Model study on horizontal variability of nutrient N/P ratio in the Baltic Sea and its impacts on primary production, nitrogen fixation and nutrient limitation

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Received: 12 January 2012 – Accepted: 17 January 2012 – Published: 31 January 2012
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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

The analysis of measured nutrient concentrations suggests that the ratio of dissolved inorganic nitrogen (DIN) alteration before and after spring blooms relative to the alteration of dissolved inorganic phosphorus (DIP) remains quite constant over the years (2000 ~ 2009). This ratio differs from the Redfield ratio and varies from 6.6 : 1 to 41.5 : 1 across basins within the Baltic Sea. If the found N/P ratios are indicators of phytoplankton stoichiometry, this would affect nutrient cycles in ecosystem models. We therefore tested the effects of using horizontally variable N/P ratio instead of fixed ratio (N/P = 10 : 1 or 16 : 1) on phytoplankton uptake and remineralization in a 3-D physical-biogeochemical coupled model ERGOM. The model results using the variable N/P ratio show systematical improvements in model performance in comparison with the fixed ratios. In addition, variable N/P ratios greatly affected the model estimated primary production, nitrogen fixation and nutrient limitation, which highlights the importance of using an accurate N/P ratio.

1 Introduction

The average phytoplankton stoichiometry is one of important features of ecosystems, which determines multiple nutrient cycles (Redfield, 1934 and 1958; Falkowski, 2000; Klausmeier et al., 2004a,b, 2007; Weber and Deutsch, 2010). Redfield (1934) noted the averaged nitrogen to phosphorus ratio in plankton is consistent with deep oceanic water. This averaged ratio has long been acknowledged as the “Redfield ratio” for phytoplankton in the world's oceans. However, laboratory studies suggest that phytoplankton are flexible in their overall stoichiometry, often matching their nutrient supply at low growth rates (Klausmeier et al., 2004a,b). Moreover, this classic elemental ratio has also long been argued against in regional oceans, and recently even been challenged for large areas in the Southern Ocean (Weber and Deutsch, 2010). In fact, any fixed elemental ratio, Redfield or otherwise, is an oversimplification when applied to
real ecosystems. Many studies have shown that the phytoplankton stoichiometry can differ among species and life stages (Minster and Boulahdid, 1987; Arrigo et al., 1999; Kress and Herut, 2001; Wong et al., 2002; Anderson and Pondaven, 2003). Moreover, Klausmeier et al. (2004b) hypothesizes that phytoplankton stoichiometry is in principle a dynamical trade-off according to ecological conditions between uptake machinery and assembly machinery. Each type of machinery has its own N/P ratio.

In the Baltic Sea, both modeling studies (Neumann, 2000; Edelvang et al., 2005; Neumann and Schernewski, 2008; Savchuk et al., 2008; Eilola et al., 2009; Maar et al., 2011; Meier et al., 2011) and observation-based studies (Osterroht and Thomas, 2000; Savchuk, 2005) often assume that the average phytoplankton stoichiometry is consistent with Redfield ratios. Only a few studies have considered Non-Redfield ratios (Shaffer, 1987; Larsson et al., 2001; Kuznetsov et al., 2008). In our previous study (Wan et al., 2011), we documented that the N/P ratio of nutrient alterations before and after spring blooms could be a good indicator to the N/P ratio of phytoplankton stoichiometry in the Baltic proper. In addition, we demonstrated that Redfield N/P ratio tends to be too high for the entire Baltic Sea and that another fixed ratio 10 : 1 is more appropriate for most areas.

In the present study, we test with a hypothesis that in each Baltic basin, the long term mean N/P ratio of nutrient alterations before and after spring blooms can be an indicator for the N/P ratio of phytoplankton stoichiometry. A horizontally interpolated 2-D distribution of N/P ratio based on observed data from nine monitoring stations in different basins is implemented in a 3-D physical-biogeochemical coupled model to test this hypothesis. As the primary production, nitrogen fixation and nutrient limitation is principally related to phytoplankton stoichiometry, this study also examines the difference between estimates based on a fixed N/P ratio versus the horizontally variable N/P ratio.
2 Data and methods

This study is an extension of the previous work of our group. For detailed description on models, see Wan et al. (2011). The following provides brief description on data and models and focuses on different scenarios’ comparison.

2.1 Data

The climatology of temperature and salinity configuring the initial and lateral boundary conditions for the physical model are from the World Ocean Atlas 2001 (WOA01, Conkright et al., 2002). The products by the operational weather model High Resolution Limited Area Model of the Danish Meteorological Institute (DMI) are used to provide atmospheric drivers for the physical model (She et al., 2007a, 2007b). The daily river runoff and bioloadings are from an operational hydrological model HBV run by the Swedish Meteorological Hydrological Institute (SMHI) (Bergström, 1976, 1992) in combination with observations from the German Bundesamt für Seeschifffahrt und Hydrographie (BSH) and climatology. The initial fields of biogeochemical model use the observed data downloaded from the website of the International Council for the Exploration of the Sea (ICES) (http://www.ices.dk/indexfla.asp) in combination with climatologies of WOA01.

2.2 Physical model

The physical model in this study is the HIROMB model, which was originally developed by BSH (Dick et al., 2001) and further developed and maintained in DMI (https://hbmsvn.dmi.dk/). HIROMB is based on the primitive geophysical fluid dynamics equations for the conservations of volume, momentum, salinity, and heat. The thermodynamic model component can resolve the reflection and absorption of shortwave radiation by the sebed in shallow water zones. The impacts from wind, atmospheric pressure, air temperature, humidity, evaporation-precipitation, and cloud cover are all
Computer model grids cover 48°33′ N to 65°51′ N and 4°05′ W to 30°15′ E with a spatial resolution of 6′ latitude and 10′ longitude, while a nested fine grid with one sixth of the coarse resolution covers the Danish Strait in order to resolve the water exchange through the narrow sills between the North Sea and the Baltic Sea. The coarse grid has 50 vertical layers and the fine grid has 52 vertical layers. The model domain includes both the Baltic Sea and the North Sea in order to provide a sufficient transition to counteract the effects from open boundaries, but the focused area is only the Baltic Sea (Fig. 1).

2.3 Biogeochemical model

The biogeochemical model is ERGOM which was developed by Neumann (2000). It has 9 state variables, including dissolved inorganic nutrients: ammonium, nitrate and phosphate; three autotrophic functional groups: diatoms, flagellates and cyanobacteria; a bulk zooplankton community; a detritus pool; and dissolved oxygen (DO). The model mathematically describes the processes of photosynthesis, nutrient uptake, growth, grazing, digestion, respiration, excretion, mortality, remineralization, nitrogen fixation, nitrification, and denitrification. This model is nitrogen-based, and phosphorus was originally coupled to nitrogen via the Redfield ratio, but the N/P ratio is variable in this study. The parameters are same as Wan et al. (2011), which are based on Neumann et al. (2002) with only a few adjusted values.

2.4 Simulation scenarios

Four simulation scenarios are implemented (Table 1) where each scenario uses identical N/P ratios for nutrient uptake and remineralization. Two scenarios use the horizontally variable N/P ratios, and the other two use fixed N/P ratios. In the first scenario considered and parameterized as surface boundary conditions. The tidal water level, the surge water level and the monthly climatology of temperature and salinity are imposed as the outer lateral conditions, and the river runoffs as the inner lateral condition.

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(V1), the N/P ratio is assumed consistent with the mean observed ratio in 2000–2009. The mean observed ratio is calculated as the mean value of surface DIN concentration alteration before and after spring blooms relative to that of DIP (Fig. 2 and Table 2). 1 February is selected as a typical winter day before spring blooms, and 1 June as a typical summer day after spring blooms. The values on 1 February and 1 June are interpolated from the monthly observed data for each year. As Scenario V1, the distribution of N/P ratio is interpolated with the ratios of seasonal deviations based on data from the well observed nine stations (Fig. 3a and Table 2). As Scenario V2, the N/P ratio distribution is interpolated with observed values from only six stations and the adjusted values: 16 : 1, 18 : 1 and 20 : 1 for Stations A, G and H, respectively (Fig. 3b). Scenario NP10 uses a fixed N/P ratio of 10 : 1 according to Wan et al. (2011) and Scenario NP16 uses the fixed Redfield N/P ratio of 16 : 1.

2.5 Efficiency of nutrient limitation

Nitrogen and phosphorus were reported as alternative limiting nutrients in the Baltic Sea (Granéli et al., 1990; Kivi et al., 1993; Zweifel et al., 1993; Danielsson et al., 2008). We define Efficiency of Nutrient Limitation (ENL) as the ratio between the duration of one nutrient limiting and the total photosynthesis duration. The limiting nutrient is determined when whose value of limitation function is the smallest among all limiting nutrients. The limitation function is a modified Michaelis-Menten formula with squared terms (Neumann et al., 2002),

$$Y(\alpha, x) = \frac{x^2}{\alpha^2 + x^2},$$

where $\alpha$ is Michaelis-Menten constant for specific algae species and $x$ is either DIN or DIP concentration. As there are three autotrophic groups, the functional group with the biggest growth rate is selected to compare the values of limitation functions. The ratio of thickness between the layer where nitrogen (phosphorus) is limiting and the entire photosynthesis-active layer is calculated as the average nutrient limitation for nitrogen
(phosphorus) for one water column. The average nutrient limitation is considered as a two-dimensional distribution with temporal variation. We consider a water column is either nitrogen limiting or phosphorus limiting, no other nutrients are considered in this study. ENL is normalized with the preliminary “ENL” for nitrogen and phosphorus. The ENL is in default for nitrogen, whose value ranges between 0 and 1. The normalized “ENL” for phosphorus equals 1-ENL.

3 Results

3.1 Model validation

As the same model was validated robust in resolving the seasonal variability in surface and the vertical profile by Wan et al. (2011), in the present study we are to validate if the model results using horizontally variable N/P ratio (Scenario V2) are better than the model results using an optimal fixed N/P ratio (Scenario NP10) based on the consistency between the simulated results and the observation data. Three aspects of model performance are examined.

3.1.1 Improvements of seasonal variability in surface waters in different basins

Nine stations J-R (Fig. 1) are selected to examine the model performance of seasonal variability of nutrients and chlorophyll-a in surface layer. The model results for chlorophyll-a are improved at stations in the Baltic proper (Fig. 4b–e), when comparing Scenario V2 to Scenario NP10. The summer bloom peaks are no longer higher than the spring bloom peaks. This is closer to observations. Chlorophyll-a in Scenario V2 is in general slightly higher than in Scenario NP10 for stations outside of the Baltic proper (Fig. 4a,g,h,i). The winter DIN concentrations in Scenario V2 are stable, no increasing trend like in scenario NP10 (Fig. 5b–e). The summer DIN surplus in Scenario NP10 is inconsistent with observations in Skagerrak and Gulf of Finland, but the results from
Scenario V2 are improved and do not show such inconsistency (Fig. 5a,i). In scenario NP10, one part of DIP consumption during spring blooms and another part during late summer blooms are inconsistent with observations, but in Scenario V2, the DIP consumption tends to be continuous for the stations in the Baltic proper, more consistent with the observations (Fig. 6b–e). There are some DIP surplus in summer in Skagerrak, Bothnian Sea and Gulf of Finland in Scenario V2, and observations also show occasional DIP surplus in summer (Fig. 6a,g,i), but the model DIP surplus in summer is larger than the observed one.

3.1.2 Improvements in temporal variation and vertical distributions

The results applying the comprehensive comparison scheme (Wan et al., 2011) show the overall effects of Scenario V2 versus NP10 (Fig. 7). Note that the values in Fig. 7 are the means over the observed grid points in a preset mesh for statistic purpose instead. If observations are roughly evenly located, the values in Fig. 7 can approach to physical means. It is a feature of the comprehensive comparison scheme, aiming to reflect the seasonal pattern and the vertical profile of model biases. The observed seasonal variability in Chlorophyll-a is closer to that in Scenario V2 than in Scenario NP10 (Fig. 7a). The improvement is reflected as a correction to the excessive summer peak height. The model DIN is closer to the observation in Scenario V2 than in Scenario NP10 (Fig. 7b). The model DIN in Scenario NP10 intends to increase over time. The model DIP is also closer to the observation in Scenario V2 than in Scenario NP10 (Fig. 7c). The vertical profile of model results has improvements in general for Chlorophyll-a, DIN and DIP in Scenario V2 in contrast to Scenario NP10 (Fig. 7d–f). The improvements happen in upper 20 m for Chlorophyll-a, below 40 m for DIN and below 80 m for DIP. Even though the improvements are not very large, the improving pattern is systematic.
3.1.3 Improvements in statistics

The statistic results clearly show the model performs better in Scenario V2 than in Scenario NP10 (Table 3). If we define the bias as the difference between the model results and the observed data, the percentage biases decrease from scenario NP10 to V2: 32% to 28% for Chlorophyll-a, 20% to 11% for DIN, and −10% to −6% for DIP. The correlation coefficients increase from 0.50 to 0.52 for DIN and from 0.89 to 0.91 for DIP, but no change for Chlorophyll-a. The standard deviation of model DIP for scenario V2 larger than that for NP10, i.e., the model DIP for scenario V2 is closer to the observed data, but no changes for Chlorophyll-a and DIN. Although the improvements in statistics are not very large, but the signal is clear that a horizontally variable N/P ratio is better an optimized fixed N/P ratio (Wan et al., 2011).

3.2 Primary production

The seasonal mean of primary production in Scenario V2 mostly ranges from \(20 \text{ g C m}^{-2} \text{ yr}^{-1}\) to \(140 \text{ g C m}^{-2} \text{ yr}^{-1}\) (Fig. 8a). The extreme values can be up to \(200 \text{ g C m}^{-2} \text{ yr}^{-1}\) in some coastal areas and estuaries. The general pattern of primary production is higher in the south than in the north, in coastal regions than in offshore regions, in estuaries than outside of estuaries. The total model primary production for the entire Baltic Sea varies seasonally, from \(10 \text{ kton C day}^{-1}\) to \(200 \text{ kton C day}^{-1}\) (Fig. 8d). The seasonal pattern is featured with the spring peak and the summer peak. The spring peak value around \(200 \text{ kton C day}^{-1}\) is much higher than the summer peak value around \(110 \text{ kton C day}^{-1}\).

In contrast to Scenario V2, the excessive primary production in Scenario NP10 increases from \(60^\circ \text{N}\) northward up to \(10 \text{ g C m}^{-2} \text{ yr}^{-1}\) at the south end of the Bothnian Bay and further up to \(30 \text{ g C m}^{-2} \text{ yr}^{-1}\) at the northern tip of the Bothnian Bay (Fig. 8b). It also increases eastward up to around \(30 \text{ g C m}^{-2} \text{ yr}^{-1}\) in the Gulf of Finland. The primary production in Scenario NP10 is mostly \(10 \sim 20 \text{ g C m}^{-2} \text{ yr}^{-1}\) higher than in the Scenario V2 in the transition zone between the Baltic Sea and the North Sea. It
is only \(0 \sim 10 \text{ g C m}^{-2} \text{ yr}^{-1}\) lower in Scenario NP10 than in Scenario V2 in the Baltic proper. The primary production in Scenario NP16 is mostly \(0 \sim 20 \text{ g C m}^{-2} \text{ yr}^{-1}\) lower than Scenario V2, but can be up to \(40 \sim 50 \text{ g C m}^{-2} \text{ yr}^{-1}\) lower in the Swedish coast of the Gotland Sea, the Gulf of Riga and other eastern coast of the Gotland Sea (Fig. 8c). The primary production in Scenario NP16 is seldom higher than in Scenario V2, only \(0 \sim 10 \text{ g C m}^{-2} \text{ yr}^{-1}\) higher in the Russian part of Gulf of Finland and \(10 \sim 20 \text{ g C m}^{-2} \text{ yr}^{-1}\) higher west of \(10^\circ\) E.

The seasonal pattern of mean primary production averaged over the entire domain in Scenario NP10 is quite similar to Scenario V2, only around \(20 \text{ g C m}^{-2} \text{ yr}^{-1}\) higher during summer blooms in Scenario NP10 than in Scenario V2 (Fig. 8d). The mean primary production in Scenario NP16 is \(10 \sim 60 \text{ g C m}^{-2} \text{ yr}^{-1}\) smaller than in Scenario V2 during spring blooms and in early summer, but around \(20 \text{ g C m}^{-2} \text{ yr}^{-1}\) higher during late summer blooms.

### 3.3 Nitrogen fixation

In 2007 \sim 2008, the nitrogen fixation in Scenario V2 occurs mainly in the southern Baltic Sea and at the entrance of the Gulf of Finland (Fig. 9a). The nitrogen fixation in Scenario V2 is mostly less than \(40 \text{ mmol N m}^{-2} \text{ yr}^{-1}\), and the integrated nitrogen fixation is no more than \(1.0 \text{ kton N day}^{-1}\) (Fig. 9d). The nitrogen fixation in Scenario NP10 occurs in the whole Southern Baltic Sea and most of the Baltic proper, and it is mostly higher than \(40 \text{ mmol N m}^{-2} \text{ yr}^{-1}\) in the Southern Baltic Sea (Fig. 9b). The nitrogen fixation in Scenario NP16 occurs in the whole southern Baltic Sea, the Baltic proper, most of the Gulf of Finland and the eastern Bothnian Sea (Fig. 9c). Its horizontal distribution tends increasing southeastwards and southwards. The highest nitrogen fixation appears in the southern coast of the Baltic Proper, up to \(200 \text{ mmol N m}^{-2} \text{ yr}^{-1}\). The total nitrogen fixation is several times higher in Scenarios NP16 and NP10 than in Scenario V2 (Fig. 9d).
3.4 Nutrient limitation

The model results show that the primary production in the Baltic Sea is mostly N-limited (ENL > 0.5, ENL is defined in Sect. 2.5), but the extent of limitation varies horizontally and differs across scenarios. In Scenario V2, it is heavily N-limited (mostly ENL > 0.8) in the Gotland Sea and in the Skagerrak and the Kattegat (Fig. 10a). The P-limited (ENL < 0.5) area is quite limited, the severe P-limited (ENL < 0.2) appears in the western Bothnian Sea and in the Gulf of Riga, other slight P-limited (0.3 < ENL < 0.5) areas include the southern coast of the Baltic proper, the eastern tip of the Gulf of Finland and the northern tip of the Bothnian Bay. In Scenario NP10, the Baltic proper, the Southern Baltic Sea, the entrance of the Gulf of Finland and the entrance of the Gulf of Riga are all N-limited (ENL > 0.7), but the Bothnian Sea, the Bothnian Bay, the Skagerrak and the Russian part of Gulf of Finland are P-limited (ENL < 0.1) (Fig. 10b). In Scenario NP16, the Baltic Sea is N-limited in general, only a few of coastal regions are P-limited (Fig. 10c). The Skagerrak, the Kattegat and the connection between the Bothnian Sea and the Bothnian Bay are heavily N-limited (ENL > 0.9). The Baltic proper is media N-limited (0.7 < ENL < 0.8), and the southern Baltic Sea is weak N-limited (0.5 < ENL < 0.7). As the entire Baltic Sea is concerned, the nutrient condition for the primary production seasons (except for during the cyanobacteria blooms) is slightly, medially and heavily N-limited in Scenario NP10, V2 and NP16, respectively (Fig. 10d). In June–September, ENL is generally low, as it is the season of likely cyanobacteria blooms, which can only be P-limited.

4 Discussion

4.1 Horizontal variability of N/P ratio

The horizontal variability of N/P ratio (Fig. 3b) is featured with a minimum around 7 : 1 in the Gotland Sea and no more than 9 : 1 in the Baltic proper, and with a northwards
increasing trend up to 18:1 in the Bothnian Sea and the Bothnian Bay and an eastwards increasing trend up to 22:1 in the Gulf of Finland. This pattern is synthesized through comparing model results among Scenarios V1, NP10, NP16. The relatively low N/P ratio in the Baltic proper is well supported by the better consistency between observations and model results of Scenario V2 than that of Scenario NP10. The out-performance of Scenario V2 over Scenario V1 (see Fig. 3a,b for N/P ratios) is very clear in the Bothnian Sea, the Bothnian Bay and the Gulf of Finland for the resultant DIP (Fig. 11d–h). DIP shows excessively surplus at the stations in those areas in Scenario V1. The adjustment in Scenario V2 relative to Scenario V1 significantly improves the consumption of DIP, but not much changes for DIN and chlorophyll-a, because the adjustment from Scenario V1 to V2 does not change the property of nutrient limitation in those areas. Therefore, the hypothesis that the long term (years 2000–2009) mean ratio of seasonal deviation of DIN relative to that of DIP indicates the stoichiometry N/P ratio is generally valid for offshore stations, except three estuarine stations A, H and I.

Wan et al. (2011) suggested that the N/P ratio in the Baltic proper is smaller than 10:1. Wan et al. (2011) reached this according to not only comparing simulation scenarios but also estimating the biological nutrient removal with observed data. We notice that there are several arguments on the N/P ratio in the Baltic proper. Osterroht and Thomas (2000) noticed that the N/P ratio of nutrient alteration before and after the growing season was much different from the Redfield ratio, however they explained the elemental ratio of nutrient uptake in the Baltic proper were consistent with the Redfield ratio, but the nutrients remineralized from freshly produced organic material had a non-Redfield ratio. Once the concept of the N/P ratio of nutrient uptake is extended to the N/P ratio of net biological removal of nutrients, it could also be alternatively explained that the elemental ratio of nutrient uptake were inconsistent with the Redfield ratio. Shaffer (1987) suggested the nutrient N/P ratio was smaller than the Redfield ratio based on sediment measurements. According to measurements, Larsson et al. (2001) concluded that the N/P ratio of elemental composition of oceanic seston is only slightly smaller than the Redfield ratio before June but much larger than the Redfield ratio later.
on until the winter recovery. We think that the N/P ratio of elemental composition of oceanic seston probably differs much from the N/P ratio nutrient uptake. Otherwise, the conclusion of Larsson et al. (2001) conflicts with two facts: that the N/P ratio of nutrient alteration before and after spring blooms is much smaller than the Redfield ratio 16 : 1 in the Baltic proper (Table 2), and that no much DIP declination is observed after mid-June. As to the N/P ratio of nutrient uptake outside of the Baltic proper, there are few relevant investigations to compare to.

4.2 Ecological impacts of horizontally variable N/P ratio

Although the horizontal variability of N/P ratio in the Baltic Sea suggested by the implemented scenario simulations needs to be verified with other investigations in the future, those simulations allow us to estimate the likely ecological impacts from using horizontally variable N/P ratio instead of a fixed one. We focus on the likely ecological impacts on primary production, nitrogen fixation and nutrient limitation.

4.2.1 Primary production

The direct measurement of primary production can be made through the classic \(^{14}\text{C}\) method. The measurements by the classic \(^{14}\text{C}\) method are generally dynamic and have only narrow representation. As pointed by Wasmund et al. (2005), data on primary production are actually limited and hard to map the seasonal and the spatial features, although there are some direct measurements (Elmgren, 1984; Wasmund et al., 2001). We compare our model results with the calculated primary production based on relevant measurements (Osterroht and Thomas, 2000; Struck et al., 2004; Wasmund et al., 2005; Savchuk and Wulff, 2007) and the recent model results (Maar et al., 2011).

Wasmund et al. (2005) estimated the net primary production in the eastern Gotland Sea was 6454 mmol C m\(^{-2}\) during the most productive period (28.3.2001~13.7.2001) which they believed were close to the annual net primary production. This value equals
77 g C m\(^{-2}\) yr\(^{-1}\). Struck et al. (2004) calculated the annual new production in the eastern Gotland Sea ranging from 247 to 588 mmol N m\(^{-2}\) yr\(^{-1}\), it equals ranging from 41 to 97 g C m\(^{-2}\) yr\(^{-1}\) if the Redfield ratio and the \(f\)-ratio 0.48 (Wasmund et al., 2005) are applied. Our modeled value in this region varies between 40 to 80 g C m\(^{-2}\) yr\(^{-1}\), which roughly fits the estimates based on measurements. The distribution pattern of primary production (Fig. 8a) is quite similar with Maar et al. (2011). Both Maar's and our model results show a northwards decreasing trend, which is consistent with the estimates of Savchuk and Wulff (2007).

The estimates of primary production depend on N/P ratio of nutrients, and even ratios of nutrients to carbon if the model does not explicitly include a state variable carbon. This recovers the uncertainty involved in primary production estimates from models. Even though the absolute value of model estimates involves uncertainty more or less, model can capture the horizontal distribution pattern and seasonal pattern reasonable well in the present study (Fig. 8a,d). As one of the three usual methods estimating primary production, the “nutrient concept” method uses the phytoplankton stoichiometry (Wasmund et al., 2005). It means some of primary production estimates even based on measurements can also include uncertainty from the selected phytoplankton stoichiometry.

The phytoplankton stoichiometry in the Baltic Sea is traditionally regarded as consistent with Redfield ratios (Neumann, 2000; Edelvang et al., 2005; Neumann and Schernewski, 2008; Savchuk et al., 2008; Eilola et al., 2009; Maar et al., 2011; Meier et al., 2011). If this is not true, the estimates of primary production might be overestimated 20 ~ 40 %, according to the impact of different N/P ratios (Fig. 8a,c).

### 4.2.2 Nitrogen fixation

As methods to measure nitrogen fixation directly are not available yet, there are no precise measurements for nitrogen fixation. We compare our model results with the estimates based relevant measurements (Niemistö et al., 1989; Hübel and Hübel, 1995;
Rahm et al., 2000; Larsson et al., 2001; Rolff et al., 2007) and other model studies (Neumann and Schernewski, 2008; Neumann et al., 2010). We estimate the total annual nitrogen fixation for the Baltic Sea is 41, 111 and 344 kton N yr\(^{-1}\) for Scenarios V2, NP10 and NP16, respectively, according to the model results (Fig. 9d). Niemistö et al. (1989) estimated the nitrogen fixation in early 1980s around 100 kton N yr\(^{-1}\). Hübel and Hübel (1995) estimated the nitrogen fixation for the Baltic proper including the Belt Sea but not the northern Baltic proper ranging 20 ~ 190 kton N yr\(^{-1}\). The estimate by Rahm et al. (2000) was 30 ~ 260 kton N yr\(^{-1}\). The estimate by Larsson et al. (2001) for years 1994 ~ 1998 was 180 ~ 430 kton N yr\(^{-1}\). The estimate by Rolff et al. (2007) reached the highest 1000 kton N yr\(^{-1}\) since ever. The model result by Neumann and Schernewski (2008) showed the nitrogen fixation varying 200 ~ 800 kton N yr\(^{-1}\) for the period 1960 ~ 2000. The result from similar model by Neumann (2010) showed the nitrogen fixation varying 80 ~ 280 kton N yr\(^{-1}\) for the period 1960 ~ 2100, with a value around 160 kton N yr\(^{-1}\) for years 2000s. In brief, our model results are in the right order, but relatively low.

The amount of nitrogen fixation in the Baltic Sea depends on the DIP availability and the N/P ratio of nutrient uptake of cyanobacteria. The DIP available for cyanobacteria mainly depends on the winter DIP level minus the DIP consumption during spring blooms which depends on the N/P ratio of nutrient uptake again. Thus the amount of nitrogen fixation significantly depends on the N/P ratio. The involvement of the N/P ratio can partially explain why the estimates of nitrogen fixation can vary one order of magnitude (Niemistö et al., 1989; Hübel and Hübel, 1995; Rahm et al., 2000; Larsson et al., 2001; Rolff et al., 2007; Neumann and Schernewski, 2008; Neumann et al., 2010).

Our model estimates in Scenarios V2, NP10 and NP16 are 41, 111 and 344 kton N yr\(^{-1}\), respectively. This reflects the significant impact of N/P ratio. We think that the Redfield ratio or even a further bigger N/P ratio for all seasons, which most of other estimates used, tend to overestimate the nitrogen fixation. If the N/P ratio of nitrogen fixation is not smaller than the Redfield ratio, in addition that the ratio of DIN
relative to DIP in river loadings is much larger than the Redfield ratio (Stålnacke et al., 1998), this might conflict with the fact that the ratio of DIN relative to DIP in total nutrient stocks is much smaller than 16 : 1 (Danielsson et al., 2008).

4.2.3 Nutrient limitation

While ocean waters are usually N-limited (Nixon et al, 1996) and freshwaters are P-limited (Schindler, 1974), the Baltic Sea, as an adjacent sea, is relatively complicated. The Baltic Sea was regarded N-limited in the Baltic proper and the Gulf of Finland, but P-limited in the Bothnian Sea and the Bothnian Bay (Granéli et al., 1990; Kivi et al., 1993; Zweifel et al., 1993; Danielsson et al., 2008). The property of nutrient limitation to primary production can vary across basins and seasons, depending on both the nutrient supplies and phytoplankton stoichiometry. Regions P-limited can be switched to N-limited when the N/P ratio is increased. For instance, the Bothnian Bay, the Bothnian Sea, the Skagerrak and the eastern end of the Gulf of Finland are P-limited in Scenario NP10, but turn to be N-limited in Scenario V2 (Fig. 10a,b).

The model result of Scenario V2 shows the Bothnian Bay is N-limited, as the N/P ratio is assumed higher 20 : 1. Zweifel et al. (1993) regarded the Bothnian Bay is P-limited. However, nitrogen was found depleted in summer (Andersson et al., 1996; Humborg et al., 2003). It means the Bothnian Bay can also be N-limited. The model result of Scenario V2 shows also the Bothnian Sea is mostly N-limited. This is consistent with Andersson et al. (1996) and Danielsson et al. (2008).

5 Summary

This investigation starts from a hypothesis that the long term (years 2000 ~ 2009) mean ratio of seasonal deviation of DIN relative to that of DIP indicates the N/P ratio in each basin in the Baltic Sea. A 3-D physical-biogeochemical coupled model is applied to test this hypothesis. The monthly series of observed DIN and DIP from nine stations in
different basins are used to generate the hypothesized N/P ratios and then interpolated for the whole Baltic Sea. The monthly series of observed surface chlorophyll-a, DIN and DIP from another nine stations and other various observations for chlorophyll-a, DIN and DIP are used to verify that the hypothesized horizontally variable N/P ratio distribution is better than an optimal fixed N/P ratio. The hypothesis is verified generally valid for observations from offshore stations, but not for three estuarine stations.

Simulations for Scenarios V2 (with the N/P ratio distribution based on the hypothesized N/P ratio but manipulated for three estuarine stations), NP10 and NP16 (fixed N/P ratios 10:1 and 16:1) are analyzed for primary production, nitrogen fixation and nutrient limitation. Scenarios V2 and NP10 have almost same primary production, and they have $10 \sim 60 \text{ g C m}^{-2} \text{ yr}^{-1}$ higher primary production during spring blooms and in early summer than Scenario NP16 does. Different N/P ratio scenarios can cause significant nitrogen fixation difference, for instance, Scenario V2, NP10 and NP16 estimate nitrogen fixation 41, 111 and 344 kton N yr$^{-1}$, respectively. Different N/P ratio scenarios can also cause significant change for the nutrient limitation property.

Acknowledgement. We would like to thank Per Berg for technical assistance with the HIROMB model code and setups, and to thank the Swedish Meteorological and Hydrological Institute and the Bundesamt für Seeschifffahrt und Hydrographie in Hamburg, Germany for providing the river data. This work was supported by European Commission FP6 projects MYCOEAN (Contract No. 218812) and MEECE (Contract No. DK18159104).

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**Table 1.** Simulation scenarios.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>Horizontally variable N/P ratio with identical values for nutrient uptake and remineralization (Fig. 3a), according to the ratios of seasonal deviations of DIN relative to that of DIP at nine stations (Table 1).</td>
</tr>
<tr>
<td>V2</td>
<td>Similar to V1, but adjusted at three estuary stations (Fig. 3b).</td>
</tr>
<tr>
<td>NP10</td>
<td>N/P ratio 10 : 1</td>
</tr>
<tr>
<td>NP16</td>
<td>N/P ratio 16 : 1</td>
</tr>
</tbody>
</table>
Table 2. N/P ratio of nutrient alterations in surface waters.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude (° N)</th>
<th>Longitude (° E)</th>
<th>DIN&lt;sup&gt;b&lt;/sup&gt; (mmol m⁻³)</th>
<th>DIN&lt;sup&gt;a&lt;/sup&gt; (mmol m⁻³)</th>
<th>DIP&lt;sup&gt;b&lt;/sup&gt; (mmol m⁻³)</th>
<th>DIP&lt;sup&gt;a&lt;/sup&gt; (mmol m⁻³)</th>
<th>∆DIN/∆DIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>58.28</td>
<td>10.51</td>
<td>6.04</td>
<td>0.30</td>
<td>0.50</td>
<td>0.22</td>
<td>20.5 : 1</td>
</tr>
<tr>
<td>B</td>
<td>56.67</td>
<td>12.12</td>
<td>6.23</td>
<td>0.25</td>
<td>0.57</td>
<td>0.07</td>
<td>12.0 : 1</td>
</tr>
<tr>
<td>C</td>
<td>55.00</td>
<td>14.08</td>
<td>3.22</td>
<td>0.20</td>
<td>0.58</td>
<td>0.18</td>
<td>7.6 : 1</td>
</tr>
<tr>
<td>D</td>
<td>55.25</td>
<td>15.98</td>
<td>2.87</td>
<td>0.23</td>
<td>0.57</td>
<td>0.18</td>
<td>6.8 : 1</td>
</tr>
<tr>
<td>E</td>
<td>57.33</td>
<td>20.05</td>
<td>3.40</td>
<td>0.22</td>
<td>0.57</td>
<td>0.09</td>
<td>6.6 : 1</td>
</tr>
<tr>
<td>F</td>
<td>58.88</td>
<td>20.32</td>
<td>4.16</td>
<td>0.20</td>
<td>0.58</td>
<td>0.08</td>
<td>7.9 : 1</td>
</tr>
<tr>
<td>G</td>
<td>60.59</td>
<td>21.09</td>
<td>6.80</td>
<td>1.16</td>
<td>0.65</td>
<td>0.14</td>
<td>11.1 : 1</td>
</tr>
<tr>
<td>H</td>
<td>63.50</td>
<td>19.82</td>
<td>6.35</td>
<td>0.99</td>
<td>0.24</td>
<td>0.04</td>
<td>26.8 : 1</td>
</tr>
<tr>
<td>I</td>
<td>60.40</td>
<td>26.49</td>
<td>17.82</td>
<td>2.46</td>
<td>0.53</td>
<td>0.16</td>
<td>41.5 : 1</td>
</tr>
</tbody>
</table>

<sup>a</sup> represents the long term mean value after spring blooms in 2000 ~ 2009;

<sup>b</sup> represents the long term mean value before spring blooms in 2000 ~ 2009;

∆ represents the value X<sup>b</sup>-X<sup>a</sup>. 
Table 3. Statistic comparison between model results and observed data for the whole Baltic Sea.

<table>
<thead>
<tr>
<th>Statistic measures/ cases</th>
<th>Chl-a (mg m(^{-3})/–)</th>
<th>DIN (mmol m(^{-3})/–)</th>
<th>DIP (mmol m(^{-3})/–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samplers OBS</td>
<td>5074</td>
<td>10529</td>
<td>10870</td>
</tr>
<tr>
<td>Observation case OBS</td>
<td>5074</td>
<td>10529</td>
<td>10870</td>
</tr>
<tr>
<td>Mean value</td>
<td>2.2</td>
<td>2.9</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>5.1</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>0.85</td>
<td>0.84</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>2.7</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>0.80</td>
<td>0.83</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>/</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>0.50</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>0.89</td>
<td>0.91</td>
</tr>
<tr>
<td>Percentage of bias</td>
<td>/</td>
<td>32%</td>
<td>28%</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>20%</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>–10%</td>
<td>–6%</td>
</tr>
</tbody>
</table>

Abbreviations: Chl for chlorophyll, DIN for dissolved inorganic nitrogen, DIP for dissolved inorganic phosphorus, DO for dissolved oxygen, OBS for observations.
Fig. 1. Bathymetry of the Baltic Sea (unit: m) and locations of selected monitoring stations. Data from stations A–I are used for generating the hypothesized N/P ratios (Table 2). Data from stations J–R are used for verifying the hypothesized N/P ratios.
Fig. 2. Surface dissolved inorganic nitrogen (black dashed cycles) and phosphorus (red dashed cycles) from stations A–I (see Fig. 1 for locations). Dissolved inorganic phosphorus is scaled up with the hypothesized N/P ratios (Table 2).
Fig. 3. N/P ratios used for Scenarios V1 (upper panel) and V2 (lower panel). The upper panel shows the N/P ratio distribution interpolated with the hypothesized N/P ratios of nine stations (Table 2). The lower panel shows the N/P ratio distribution manipulated. Unit: mmol m⁻³.
Fig. 4. Comparison between Scenario V2 (red curve) and Scenario NP10 (green curve) for surface chlorophyll-a in contrast with observations (black dashed cycles). Units: mg m\(^{-3}\).
Fig. 5. Comparison between Scenario V2 (red curve) and Scenario NP10 (green curve) for surface dissolved inorganic nitrogen in contrast with observations (black dashed cycles). Units: mmol m$^{-3}$. 
Fig. 6. Comparison between Scenario V2 (red curve) and Scenario NP10 (green curve) for surface dissolved inorganic phosphorus in contrast with observations (black dashed cycles). Units: mmol m$^{-3}$. 
Fig. 7. Comprehensive comparison between Scenario V2 (red curve) and Scenario NP10 (green curve) for in contrast with observations (black dashed cycles). Panels A, B and C show the seasonal pattern of model biases for chlorophyll-\(a\), dissolved inorganic nitrogen and phosphorus, and Panel D, E and F for their vertical profiles, respectively (vertical axes for depth, unit: m).
Fig. 8. Comparison of primary production among Scenarios V2, NP10, NP16. Panel A shows the annual mean primary production of Scenarios V2, Panel B (C) for the deduction of Scenario NP10 (NP16) minus V2. Panel D shows the seasonal patterns of mean primary production integrated horizontally, with black, red and green curves for Scenarios V2, NP10 and NP16, respectively.
Fig. 9. Comparison of nitrogen fixation among Scenarios V2, NP10, NP16. Panels A, B, C show the annual mean nitrogen fixation for Scenarios V2, NP10 and NP16, respectively. Panel D shows the seasonal patterns of mean nitrogen fixation integrated horizontally, with black, red and green curves for Scenarios V2, NP10 and NP16, respectively.
Fig. 10. Comparison of nutrient limitation among Scenarios V2, NP10, NP16. Panels A, B, C show the annual mean nutrient limitation for Scenarios V2, NP10 and NP16, respectively. Panel D shows the seasonal patterns of mean nutrient limitation integrated horizontally, with black, red and green curves for Scenarios V2, NP10 and NP16, respectively.
Fig. 11. Comparison between Scenario V2 (red curve) and Scenario V1 (green curve) for surface dissolved inorganic phosphorus in contrast with observations (black dashed cycles). Units: mmol m$^{-3}$. 