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A nitrogen source in spring in the surface mixed-layer of the Baltic Sea: Evidence from total nitrogen and total phosphorus data

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ABSTRACT

The combined mass balance for total nitrogen (TN: concentrations of organic + inorganic nitrogen compounds) and total phosphorus (TP: concentrations of organic + inorganic phosphorus compounds) at 12 stations in the Baltic Sea for the period 1995–2013 clearly indicated the existence of a significant nitrogen source in the surface mixed layer in May of up to 86 mmol m^{-2} $month^{-1}$ at the Baltic Proper stations. The analysis is based on monthly changes in TN with reference to the concentrations in April, and taking into account the atmospheric deposition of inorganic nitrogen compounds and the sedimentation of particulate organic nitrogen. The nitrogen source is closely linked to the consumption of excess phosphate and thus to the production of organic matter in the surface mixed-layer. Processes such as early nitrogen fixation and nitrogen transport by migrating plankton organisms are discussed as possible causes for the nitrogen input into the surface mixed layer in May. The long-term mean of the nitrogen source amounted to 55 mmol m^{-2} in the Baltic Proper corresponding to a regional nitrogen input of 83 kt. We also obtained data for the mid-summer nitrogen fixation of 141 mmol m^{-2} which corresponds to an input of 202 kt.

1. Introduction

As the availability of nitrogen often limits biological production in the world ocean it is aimed to determine the marine nitrogen budget on global and regional scales (see reviews by Gruber and Galloway, 2008; Voss et al., 2013; Zehr and Kudela, 2011). Marine nitrogen fixation makes globally a substantial contribution to the nitrogen budget and is the only source of new nitrogen in the ocean, while the microbial pathways denitrification and anammox lead to a net loss of fixed nitrogen (Codispoti, 2007; Gruber and Sarmiento, 1997; Voss et al., 2013).

Our study area is the Baltic Sea which is a shallow brackish, semi-enclosed sea where intermittent salt water inflows from the North Sea mix with river runoff and precipitation. The riverine input of dissolved inorganic nitrogen, DIN, is a major nitrogen source of the Baltic Sea (annual DIN load: 569 kt yr^{-1}) and is particularly large along the southern and southeastern coastlines (Rahm and Danielsson, 2007). The other two important nitrogen sources are atmospheric deposition, estimated at between 230 kt yr^{-1} in 1995 and 199 kt yr^{-1} in 2006 (Bartnicki et al., 2011), and the well and unambiguously documented mid-summer N_2-fixation of 434 kt yr^{-1} (Wasmund et al., 2005). The importance of the mid-summer N_2-fixation has been demonstrated by many field investigations (e.g. Kahru et al., 2007; Larsson et al., 2001; Rolff et al., 2007; Stal et al., 2003; Wasmund et al., 2001). The heterocystous and aggregate-forming cyanobacteria, namely *Aphanizomenon flos-aquae*, *Nodularia spumigena* and *Anabaena* spp., are the important nitrogen fixers of the Baltic summer phytoplankton blooms. But also diazotrophic pico- and nanocyanobacteria contribute significantly to the N_2-fixation (Wasmund et al., 2001). Nitrogen fixation rates in spring are typically very low in the Baltic Sea. Wasmund et al. (2005) report rates in May between 0.055 and 0.260 mmol m^{-2} d^{-1} in contrast to mid-summer rates of up to 3.69 mmol m^{-2} d^{-1}. Bentzon-Tilia et al. (2014) are the first that measured substantial N_2-fixation of up to 83 nmol l^{-1} day^{-1} in the surface water (=1.2 mmol m^{-2} d^{-1}, assuming a surface mixed layer depth of 15 m) in two temperate estuaries of the Baltic Sea in winter time at temperatures as low as 2.5 °C. They describe a diverse diazotrophic community of heterotrophic, photoheterotrophic and heterocystous cyanobacteria. However, biogeochemical models of the Baltic Sea typically implemented a strong temperature dependence of N_2-fixation and that the activity becomes virtually zero below 12 °C (Eilola et al., 2009; Neumann, 2000; Savchuk, 2002).

Investigations of the Baltic nitrogen budget were also performed on the basis of high-resolution CO_2 partial pressure, pCO_2, measurements on a cargo ship which were used to determine the net community production and based on the C/N ratio of the particulate organic matter, POM, to quantify the nitrogen fixation (Schneider et al., 2009, 2014). In addition to the drawdown of pCO_2 and of the related total CO_2, C_T, during the cyanobacteria bloom in mid-summer, it was found that the decrease of C_T during the spring bloom in the central Baltic Sea continued after the complete exhaustion of nitrate by mid-April (Omstedt et al., 2014) in the upper 50–60 m (Wasmund et al., 2005). As this

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went along with the consumption of excess phosphate that still existed after the nitrate depletion, it was interpreted as a continuation of the net biomass production during the post-spring bloom period in April/May. A mass balance for total nitrogen (TN: DIN + particulate and dissolved organic nitrogen concentrations) that was based on data from the Swedish monitoring station BY15 in the eastern Gotland Sea (Fig. 1) indicated an external TN source already by the end of April and in May. Since production of POM requires nitrogen and since the atmospheric deposition of DIN is by far too low to cover the nitrogen demand of the post-nitrate bloom, it was concluded that a nitrogen source must exist in this period. The source itself, however, could not be identified based on the data. Several possible nitrogen sources were discussed by Schneider et al. (2009). Among these are the use of organic nitrogen for production, the transfer of nitrogen from the existing POM pool and finally N_2-fixation that was termed "cold fixation" because the post-nitrate bloom started for some years already by mid-April when temperatures can be as low as 2–3 °C. Kuznetsov et al. (2011) implemented in a one-dimensional model for the central Gotland Sea two diazotrophic groups, one of them is not limited by temperature but is strongly phosphate-limited and is able to fix nitrogen during April/May. With this approach they could improve the model's ability to reproduce sea-surface phosphate and pCO_2 dynamics in spring. Also Kreus et al. (2014) performed one-dimensional model experiments for the Gotland Sea to explain the observed drawdown in DIP and pCO_2 levels after the spring-bloom. They conclude that this pattern does not require N_2-fixation but can be sufficiently achieved when considering variable cellular C:N:P stoichiometry of phytoplankton and a temporal decoupling between nutrient uptake and phytoplankton growth. However, the contribution of this process seems to be overestimated as the simulated surface water POC:PON ratios by Kreus et al. (2014) are as high as 15 in spring and thus much higher than the measured values of 8 to 9 in spring 2001 by Schneider et al. (2003).

With this study we are refining the previous analysis of the total nitrogen budget that was confined to the central station in the Gotland Sea (Omstedt et al., 2014; Schneider et al., 2009). In order to scrutinize the existence of a nitrogen source in May after the nitrate fuelled spring bloom, total nitrogen and total phosphorus concentration data available through the Swedish National Monitoring Programme (SMHI) were statistically evaluated. The analysis comprises 19 year time series data (1995–2013) from 12 stations in the Baltic Proper and the Bothnian Sea.

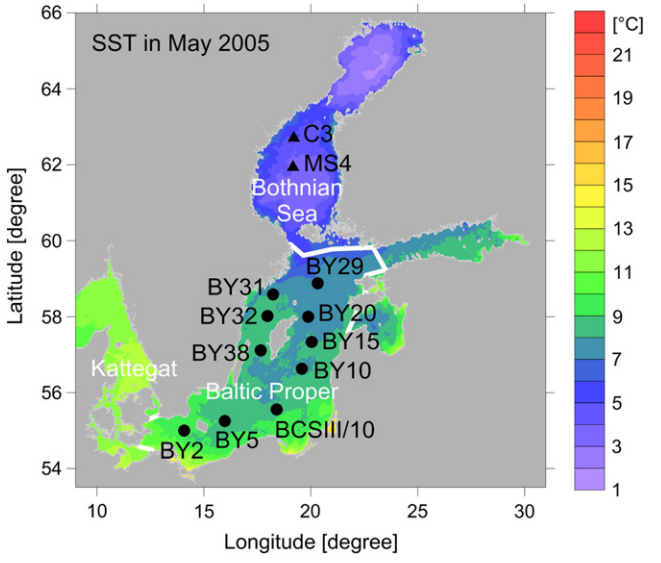

Fig. 1. Stations of the Swedish National Monitoring Programme (SMHI) considered for the evaluation of total nitrogen and total phosphorus concentrations. The sea surface temperature distribution in May 2005 is based on Advanced Very High Resolution Radiometer (AVHRR) satellite data.

2. Methods

2.1. The data base

A large number of stations are visited monthly within the Swedish National Monitoring Programme (SMHI) for the determination of a comprehensive set of biogeochemical variables including total phosphorus concentration, TP, and total nitrogen concentration, TN. For our study we used a 19 year time series data (1995–2013) of 12 open sea stations located in the Baltic Proper and the Bothnian Sea (Fig. 1). Shallow coastal stations (<50 m) were not considered because they are directly affected by exchange processes at the sediment surface which are difficult to quantify in a mass balance. Samples were taken at depth intervals of 5 m between the surface and 20 m and at intervals of 10 m between 20 m and the halocline.

For the determination of TN and TP, unfiltered samples were digested with an oxidation reagent consisting of an alkaline solution of peroxodisulfate and boric acid. Through this the organic matter is oxidized and organic nitrogen and phosphorus are released as nitrate and phosphate, respectively, which together with the initial nitrate and phosphate concentrations are analyzed by the classical photometric methods (Grasshoff et al., 1999). The relative error of the analytical results amounts to 4% and 2% for TN and TP, respectively, at concentration levels encountered in the Baltic Sea (Valderrama, 1981).

2.2. The mass balance approach

A mass balance for total nitrogen was used to detect and quantify the nitrogen source on the basis of C_T and PO_4^{3-} depletion occurring after the nitrate concentrations have approached zero in early spring. The mass balance is based on the assumption that any changes in the surface water TN can only be caused by sedimentation of POM and by atmospheric deposition of DIN (Larsson et al., 2001; Rolff et al., 2007). This implies that the surface water TN is not significantly affected by either lateral or vertical transport. This assumption is justified since a thermal surface layer develops with the onset of the spring bloom and is continuously flattening from about 30 m in April to about 15 m in midsummer (Lass and Matthäus, 2008). Any potential effects of vertical and lateral transports on the TN budget will be addressed in the context of an uncertainty analysis of the budget calculations.

The observed accumulated change in a specific month, ΔTN, with respect to the TN concentration in an appropriate reference month is then given by:

$$\Delta TN = \Delta TN^{atm} - \Delta TN^{sed} + \Delta TN^{us} \quad (1)$$

with:

ΔTN^{atm} accumulated DIN input by atmospheric deposition since the reference month as mmol m^{-3};
ΔTN^{sed} accumulated change in TN concentration caused by sedimentation since the reference month as mmol m^{-3};
ΔTN^{us} accumulated change in TN concentration caused by an unknown sink/source since the reference month as mmol m^{-3};

and:

$$\Delta TN^{atm} = F_{DIN}^{atm} \cdot n / z_{mix} \quad (2)$$

with:

z_{mix} mixed layer depth;
F_{DIN}^{atm} atmospheric deposition flux of DIN as mmol m^{-2} $month^{-1}$;
n months since the reference month.

For the atmospheric DIN deposition we used a uniform value of 3 mmol m^{-2} $month^{-1}$ (Bartnicki et al., 2011). Since the mixing depth