

**N<sub>2</sub>-fixation**

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# The role of N<sub>2</sub>-fixation to simulate the pCO<sub>2</sub> observations from the Baltic Sea

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## Abstract

Measurements in the central Baltic Sea have shown that dissolved inorganic carbon (DIC) concentrations in the upper water column continue to decrease even after complete depletion of dissolved inorganic nitrogen (DIN). To explain this observation, a new external supply of nitrogen is required without a concomitant supply of inorganic carbon. The primary proposed candidate process is N<sub>2</sub>-fixation. In order to address this question in the eastern Gotland Sea, a biogeochemical model containing nine state variables including diatoms, flagellates, and nitrogen fixing cyanobacteria, was coupled to a 1D physical model. The results from the winter period until the onset of the spring bloom of 1997 gave reasonable surface water values for partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) compared with measurements of the *p*CO<sub>2</sub>. However, the model failed to simulate the observed *p*CO<sub>2</sub> drawdown for the period from the end of the spring bloom until late summer. Even after introducing a seasonal dissolved organic carbon (DOC) excess production and varying different process parameterization the simulated *p*CO<sub>2</sub> values did not improve. Only the shift from a sharp to a moderate temperature dependency in addition to an increase in the C:P ratio of the nitrogen fixing cyanobacteria made it possible for the model to match the *p*CO<sub>2</sub> observations. The resulting total nitrogen fixation (167 mmol m<sup>-2</sup> a<sup>-1</sup>) exceeds previous measurement-based estimates but is in good agreement with recent rate measurement based estimates.

## 1. Introduction

It is standard practice to use the concept of constant stoichiometric ratios, i.e. the so called Redfield ratio (Redfield et al., 1963) concept, between carbon (C), nitrogen (N) and phosphorus (P) in fresh organic material, to derive the net carbon balance from photosynthesis and respiration from changes in nutrient concentrations in the euphotic zone (Dugdale and Goering, 1967). However, measurements in various oceanic regions have shown that dissolved inorganic carbon (DIC) concentrations in the upper

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water column continue to decrease even after depletion of dissolved inorganic nitrogen (Sambrotto et al., 1993; Michaels et al., 1994; Gruber et al., 1998; Thomas et al., 1999; Körtzinger et al., 2001). The reasons for this decoupling between carbon and nitrogen are still not completely understood. Possible explanations include the loss of CO<sub>2</sub> by air-sea exchange, high C:N ratio in particulate organic matter (POM), the production of labile and semi-labile dissolved organic matter (DOM) and lateral transport (Sambrotto et al., 1993; Bates et al., 1996; Six and Maier-Reimer, 1996; Gruber and Sarmiento, 1997; Thomas et al., 1999; Kähler and Koeve, 2001; Körtzinger et al., 2001). Previously, N<sub>2</sub>-fixation was considered not to be a candidate process, as its rate were deemed to be to small (Larsson et al., 1985; Sambrotto et al., 1993). More recent studies suggest however that N<sub>2</sub>-fixation has been underestimated as a significant source for bio-usable nitrogen and therefore could play a major role in explaining the drawdown of DIC in the summer (Capone et al., 1997; Karl et al., 1997; Capone, 2001; Zehr et al., 2001). As a result, it has been recognized that incorporating N<sub>2</sub>-fixation into biogeochemical models has become necessary for any model attempting to simulate upper ocean biogeochemical cycles (Bissett et al., 1999; Savchuk and Wulff, 1999; Neumann, 2000; Hood et al., 2001; Capone, 2001; Fennel et al., 2001; Anderson and Pondaven, 2003).

Observations from the eastern Gotland Sea (Schneider et al., 1999, 2003) show a similar summertime drawdown as was first described for Bermuda by Michaels et al. (1994). N<sub>2</sub>-fixation has been proposed as a possible mechanism in this region as well (Schneider et al., 2003), but this attempt is equivocal in how far N<sub>2</sub>-fixation can be held responsible to explain the observed summertime drawdown in CO<sub>2</sub>, since N<sub>2</sub>-fixation rates are not available for the early summer. The purpose of this study here is to investigate how far N<sub>2</sub>-fixation is indeed the likely mechanism to explain these observations. We adopt a modeling approach, where we use an existing ecosystem model coupled to a one-dimensional physical model to highlight the processes driving the upper ocean carbon cycle. DIC and alkalinity were added as additional state variables and the effects of different processes such as CO<sub>2</sub> air-sea exchange and biological production

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on the surface water CO<sub>2</sub> were tested.

## 2. Model description

### 2.1. The physical model

The physical model is a one-dimensional version of the Modular Ocean Model (MOM) 2.2 (Pacanowski et al., 1990). Similar models have been successfully applied to the Baltic Sea (Lehmann, 1995; Fennel and Neumann, 1996). The one-dimensional model gives reasonable temperature values and develops a seasonal thermocline with realistic mixed layer depths. The model has 42 vertical layers with a constant resolution of 6 m corresponding to the deepest point in the eastern Gotland Sea. The Richardson-number model of Pacanowski and Philander (1981) accounts for the vertical mixing. In this paper, the time step for the model simulation is 10 min.

### 2.2. The ecosystem model

The nine-compartment ecosystem model by Neumann (2000) was developed to describe a nitrogen cycle within the Baltic Sea. The model accounts for processes like primary production, respiration, remineralization, sedimentation, resuspension, nitrogen fixation, denitrification, and zooplankton grazing on primary producers. The nutrient state variables are dissolved nitrate, ammonium, as regenerated from nitrate, and phosphate. The primary producers are divided into three functional groups called diatoms, flagellates, and cyanobacteria. The *diatoms* represent large phytoplankton and dominate the spring bloom. Their growth rate is dependent on the availability of nitrate but is independent of temperature. *Flagellates* represent smaller cells. They get an advantage at lower nutrient concentration, i.e. they take up mostly ammonium, and hence account for for the “regenerated” production during summer. The temperature

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dependency of their growth rate ( $TLIM_{FLA}$ ) is expressed as:

$$TLIM_{FLA} = 1 + \frac{T^2}{T_{FLA}^2 + T^2} . \quad (1)$$

Here,  $T_{FLA}$  is a constant temperature set to 10°C, and  $T$  is the actual water temperature (in °C).

*Cyanobacteria* are able to convert elemental nitrogen to ammonium and therefore constitute a source of new nitrogen to the system. This functional group is able to out-compete other phytoplankton groups when nitrate and ammonium concentrations are low, and their limiting nutrient is phosphate. In addition, a negative sinking velocity is attributed to these cells accounting to their ability to accumulate at the sea surface. This parameterization for N<sub>2</sub>-fixation is based on observations in the Baltic Sea (Wasmund, 1997). In order to describe the influence of high water temperature on the growth rate of cyanobacteria ( $TLIM_{CYAN}$ ) a Fermi function is used to suppress growth in water colder than 16°C, i.e. the constant temperature  $T_{CYAN}$  is set to 16°C:

$$TLIM_{CYAN} = \frac{1}{1 + \exp(T_{CYAN} - T)} . \quad (2)$$

Here again,  $T$  is the actual water temperature.

We extended this model including a CO<sub>2</sub> chemistry formulation with DIC as a state variable and alkalinity as a constant, explained later in the text. These variables are needed to calculate the partial pressure of CO<sub>2</sub> ( $pCO_2$ ), which determines the direction and magnitude of the exchange of CO<sub>2</sub> across the air-sea interface. We use the parameterization for the gas transfer velocity  $k$  of Wanninkhof (1992), which gives a square dependency of the wind speed. Since the seasonal amplitude of atmospheric  $pCO_2$  is small compared to the seasonal amplitude of  $pCO_2$  in the Baltic Sea (Kuss et al., 2004), we set the atmospheric CO<sub>2</sub> partial pressure to a constant 364  $\mu$ atm (Thomas and Schneider, 1999). Changes in DIC concentrations in the model layers

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are caused by vertical diffusion of DIC and due to biological processes, i.e. the formation and degradation of particulate organic carbon (POC). This is done by coupling the nitrogen fluxes out of the ecosystem model to corresponding carbon transformations according to constant stoichiometric ratios (Redfield et al., 1963). At the surface, DIC concentrations are also altered by the air-sea gas exchange.

### 2.3. CO<sub>2</sub> chemistry

The partial pressure of CO<sub>2</sub> of the surface water is calculated from DIC, alkalinity, pressure, temperature, and salinity using the equations for carbon chemistry from DOE (1994). The equilibrium constants are calculated by Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). The solubility of CO<sub>2</sub> is taken from Weiss (1974).

Since a 1D-model is applied to answer the question addressed in this paper, the alkalinity is kept constant over the entire model period. This is in contrast to observations which show a considerable temporal and spatial variability of alkalinity in the Eastern Gotland Sea. This is due to different alkalinities in river water which mix at varying proportions with Baltic Proper water in the eastern Gotland Sea and thus lead to varying and complex alkalinity/salinity relationships (Ohlson, 1998; Thomas and Schneider, 1999). However, the effect of DIC changes on the  $p\text{CO}_2$  is almost independent of the alkalinity at the alkalinity range encountered in the Gotland Sea. Hence, it is justified to use the  $p\text{CO}_2$  measured at different background alkalinities to validate the DIC changes simulated by our model at a fixed mean alkalinity. In contrast, the measured DIC concentration may not be used for a comparison with the model results, since it varies almost proportional to the background alkalinity.

Internal changes in alkalinity in a given water mass may occur by nitrate consumption/release and calcium carbonate formation/dissolution and act directly upon the  $p\text{CO}_2$ . However, in the Baltic Sea, the effect of calcium carbonate production on the marine carbon system is nearly negligible due to the low  $\text{CO}_3^{2-}$  concentration throughout most of the year. The effect of alkalinity changes due to nitrate consumption in the Baltic Sea on the  $p\text{CO}_2$  of less than 15  $\mu\text{atm}$  is small compared to the large seasonal

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$p\text{CO}_2$  amplitude (HELCOM, 1996) and is treated as negligible in this study.

Figure 1 provides a diagram of the processes and state variables that are accounted for in the model.

#### 2.4. Data availability for the eastern Gotland Sea and model setup

5 The eastern Gotland Sea is a suitable testbed for modeling studies aimed at understanding the underlying mechanisms that drive the seasonal upper ocean  $\text{CO}_2$  cycle due to the high availability of carbon-related data collected during intensive field campaigns in the last ten years (Thomas and Schneider, 1999; Thomas et al., 1999; Schneider et al., 1999; Osterroht and Thomas, 2000). In order to generate representative values for the eastern Gotland Sea, continuous measurements of sea surface  $p\text{CO}_2$  and deep profiles for salinity, temperature and DIC concentrations were averaged within a box of the eastern Gotland Sea (Fig. 2).

10 The model simulations in this work describe a one year cycle for the time period February 1997 until January 1998. Our choice of starting the simulations in February 1997 was based on this being the first time period with good observations to initiate the model. Observation to compare the model results are available for May 1997 and November 1997. In order to augment our database, we assume interannual variability is negligible and incorporate  $p\text{CO}_2$  data from October 1996 and July 1998 (Schneider et al., 1999). Since this is the first time this kind of investigation has been conducted for the Baltic Sea, we must accept the uncertainties evolved out of this incomplete data availability. For the model setup, the box averaged profiles for temperature, salinity, and DIC concentrations were used as initial values. Alkalinity was calculated from the initial values for temperature, salinity, DIC and  $p\text{CO}_2$ . Wind and air temperature data were taken from the weather forecast model HIRLAM (<http://www.dmi.dk>). Heat fluxes were provided out of BALTEX results (<http://w3.gkss.de/baltex>), and input values for atmospheric nitrate deposition were taken from Schulz et al. (1999).

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### 3. Results

We present first results from our standard simulation. We will have to realize quickly, however, that this simulation fails to attain the very low summertime  $p\text{CO}_2$  values despite the fact that we included  $\text{N}_2$ -fixation on our model results. Figure 3 shows the results of the upper model layer of the standard simulation. In the following, we will describe the simulated  $p\text{CO}_2$  and discuss the main underlying causes. We start in the winter and present and discuss results for subsequent seasons.

The relatively high initial  $p\text{CO}_2$  values decrease during February due to a decrease in sea surface temperature (SST) and in DIC concentration, whereby the latter decrease is mainly a result of the loss of  $\text{CO}_2$  to the atmosphere by gas exchanges. In March, the effect of increasing SST and ongoing decrease in DIC concentration on the  $p\text{CO}_2$  development are counteracting and cause an almost steady  $p\text{CO}_2$  for about a month. At the end of April, a drastic  $p\text{CO}_2$  decrease is simulated due to a rapid decrease in DIC caused by the onset of a diatom dominated spring bloom.

The simulated  $p\text{CO}_2$  reaches its lowest value at the beginning of May, when the spring bloom comes to an end because of complete nitrate depletion. Comparison shows that the simulated  $p\text{CO}_2$  for May is in good agreement with the observations. The end of the spring bloom makes also a change in the dominant functional group with flagellates taking over from the diatoms. Flagellates benefit from “regenerated” nutrients, i.e. no net DIC uptake with no further DIC drawdown, and the dominant process controlling the simulated  $p\text{CO}_2$  after the spring bloom is the increase in SST. At the beginning of July, the SSTs are high enough for cyanobacteria to become established. Their growth adds new nitrogen to the surface water and hence permit additional uptake of inorganic carbon to occur. This process, in addition to outgassing of  $\text{CO}_2$ , leads to a decrease in DIC from early July on. This counteracts the effect of increasing SST on the simulated  $p\text{CO}_2$  and leads to a decrease in  $p\text{CO}_2$ . Although the model is able to reproduce a low  $p\text{CO}_2$  value that represents the spring bloom, it is not capable of simulating the observed low  $p\text{CO}_2$  values in summer.

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The simulated  $p\text{CO}_2$  continues to decrease and, in August, the surface water is undersaturated in  $\text{CO}_2$  with respect to the atmosphere. Hereafter, the water stays undersaturated until the end of October, allowing  $\text{CO}_2$  flux into the water. From September to October,  $p\text{CO}_2$  variations are relatively small due to the counteracting processes of cooling and an increase in DIC due to mixed layer deepening. In October, the simulated  $p\text{CO}_2$  value is again in good agreement with the observed value.

From November to January, an oversaturation in  $\text{CO}_2$  with respect to the atmosphere is simulated, despite decreasing temperatures due to mixing of DIC enriched water from deeper layers into the surface. This leads to an outgassing of  $\text{CO}_2$  into the atmosphere. The simulated  $p\text{CO}_2$  for November differs only slightly from the observations. The low biological productivity during summer partly explains the difference between the starting value and the model result after one year of simulation.

In summary, the model simulations for  $p\text{CO}_2$  give reasonable results for the winter period until the onset of the spring bloom. The observed increase of  $p\text{CO}_2$  in late fall and winter are resolved by the model, although the simulated  $p\text{CO}_2$  underestimates the observations in mid-winter. However, a large discrepancy between model simulation and observations is found during the summer period. Although the model simulates the observed nitrate concentration in the surface water and also adds additional nutrients into the surface by including  $\text{N}_2$ -fixing cyanobacteria, it cannot simulate the  $\text{CO}_2$  undersaturation of the midsummer surface water in the eastern Gotland Sea. Obviously, processes are missing or underrepresented in the model that can cause an additional DIC drawdown in order to compensate the temperature induced increase in  $p\text{CO}_2$ . In the following section, we describe the effects of improvements of the model parameterizations of the  $\text{CO}_2$  exchange across the air-sea interface, and a higher C:N stoichiometric ratio for POM as well as for DOM, that we added to the model.

The gas transfer velocity,  $k$ , is often expressed as a function of the wind speed ( $U$ ), but ill known relationships arise in uncertainties of air-sea fluxes. Compared to a  $k$  expressed as a squared function of the wind speed (Wanninkhof, 1992), a cubic dependency generally leads to a smaller gas transfer velocity on low, and to a larger  $k$

on high wind speeds. The observed CO<sub>2</sub> undersaturation in the surface waters with respect to the atmosphere during summer indicates uptake of atmospheric CO<sub>2</sub> in the eastern Gotland Sea, i.e. the air-sea gas exchange cannot be a candidate process to explain ongoing DIC drawdown during summertime. However, since in summer wind velocities are usually low compared to winter values, a cubic function for  $k$  reduces the CO<sub>2</sub> uptake by the surface water in summer, and hence reduces the increase of DIC due to atmospheric CO<sub>2</sub> uptake after the spring bloom. Therefore, the air-sea flux parameterization by Wanninkhof (1992) is substituted by a cubic dependency of the wind speed for  $k$  determined for the eastern Gotland Sea by Kuss et al. (2004):

$$k = 0.037 U_{10}^3 \left( \frac{Sc}{660} \right)^{-\frac{1}{2}} \quad (3)$$

Here,  $Sc$  is the Schmidt number and  $U_{10}$  the wind velocity 10 m above the sea surface.

Variations in the model DIC concentration due to biological processes are linked by a constant elemental ratio to the nitrogen cycle. Compared to the traditional Redfield ratio of 106C:16N (Redfield et al., 1963), measurements of POM in the eastern Gotland Sea indicate a slightly elevated C:N ratio of 8.1, i.e. a possible indicator for preferential N recycling (Nagel, 1999). This ratio is applied to all variables that contribute to the model POM. In contrast to e.g. the Sargasso Sea (Anderson and Pondaven, 2003), no significant elevated C:N ratio for detritus, part of POM, is reported. Therefore, the model detritus contains the same C:N ratio as the other POM variables.

According to our understanding, the formation of POM leads to the formation of labile and semi-labile, or freshly formed, DOM. The formation of nitrogen depleted DOM, i.e. with a high C:N ratio, has been discussed as a possible explanation to allow more carbon to be fixed per unit of available nitrate (Sambrotto et al., 1993; Toggweiler, 1993; Kähler and Koeve, 2001). Measurements in nitrate-depleted surface waters have shown that freshly formed DOM may have a high C:N ratio (i.e. preferential N

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recycling) and hence contributes to a seasonal CO<sub>2</sub> drawdown (Williams, 1995; Kähler and Koeve, 2001).

The formation processes for DOM are manifold and only in part understood. As a consequence, different model parameterization for DOC production have been applied (Fasham et al., 1990; Six and Maier-Reimer, 1996; Slagstad et al., 1999; Anderson and Pondaven, 2003). In our simulation we have used an approach similar to Slagstad et al. (1999) and the relevant amount of DOC determined from measurements is taken into account. This amount, estimated by using a data set for the years 1994 to 2000 (Klaus Nagel, unpublished data), yield in a seasonal increase of 35 μmol kg<sup>-1</sup> (Leinweber, 2002) with a C:N ratio of 18.8. This high C:N ratio leads to an excess CO<sub>2</sub> fixation that amounts to about 60% of freshly produced DOM. To account for this effect, DIC is removed with a fixed rate for every time step over a time period of three months, starting directly after the onset of the spring bloom (Schneider et al., 2003). The same amount is added continuously over a period of three months, beginning in November, to the inorganic pool to account for remineralization of DOM.

The combined effect of the previous processes still does not lead to reasonable agreements with observations (Fig. 4). Therefore, N<sub>2</sub>-fixation is proposed as the underestimated process in the model that is needed to match the observations.

#### 4. Discussion

Various biogeochemical studies point towards a much greater role for marine nitrogen fixation to explain “carbon overconsumption” (Gruber and Sarmiento, 1997; Gruber et al., 1998; Capone, 2001; Zehr et al., 2001). Therefore, the formulation for N<sub>2</sub>-fixation in the presented model is revised. In the following two sections we present the reasons for an alternate parameterization for N<sub>2</sub>-fixing cyanobacteria. The chronology describes the time when N<sub>2</sub>-fixation can occur and the efficiency describes the amount of how much N<sub>2</sub>, and therefore CO<sub>2</sub>, can be fixed.

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## 4.1. Chronology

The simulated cyanobacteria (diazotroph) biomass maximum in late summer coincides with observations of highest N<sub>2</sub>-fixation rates between July and August (Niemistö et al., 1989; Ohlendieck et al., 2000; Neumann, 2000; Wasmund et al., 2001; Larsson et al., 2001; Elmgren and Larsson, 2002). However, our simulated N<sub>2</sub>-fixation rates for the period from November 1997 until October 1998 in the central Baltic Sea are much smaller than observations suggest (Wasmund et al., 2001; Neumann, 2000) (Table 1).

The highest N<sub>2</sub>-fixation rates are usually reported for late summer, but satellite data reveal an accumulation of diazotrophs as early as June in 1997. However, satellite observations can only detect diazotrophs that are accumulated at the sea surface and therefore cannot be used to calculate the total biomass for diazotrophs (Wasmund et al., 2001). *Aphanizomenon* are generally distributed in the upper water column between 10 and 20 m and therefore can not be detected by satellites. However, observations at station “Landsort Deep” in the western Gotland Sea report higher biomasses of *Aphanizomenon* for May and June 1997 compared to former years (Larsson et al., 2001). The analysis of satellite data in addition to observations in subsurface waters suggest that elevated nitrogen fixation rates may already occur “before” late summer. Hence, to account for an earlier onset in cyanobacterial growth, a change from a sharp to a moderate temperature dependency on N<sub>2</sub>-fixing cyanobacteria ( $TLIM_{CYAN}$ ), similar to the parameterization used for flagellates in this model, is suggested:

$$TLIM_{CYAN} = 1 + \frac{T^2}{T_{CYAN}^2 + T^2}. \quad (4)$$

Here,  $T$  is the actual water temperature and the temperature  $T_{CYAN}$  is set to 15°C for N<sub>2</sub>-fixing cyanobacteria. This change allows the cyanobacteria to grow independent from temperature but with an advantage under high water temperatures.

This modified temperature dependency for the growth rate of diazotrophs allows the onset of N<sub>2</sub>-fixation almost immediately after the spring bloom has exhausted surface

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nitrate. The largely increased addition of new nitrate results in a second  $p\text{CO}_2$  minimum after a short period of increasing  $p\text{CO}_2$  due to increasing sea surface temperatures (Fig. 5). Although this parameterization leads to  $\text{CO}_2$  undersaturated surface waters with respect to the atmosphere, it still does not simulate the observed very low  $p\text{CO}_2$  values in summer. The reason for the increase of  $p\text{CO}_2$  in the simulations after the second minimum is an earlier depletion of phosphorus associated with the earlier onset of diazotrophic growth. The maximum of  $\text{N}_2$ -fixation has shifted from late to early summer, and in the late summer primary production only occurs due to regenerated production, mostly flagellates. Hence, without a further decrease of DIC, the high water temperatures dominate the effect on the  $p\text{CO}_2$  and cause the simulated increase. The depression of diazotrophic blooms in late summer does not coincide with observations; therefore, the role of phosphorus as a limiting factor for diazotrophic growth is discussed next.

#### 4.2. Efficiency

$\text{N}_2$ -fixing cyanobacteria seem to be favored over other primary producers under nitrogen-depleted conditions but are still supposed to be limited by phosphorus and iron. It is known that iron is required for the growth of phytoplankton cells and nitrogen fixation. Laboratory experiments have shown growth dependency for *Nodularia spumigena*, a species common in the Baltic Sea, on iron availability (Paczuska and Kosakowska, 2003). However, the concentration of bioavailable iron in the Baltic Sea is reported to be high enough for cyanobacteria to bloom (Rydin et al., 2002). Therefore, it seems appropriate to ignore iron as a possible limiting factor in our model simulations.

But even under phosphorus-depleted conditions diazotrophs can still be observed in the Baltic Sea, even until September or October (Leppänen et al., 1988; Wasmund et al., 2001). How diazotrophs overcome this apparent phosphorus deficiency is still unknown. Wasmund et al. (2001) assume the existence of an additional phosphorus source and suggest a phosphate uptake of diazotrophs from deeper water (20 m) due to vertical migration, a hypothesis first proposed by Karl et al. (1992). It is also known

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that some marine algae are capable of internal phosphate storage (Copin-Montégut and Copin-Montégut, 1983; Andersen et al., 1991). Under phosphate-depleted conditions, the internal phosphate source can be used and may result in an C:P ratio in POM that exceeds the Redfield ratio. Observations for *Trichodesmium* in the tropical North Atlantic indicate an N:P ratio close to the Redfield ratio under phosphorus-replete conditions; whereas, under phosphorus-depleted conditions the N:P ratio can increase up to 100:1 (Capone, 2001). Similar to these observations, the C:P ratios in POM, mostly diazotrophs, at station “Landsort Deep” in the western Gotland Sea indicates a C:P ratio of up to 420:1 under phosphorus-depleted conditions (Larsson et al., 2001). Although the driving processes are still unknown, these observations make it clear that a link between carbon and phosphorus by the traditional stoichiometric ratio for diazotrophs would lead to an underestimation of  $N_2$ -fixation rates.

In our standard simulation, the growth of diazotrophs is limited by phosphorus that is taken up according to the Redfield ratio. In other biogeochemical models, different parameterizations have been proposed to account for  $N_2$ -fixation. For example, Hood et al. (2001) assume *Trichodesmium* is capable of obtaining or retaining the phosphorus required to support growth; i.e. there is no phosphorus limitation for *Trichodesmium* in the model. Fennel et al. (2001) assume a stoichiometric N:P ratio of 45 for *Trichodesmium* at station ALOHA which is based on observations. In order to increase the efficiency of  $N_2$ -fixation in our model and thus to align the simulated midsummer  $pCO_2$  with the measurements, we increased the phosphorus availability by a factor of 2. This manipulation is equivalent to a doubling of the C:P ratio in these cells. In contrast, the growth of diatoms in early spring is not affected by this enhanced phosphorus concentrations because it is limited only by nitrate. Flagellates only account for the “re-generated” production, therefore they do not account for additional DIC drawdown due to an enhanced availability of phosphorus. Hence, simulated changes in  $pCO_2$  can be directly related to the cyanobacteria.

The resulting model simulations are now able to describe the observations (Fig. 6). The increase of the C:P ratio leads to pronounced  $N_2$ -fixation rates after the spring

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bloom, and the simulated  $p\text{CO}_2$  in June is even lower than the observed value for July 1998. A very low  $p\text{CO}_2$  value of approximately  $160 \mu\text{atm}$  was detected on a cruise in June 2001 (Schneider et al., 2003) and confirms the adequacy of the model parameterization. The resulting total nitrogen fixation ( $167 \text{ mmol m}^{-2} \text{ a}^{-1}$ ) exceeds previous estimates but is in good agreement with recent measurement based estimates for 1997 (Table 1).

The large input of nitrogen results in an unrealistic increase of nitrate concentration in the upper water column at the end of the simulation, that so far cannot be compensated, although we account for denitrification in the model. To balance the increase in the upper layers, the sinking velocity of detritus is increased to  $6.5 \text{ m d}^{-1}$ , a value well within the range found in literature (Fasham et al., 1993; Jørgensen, 1994; Haupt et al., 1999). The same approach is made by Hood et al. (2001) for the same reason, who assume a sinking velocity of  $12 \text{ m d}^{-1}$ .

The additional availability of regenerated nutrients also stimulates the growth rate of flagellates in the model that is inconsistent with observations. However, adjusting the growth rate within a reasonable range, in this case to a maximal uptake rate of  $0.85 \text{ d}^{-1}$  and a half-saturation constant of 0.1 (Jørgensen, 1994; Fennel, 1998), lead again to reasonable results.

## 5. Conclusions

The focus of this work was to quantify the processes driving the seasonal carbon cycle in the surface water of the eastern Gotland Sea by the use of an ecosystem model. This ecosystem model describes a nitrogen cycle within the Baltic Sea that fits the observations (Neumann, 2000). However, the inclusion of  $\text{CO}_2$  into the ecosystem model reveals underestimated processes during summertime, possibly an underestimation of  $\text{N}_2$ -fixation. Next to a higher C:N ratio in POM, an additional DOC sink term and a smaller uptake of atmospheric  $\text{CO}_2$ , only the drastic change of the parameterization for  $\text{N}_2$ -fixation makes it possible to simulate the observed  $p\text{CO}_2$  values. Therefore, includ-

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ing CO<sub>2</sub> into ecosystem models is a powerful tool in quantifying processes concerning the ecosystem.

Although the model results seem reasonable, it needs to be confirmed with measurements of N<sub>2</sub>-fixation rates. Another problem due to this strong nitrogen source in the model is that there must be an additional sink for nitrogen to balance the system. One possibility may be to account for anammox (Dalsgaard et al., 2003), another form of denitrification, in the model results. Also, the behavior of diazotrophs under phosphate-depleted situation is still not well understood. Although the presented parameterization gives reasonable results, assuming a fixed C:P ratio is probably not the best choice. For future parameterization, e.g. a variable C:P ratio for diazotrophs may reduce an early phosphate limitation in the model and hence may better fit the observations. As mentioned earlier, iron does not seem to limit the growth of cyanobacteria in the Baltic Sea. However, including iron as a limiting factor might help to increase the ability to achieve better horizontal distribution within 3D-model results.

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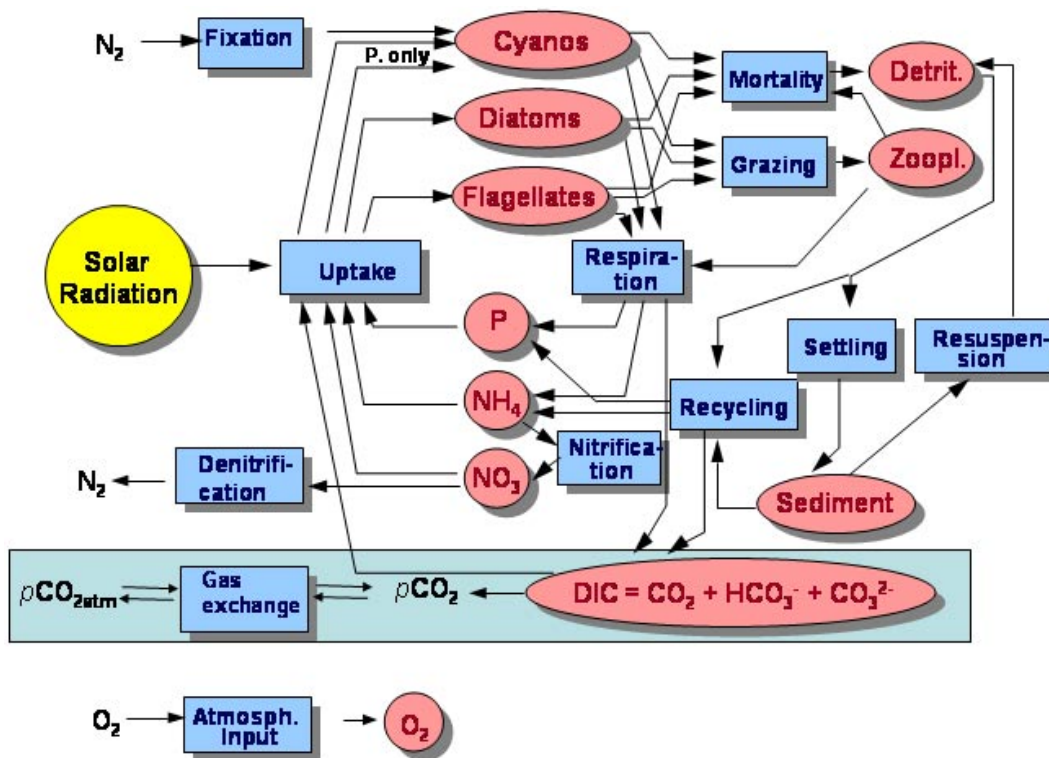
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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)**Table 1.** Selected N<sub>2</sub>-fixation rates for the eastern Gotland Sea.

| Reference                               | Method                 | N <sub>2</sub> -fixation rate<br>in the eastern Gotland Sea<br>(mmol N m <sup>-2</sup> a <sup>-1</sup> ) |
|---|------------------------|--|
| <b>this study</b>                       | <b>C model budget</b>  | 167  |
| <a href="#">Niemistö et al. (1989)</a>  | net samples            | 27.1–55.7  |
| <a href="#">Rahm et al. (2000)</a>      | P-Budget               | 14.3–214   |
| <a href="#">Larsson et al. (2001)</a>   | N-Budget               | 113–140 (1997)   |
| <a href="#">Wasmund et al. (2001)</a>   | <sup>15</sup> N-Tracer | 125 (1997–1998)  |
| <a href="#">Schneider et al. (2003)</a> | C budget               | 320±50 (2001)  |

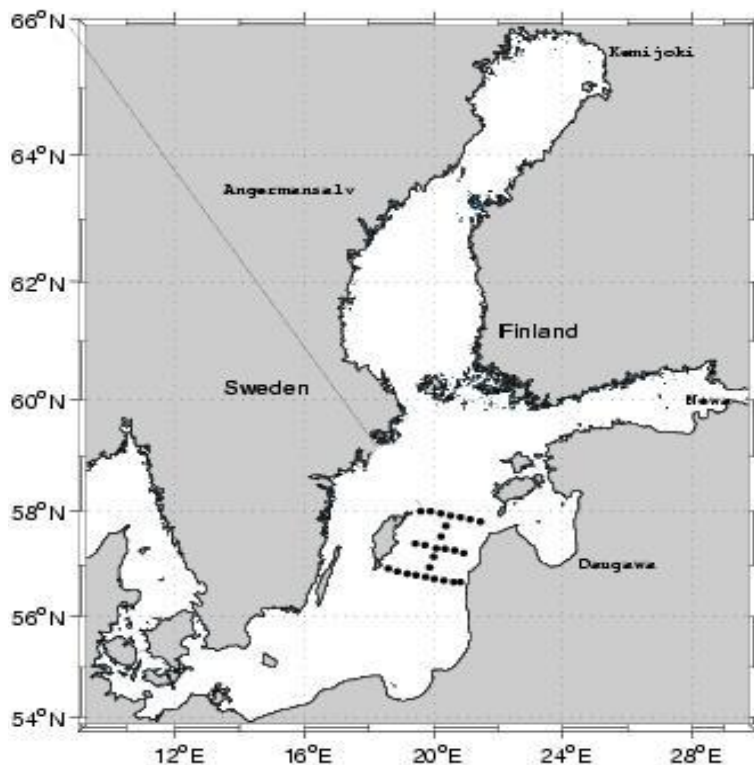
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**Fig. 1.** Conceptual ecosystem model. Circles are for state variables and rectangles for processes, respectively. In detail: state variables are: ammonium (NH<sub>4</sub>), nitrate (NO<sub>3</sub>), phosphate (P), dissolved inorganic carbon (DIC), flagellates, diatoms, cyanobacteria (Cyanos), detritus (Detrit.), zooplankton (Zoopl.), oxygen (O<sub>2</sub>), and sediment.

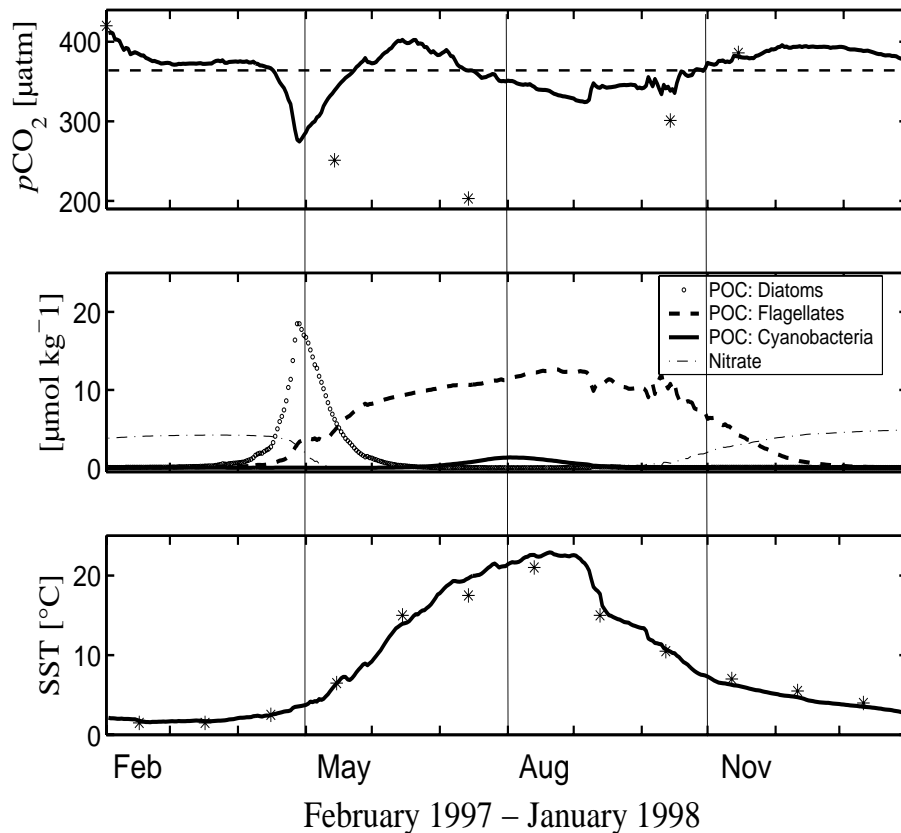
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**Fig. 2.** Map of the Baltic Sea. Points indicate the positions of the stations in the eastern Gotland Sea that have been investigated for inorganic carbon during several cruise campaigns.

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**Fig. 3.** Simulated annual cycle for the period February 1997 until January 1998. **(a)** simulated  $p\text{CO}_2$  (solid line) compared with observations (stars) (in  $\mu\text{atm}$ ). **(b)** POC: diatoms (dots), POC: flagellates (dashed line), POC: cyanobacteria (solid line), nitrate (dots) (in  $\mu\text{mol kg}^{-1}$ ). **(c)** SST (solid line) compared with observations (<http://www.bsh.de>) (stars) (in  $^{\circ}\text{C}$ ).

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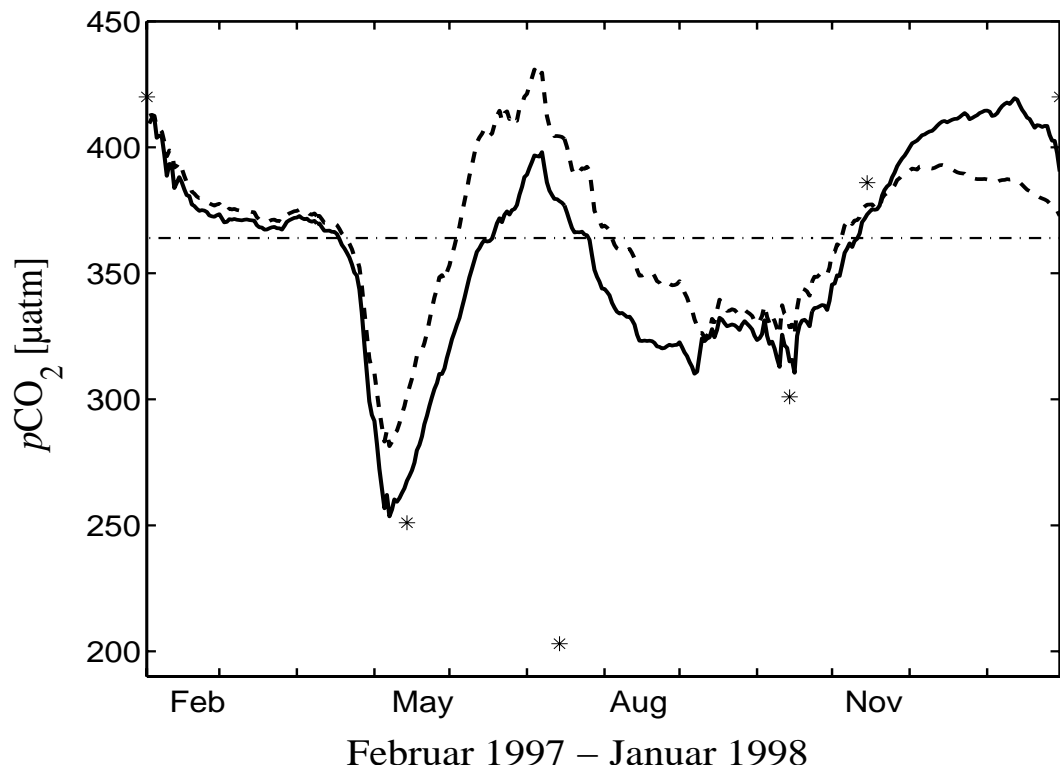
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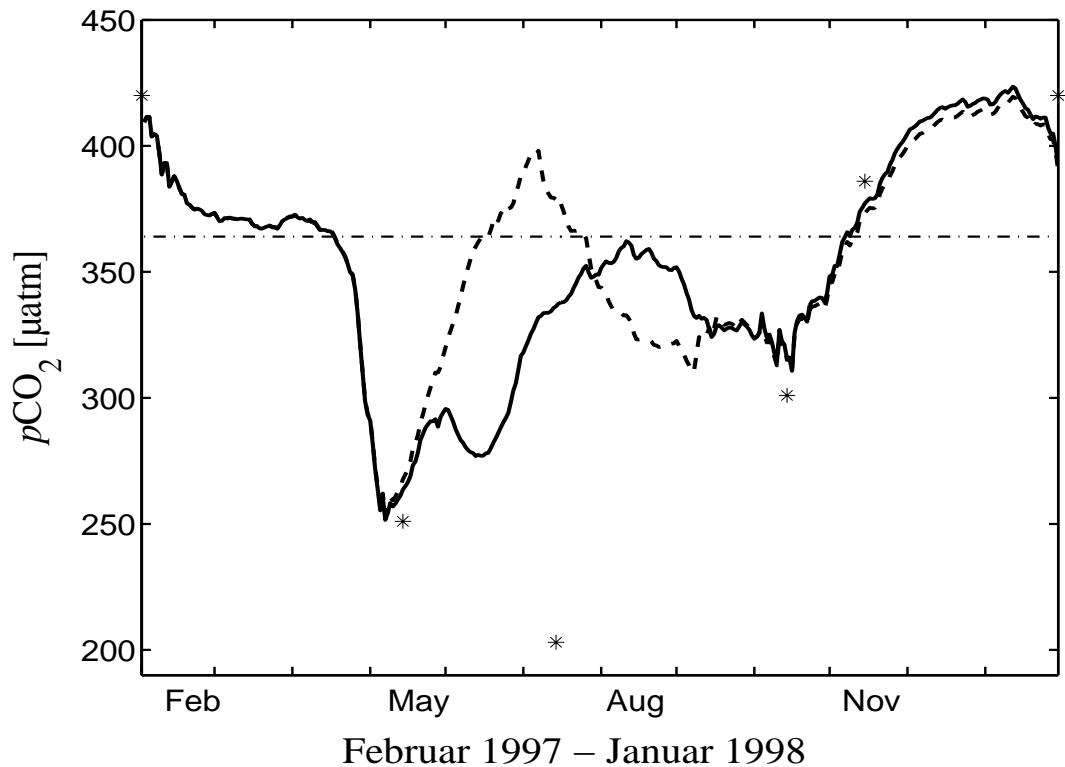
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**Fig. 4.** Modified simulated  $p\text{CO}_2$  (solid line) compared to  $p\text{CO}_2$  simulations with initial parameterizations (dashed line) and measured  $p\text{CO}_2$  (stars).

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**Fig. 5.** Modified simulated  $p\text{CO}_2$  with change in chronology parameterization for  $\text{N}_2$ -fixing cyanobacteria (solid line) compared to previous modified  $p\text{CO}_2$  simulations (dashed line; see solid line in Fig. 4) and measured  $p\text{CO}_2$  (stars).

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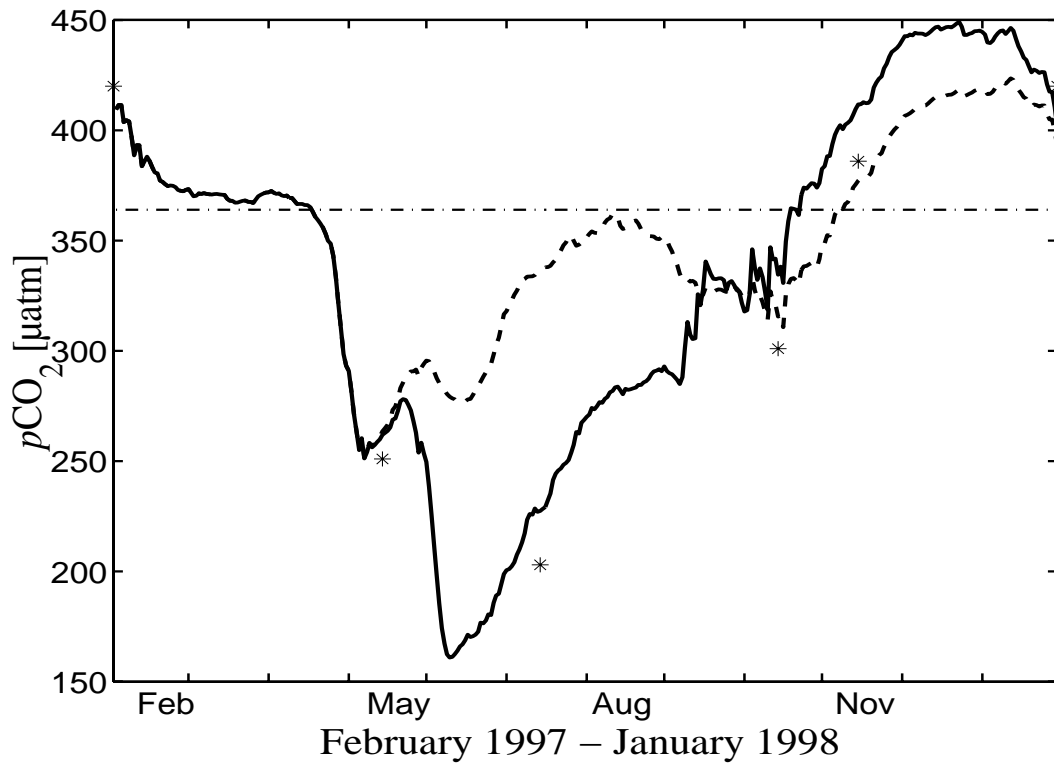
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**Fig. 6.** Modified simulated  $p\text{CO}_2$  with change in efficiency parameterization of  $\text{N}_2$ -fixing cyanobacteria (solid line) compared to previous modified  $p\text{CO}_2$  (dashed line, is solid line in Fig. 5) and measured  $p\text{CO}_2$  (stars).

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