portion (<1%) of the biomass is deposited as sediment; the rest is mineralised and recycled (de Haas et al., 2002). On shallow sea floors of the southern, central and eastern North Sea, wind-induced currents, tides, and/or wave action resuspend the sedimented material, and residual currents transport it to depositional areas where energy at the sea floor is low enough to preclude resuspension (Eisma, 1990; Puls and Sündermann, 1990).

Such depositional areas comprise around 1/3 of the sea floor in the North Sea, and the largest depositional centre is the Skagerrak. The Skagerrak is part of the epicontinental North Sea and is connected to the brackish Baltic Sea via the Kattegat (Fig. 1). The Skagerrak is a deep basin (maximum depth 700 m) with an average depth of 200 m and a counter-clockwise water circulation

(Svansson, 1975) that entrains Baltic Sea outflow (salinity of 25 to 30) and North Sea water (salinity 33 to 35). As the water depth increases and the current speed of the cyclonic gyre is reduced, fine-grained sediment is deposited in the northeastern and central parts of the basin (Rodhe and Holt, 1996) at a relatively high rate of up to 1 cm per year. The Skagerrak (and Norwegian Trench to the Northwest) account for 50–70% of all the suspended matter permanently buried in the North Sea. One of the major sources for material buried in the Skagerrak is the Southern North Sea (Van Weering et al., 1993), which is subject to most severe eutrophication phenomena and input of river-borne nutrients.

The Kattegat (water depth <70 m) water circulation is characterized by inflow of salty water from the Skagerrak at depth, and outflow of brackish water of Baltic Sea origin at the surface. According to Carstensen et al. (2006) discharge is collected from a total land area of roughly 16,000 km² in Denmark and 21,000 km² in Sweden. In Denmark 63% of the watershed is arable land and pasture, in Sweden 18%. Sediments in the Kattegat reflect local processes of sediment production and transport. The sea floor is depositional only in deep channels, whereas in shallow waters there is no net deposition (Christiansen et al., 1997). Normally, there is no flux of nutrients from the Skagerrak to the Kattegat (Rydberg et al., 1996). Typically, the winter nitrate concentrations in the Kattegat exceed concentrations expected from mere conservative mixing between Skagerrak and Baltic Sea waters (Rasmussen et al., 2003), which also suggests inputs of nitrogen (and other nutrients) from regional sources on land and from the atmosphere. Therefore, the local nitrogen load from freshwater discharge of bordering countries into the Kattegat area, which has varied between 50 and 150 kt/a in the period from 1989 to 2002 (Carstensen et al., 2006), to a large extent determines the isotope signature of nitrogen in sediment in the Kattegat.

3. Materials and methods

3.1. Surface sediments

Analyses of elemental composition and $\delta^{15}\text{N}$ were done on 214 surface sediment samples (0–1 cm) collected by grab sampling on various expeditions performed by various institutions between 1986 and 2003. All samples had been dried prior to storage. To exclude artefacts of sample storage, we checked that the concentrations of total N had not changed systematically from those measured at the time of sampling. Due to bioturbation in the upper sediment layer, the modern data set smoothes any possible variability over approximately two decades, and thus is comparable to the temporal resolution achieved by dated sediment series. The bulk of the isotope data from the Kattegat has been previously published by Voss et al. (2005).

3.2. Multicores and gravity cores

The five multicores (MUCs) and gravity cores (GCs) were collected on expedition *R/V Alkor-159* (2000) (Fig. 1; see also Table 1 for core positions). MUCs were extruded on board and sliced in 1 cm intervals, gravity cores were sampled in the laboratory with sawn-off syringes pushed into the core faces. Both types of sediment samples were frozen, freeze-dried and homogenized for subsequent measurements.

3.3. Chemical and isotopic analyses of sediment samples

Aluminum concentrations were determined after acid digestion of sample splits and determination of Al with an ICP-OES instrument at IOW (Emeis et al., 1998). For organic carbon analysis the <63 μm sediment fraction was weighed into silver cups, acidified with HCl to remove carbonate, dried at 60 °C over night and pressed into pellets. For total nitrogen and N-isotope analysis, tin cups were used, and no acidification was necessary. The sand-free size fraction was chosen

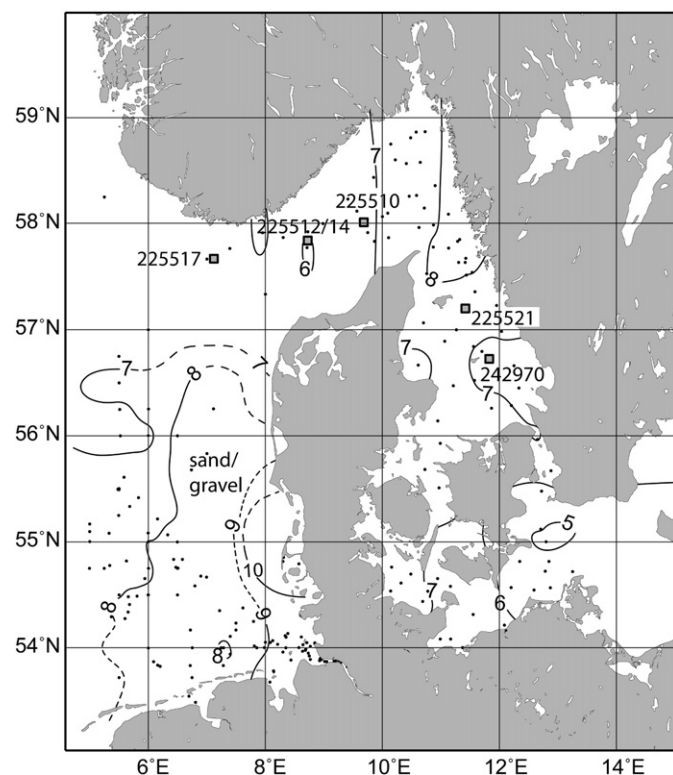


Fig. 1. Map of $\delta^{15}\text{N}$ in surface sediments of the North Sea–Baltic Sea area and core locations. Surface sediment data east of 10°E have been previously published by Voss et al. (2005).

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