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Non-Redfieldian Dynamics Explain Seasonal pCO₂ Drawdown in the Gulf of Bothnia

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RESEARCH ARTICLE

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Non-Redfieldian Dynamics Explain Seasonal pCO₂ Drawdown in the Gulf of Bothnia

Key Points:

- Observed pCO₂ and nutrient dynamics are captured by simulating non-Redfieldian phytoplankton C:N:P ratios and extracellular DOC production
- The atmospheric CO₂ uptake is halved if using the Redfield ratio to determine carbon assimilation
- The model suggests a more productive Gulf of Bothnia than previous measurements

Supporting Information:

- Supporting Information S1

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Abstract High inputs of nutrients and organic matter make coastal seas places of intense air-sea CO₂ exchange. Due to their complexity, the role of coastal seas in the global air-sea CO₂ exchange is, however, still uncertain. Here, we investigate the role of phytoplankton stoichiometric flexibility and extracellular DOC production for the seasonal nutrient and CO₂ partial pressure (pCO₂) dynamics in the Gulf of Bothnia, Northern Baltic Sea. A 3-D ocean biogeochemical-physical model with variable phytoplankton stoichiometry is for the first time implemented in the area and validated against observations. By simulating non-Redfieldian internal phytoplankton stoichiometry, and a relatively large production of extracellular dissolved organic carbon (DOC), the model adequately reproduces observed seasonal cycles in macronutrients and pCO₂. The uptake of atmospheric CO₂ is underestimated by 50% if instead using the Redfield ratio to determine the carbon assimilation, as in other Baltic Sea models currently in use. The model further suggests, based on the observed drawdown of pCO₂, that observational estimates of organic carbon production in the Gulf of Bothnia, derived with the ¹⁴C method, may be heavily underestimated. We conclude that stoichiometric variability and uncoupling of carbon and nutrient assimilation have to be considered in order to better understand the carbon cycle in coastal seas.

1. Introduction

A substantial part of the global air-sea CO₂ exchange takes place in marginal seas. Estuaries and inner parts of coastal systems are usually sources of CO₂ to the atmosphere due to high inputs of terrestrial organic matter and river water oversaturated in CO₂, whereas outer parts of the continental shelf, and coastal seas in general, are CO₂ sinks (Bauer et al., 2013; Borges et al., 2005; Cai, 2011; Laurelle et al., 2010; Raymond et al., 2013; Regnier et al., 2013). This carbon drawdown is a consequence of large phytoplankton blooms occurring where stratification, light regime, and nutrient conditions are suitable for phytoplankton growth.

Drastic changes in freshwater and organic matter supply, affecting the carbon balance, are envisaged for high latitude coastal seas with a warming climate (Semiletov et al., 2016). At the same time, a reduction in sea-ice cover is expected to affect the air-sea CO₂ exchange, both directly, and indirectly by altering the productive season (Arrigo et al., 2008; Semiletov et al., 2004). To predict what direction global warming affects high latitude coastal seas and their functioning as a CO₂ sink or source to the atmosphere, a better understanding of the mechanisms that underlie the dynamics of organic matter, bacterial, and primary production in the coastal seas, and an improvement of their representation in biogeochemical models, are needed.

The Gulf of Bothnia (Figure 1), the Northern part of the Baltic Sea, is a subarctic estuary that is partly to completely ice-covered during winter (Granskog et al., 2006). The rivers draining into the basin run through pristine boreal areas and bring relatively high concentrations of organic nutrients and carbon (Humborg et al., 2003; Stepanauskas et al., 2002), which have a large impact on the biogeochemistry and carbon

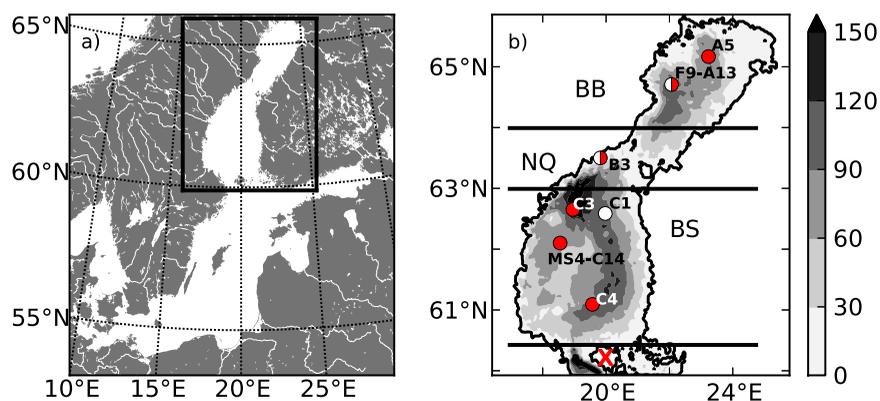


Figure 1. (a) Map of the Baltic Sea. The rectangle shows the location of the model configuration. (b) Model bathymetry with filled depth contours in meters. The circles show the location of monitoring stations from which data have been collected for model validation. Red color indicates that there are measurements of temperature, salinity, nutrients, and chlorophyll, while white indicates measurements of PAR, salinity, and primary production. The three different subbasins the Bothnian Bay (BB), the Northern Quark (NQ), and the Bothnian Sea (BS) are separated by horizontal black lines. The red cross indicates the location of the island of Åland.

cycling of the gulf (Sandberg et al., 2004; Wikner & Andersson, 2012). The northernmost basin, the Bothnian Bay (BB, Figure 1) has been found to be a weak source of CO_2 to the atmosphere, while the southernmost basin, the Bothnian Sea (BS), acts as a sink (Löffler et al., 2012). Because of low sediment-water fluxes of phosphate, and the low input of phosphate from rivers, primary production in the Bothnian Bay is severely phosphorus limited (with winter phosphate concentrations of about 0.05 mmol m^{-3}), in contrast to the more nitrogen limited southern basins of the Baltic Sea (Andersson et al., 1996). Several studies with physical-biogeochemical models have been carried out to estimate the carbon and nutrient fluxes in the Baltic Sea (Edman & Andersson, 2014; Eilola et al., 2011; Gustafsson et al., 2014a; Kuznetsov & Neumann, 2013). Yet, none of these models have been able to realistically reproduce the carbon fixation and the nutrient uptake in the Bothnian Bay. In the Bothnian Sea, the nutrient uptake is in general well reproduced, but the models fail when it comes to carbon assimilation and primary production (Gustafsson et al., 2014a).

The models used in these studies have, like most marine biogeochemical models, a phytoplankton formulation that assumes the Redfield ratio (Redfield, 1934, 1958) to determine phytoplankton carbon and nutrient assimilation and the production of organic matter. In this kind of formulation, the uptake of carbon and nutrients is directly linked to the uptake of the most limiting nutrient, and the internal carbon:nitrogen:phosphorus (C:N:P) ratios of the phytoplankton and the organic matter are fixed. However, this is a crude and in many cases an invalid assumption (Flynn, 2003, 2010), since the internal C:N:P ratios of phytoplankton can deviate far from the Redfield ratio (Bertilsson et al., 2003; Geider & La Roche, 2002; Goldman et al., 1979; Leonardos & Geider, 2004; Spilling et al., 2015), in particular during times of nutrient limitation. Especially in the phosphorus limited Bothnian Bay these models can be expected to fail, and nutrient measurements from this area do suggest that the ratio of N:P assimilation exceeds the Redfield ratio by far (Eilola, 2009). Another feature the fixed-stoichiometric models do not capture is the carbon overflow process and the production of extracellular DOC, which can make up a large part of the primary production when there are not enough nutrients to bind the fixed carbon into biomass (Kaltenböck & Herndl, 1992; Obernosterer & Herndl, 1995; Puddu et al., 2003; Spilling et al., 2016).

Several recent papers have emphasized the need to move from fixed stoichiometric models to the use of a new generation of plankton models with a more mechanistic representation of physiological processes (Allen & Polimene, 2011; Flynn, 2010; Glibert et al., 2013). Especially when modeling the biogeochemistry of coastal and semienclosed seas, physiological flexibility of phytoplankton is required to deal with transitions between phosphorus and nitrogen limitation, between oligotrophic and eutrophic waters, changes in light conditions, and high organic matter loadings (Baretta-Bekker et al., 1995; Bauer et al., 2013; Blackford et al., 2004). The phytoplankton formulation in mechanistic models is often based on the philosophy of Droop's quota model (Droop, 1968, 1973, 1974), where the stoichiometric flexibility of the phytoplankton is taken into account. This allows for a decoupling of the nutrient and carbon assimilation, which has been shown to

be more suitable when modeling carbon fixation and uptake of more than just one species of nutrient, compared with models with fixed stoichiometry (Ayata et al., 2013; Christian, 2005; Flynn, 2003, 2010). Until present, many different physiological models of varying complexity have been developed that take into account different aspects of stoichiometric flexibility (e.g., Geider et al., 1998; Ghyoot et al., 2015; Klausmeier et al., 2004; Omta et al., 2009; Pahlow & Oschlies, 2013; Talmy et al., 2014). However, only a few models considering variable C:N:P in phytoplankton have been applied to larger regional areas and 3-D ocean circulation models (e.g., Ayata et al., 2014; Baretta-Bekker et al., 1995; Tagliabue & Arrigo, 2005; Vichi et al., 2007a).

Here we test, for the first time, a flexible-stoichiometry model coupled to a 3-D circulation model of the Gulf of Bothnia, to examine how stoichiometric flexibility and extracellular DOC production can explain seasonal nutrient and CO₂ dynamics at different contrasting sites. Flexible-stoichiometry models have previously been applied for primary production studies in sea-ice in the Gulf of Bothnia and the Gulf of Finland (Tedesco et al., 2010, 2017; Thomas et al., 2017). For pelagic biogeochemistry, flexible-stoichiometry models have been used for 1-D studies at specific locations (Kreus et al., 2015a, 2015b; Vichi et al., 2004), and for modeling cyanobacteria in a dynamic 3-D model (Kuznetsov et al., 2008), but only in the central Baltic Sea and the Gulf of Finland. Wan and Hongsheng (2014) implemented a spatially varying, but still dynamically fixed, phytoplankton N:P ratio in a 3-D model for the Baltic Sea. It led to an improvement in modeled nutrient dynamics, but they did not include data from, nor validate their model for, the central Bothnian Bay where the most extreme N:P ratios are found.

The main objectives of this study are (i) to present and validate a coupled physical-biogeochemical 3-D model with flexible stoichiometry, for the first time applied to the Gulf of Bothnia, and particularly (ii) to demonstrate the importance of having a flexible stoichiometry-approach, compared to a fixed stoichiometry approach, for the seasonal pCO₂ and nutrient dynamics as well as the organic carbon production and the air-sea CO₂ exchange in this area.

The outline of the paper is as follows. In section 2, the physical and biogeochemical models are introduced. Further the two simulations, one with variable and one with fix stoichiometry, and the observational data that have been used for model validation are described. In section 3, the two simulations are compared to observations of macronutrients, chlorophyll, and pCO₂. Even though measurements of primary production are known to be difficult to interpret, the modeled primary production is also compared to measured primary production by the ¹⁴C method. The modeled seasonal evolution of the phytoplankton stoichiometry in variable stoichiometry case is presented. In section 4, the importance of the variable stoichiometry for nutrient and carbon cycling in the Gulf of Bothnia is discussed. We further discuss our finding that the primary production needed to simulate the seasonal pCO₂ dynamics is severalfold higher than the observed primary production.

2. Model Setup

2.1. Physical Model

A NEMO (Nucleus for European Modelling of the Ocean, <http://www.nemo-ocean.eu>, Madec et al., 2016) configuration for the Gulf of Bothnia (Figure 1), from now on NEMO-GoB, was created from the NEMO-Nordic setup (Hordoir et al., 2013, 2015). NEMO-Nordic is a 3-D hydrodynamic model of the Baltic and the North Seas based on NEMO 3.6 (Madec et al., 2016) and the LIM3 sea-ice model (Vancoppenolle et al., 2009). The NEMO-GoB configuration was set up with a 2 nautical mile (3,704 m) horizontal resolution and 36 vertical levels (z coordinates) and with an open boundary located in the Åland Sea at 59.9°N, South of the island of Åland (Figure 1). The open boundary conditions were created from the simulation output of the full Nemo-Nordic setup. The baroclinic and barotropic modes at the open boundaries are computed with a Flow Relaxation Scheme (Davies, 1976; Engedahl, 1995) and Flather conditions (Flather, 1994), respectively (Madec et al., 2016). Daily output of the sea surface height was used, as the sea-level variability governing the barotropic exchanges in the Baltic Sea can be described accurately on a daily timescale. The baroclinic exchange consists of an outflow toward the Baltic Sea in surface waters, which means that the information in terms of temperature and salinity at the open boundary is mostly pushed out of the computational domain. Below the level of the halocline, this information travels into the computational domain, but the variability is less than above the halocline. Therefore, temperature and salinity fields that are used for the open boundary condition are monthly values only.

Initial conditions for salinity and temperature were extracted from the same simulation as used for the open boundary conditions. Hourly atmospheric data from a downscaled ERA40 simulation (Samuelsson et al., 2011) and daily river runoff data from the hydrological model EHYPE (Donnelly et al., 2016) were used as model forcing.

A validation of the physical model is presented in section 3.1.

2.2. Biogeochemical Model

The Biogeochemical Flux Model (BFM; <http://bfm-community.eu>) (Vichi et al., 2007b, 2015b) is a stoichiometric biogeochemical model that has been coupled to 3-D ocean circulation models. It has been applied both to the global ocean and to various regional seas (Lazzari et al., 2016; Vichi & Masina, 2009; Vichi et al., 2003, 2004, 2007a), and derives from the ERSEM model (Baretta et al., 1995), originally adapted for the North Sea. BFM explicitly describes, in its standard configurations, the fluxes of carbon, oxygen, nitrogen, phosphorus, and silicon (Si) between inorganic, nonliving organic, and living organic matter in the lower trophic levels of the marine ecosystem. It has four phytoplankton functional groups (diatoms, flagellates, picophytoplankton, and large phytoplankton), four zooplankton groups (heterotrophic nanoflagellates, microzooplankton, carnivorous, and omnivorous mesozooplankton), and one group of bacteria that represents both aerobic and anaerobic bacteria. In all plankton functional groups, the content of C, N, P (and Si in case of diatoms) is modeled explicitly, which allows the internal C:N:P(Si) ratios to vary dynamically. BFM has four types of organic matter: labile, semilabile, and semirefractory dissolved organic matter (DOM) as well as labile particulate organic matter (POM). The labile DOM and POM both contain C, N, and P, with dynamic C:N:P ratios, while the semilabile and semirefractory DOM only consist of C. The inclusion of bacteria and organic matter dynamics makes it possible to simulate not only the classical food chain, but also the microbial food web (Lazzari et al., 2016), which has been shown to play an important role especially in the Northern Baltic Sea (Sandberg et al., 2004; Wikner & Andersson, 2012). A new state variable was added to the model to represent terrestrial DOM, also with dynamic C:N:P ratios. It is subject to a linear decay with a time scale of 1 year to represent microbial and photochemical remineralization (Fransner et al., 2016) (Appendix A1).

2.2.1. Nutrient and Carbon Fixation

The phytoplankton nutrient and carbon uptakes in BFM are decoupled, which makes it possible for carbon fixation to occur also in nutrient limited conditions. The carbon fixation is ultimately determined by the temperature and light conditions as well as by the carbon and Chl-a content in the phytoplankton. The nutrient uptake, which partially is based on Droop kinetics (Droop, 1973), is regulated so that the internal C:nutrient ratios in the phytoplankton are kept within certain ranges. If there are more than enough nutrients to keep the C:nutrient ratios at optimal levels (assumed to be Redfield), the phytoplankton can, to a certain extent, assimilate, and store the nutrients for future use (i.e., luxury consumption, Baretta-Bekker et al., 1997). If there are not enough nutrients in the surrounding water to bind the fixed carbon into biomass, the phytoplankton can use internally stored nutrients. If neither the internal pool of the phytoplankton nor the surrounding water contains enough nutrients, a part, or all of the fixed carbon is released as extracellular (semilabile) DOC (Vichi et al., 2004, 2015b).

The stoichiometry of the phytoplankton, which is regulated by carbon and nutrient assimilation as described above, affects the losses of biomass due to nutrient stress, and the chlorophyll synthesis. The more the cellular stoichiometry deviates from the optimal stoichiometry, the more stressed the phytoplankton are. The growth rate, which is dependent on the phytoplankton biomass and their chlorophyll content, is therefore indirectly related to the nutrient status of the cells, in contrast to Droop's quota model where the growth relates directly to the cellular nutrient status.

A summary of the model equations governing the carbon and nutrient assimilation is found in Appendices A3, A4, and A5. For a more detailed description, the reader is referred to the BFM manual (Vichi et al., 2015b), as well as Lazzari et al. (2016) and Baretta-Bekker et al. (1997).

2.2.2. Benthic Submodel

A simple benthic return submodel (Polimene et al., 2006) was added to the configuration. Sedimenting organic matter that reaches the seafloor goes into the sediment pools of organic C, N, P, and Si. In the sediments, a fraction of the deposited matter is remineralized and returns to the water column with a constant rate, and a fraction is permanently buried. The phosphorus release from sediments is known to depend on the salinity of bottom waters (Blomqvist et al., 2004). A salinity-dependent parameterization was therefore

created, where the flux of phosphorus out of the sediments is set to zero below a threshold salinity of 5.3. Salinity-dependent parameterizations for sediment-water phosphorus fluxes are also used in other Baltic Sea models (Eilola et al., 2009; Savchuk et al., 2012). A constant release of $1.5 \text{ mmol Eq m}^{-2} \text{ d}^{-1}$ of alkalinity from the sediments was added to the configuration. This is close to the mean alkalinity release of $1.6 \text{ mmol Eq m}^{-2} \text{ d}^{-1}$ calculated for the Gulf of Bothnia by Gustafsson et al. (2014b), who concluded that a source of alkalinity is needed in the sediments in order to simulate the alkalinity of the Baltic Sea.

2.2.3. Underwater Light Regime

The background light extinction coefficient in BFM is well adapted for open ocean conditions and is by default tuned to the optical attenuation of pure water, and linearly modulated by the chlorophyll and particulate organic carbon (POC) concentrations. In the Baltic Sea, however, the water tends to get more turbid as salinity decreases as a result of the high input of colored dissolved organic matter (CDOM) from the rivers. As the CDOM is not modeled explicitly, the light extinction coefficient's dependency on the CDOM concentration is parameterized as a function of salinity. This has been done earlier in modeling studies for the Baltic and North seas (Maar et al., 2011; Neumann et al., 2015). For the current study the salinity dependency of the specific attenuation coefficient was estimated by first creating a linear extrapolation of measurements of Photosynthetic Available Radiation (PAR) and salinity at stations F9-A13, B3, and C1 in the Gulf of Bothnia (Figure 1). As the measured PAR-field also includes the effect of chlorophyll and POC, the CDOM-salinity dependency had to be fine-tuned in order to reproduce the measured PAR. The derived parameterization is shown in Appendix A2.

2.2.4. Coupling to the Physical Model

BFM was coupled online to, and run with the same time step as, NEMO-GoB. A description of the technical details of the coupling between BFM and NEMO can be found in Vichi et al. (2007a, 2015a). An adaptation of the flow-relaxation scheme used for the open boundary conditions for the active tracers was done to obtain open boundary conditions for the biogeochemical tracers. As there is no regularly visited monitoring station in the Åland Sea, a set of boundary conditions for phosphate, nitrate, ammonium, and oxygen was created from a simulation with NEMO-Nordic-SCOBI (Kuznetsov et al., 2016), an ecosystem model covering the whole Baltic Sea. The boundary condition for Total Alkalinity (TA) was calculated as a function of salinity (Gustafsson et al., 2014b), where the salinity field was taken to be the same as used for the salinity boundary condition. The Dissolved Inorganic Carbon (DIC) boundary conditions were thereafter calculated from the TA, based on the DIC-TA relationship in Thomas and Schneider (1999). For terrestrial dissolved organic carbon, the boundary conditions were taken from the simulations in Fransner et al. (2016). The boundary conditions for terrestrial dissolved organic nitrogen (DON) and phosphorus (DOP) were calculated by dividing the boundary conditions for terrestrial DOC by the C:N and C:P ratios of the terrestrial organic matter in the rivers. These ratios were calculated from the same river data as used for the river loads, which are further described below. The boundary conditions of all other state variables were set to spatially and temporally constant values.

River loads of DOC, DIC, and TA were created from 5 years (1996–2000) of monthly measurements of concentrations in 50 rivers (Fransner et al., 2016). For Si and inorganic and organic P and N, the river forcing was created from 30 years (1970–2000) of combined modeling and measurement of concentration data from the Baltic Environmental Database (BED, <http://www.balticnest.org/bed>). The DIN (dissolved inorganic nitrogen) was assumed to consist of 90% nitrate and 10% ammonium, which was estimated from nutrient measurements in Swedish rivers (SLU environmental database, <http://miljodata.slu.se/mvm/>). The particulate organic fractions of C, N, and P were assumed to be 10% of the total riverine input of organic C, N, and P. Our particulate fractions are smaller than the particulate fractions measured in Baltic Sea rivers by Stepanauskas et al. (2002; 47 and 18% of the organic P and N, respectively). However, their measurements were taken in June–July 1999, and they concluded that a major part of the particulate material came from phytoplankton. These fractions are therefore not representative for the whole year and we consequently chose smaller fractions. Twenty percent of the riverine input of DOC was assumed to be refractory based on Fransner et al. (2016). The refractory part is not modeled explicitly and was simply removed from the river load. Similarly, for the riverine DOP and DON, 20 and 40% were set to refractory, respectively. Atmospheric deposition of ammonium, nitrate, and phosphate was obtained from the BED database. The inorganic carbon system was forced with atmospheric $p\text{CO}_2$ levels from the Barrow station in Alaska (<https://www.esrl.noaa.gov/gmd/obop/brw/>), which have been shown to differ by only 3 ppm from the $p\text{CO}_2$ levels in the Baltic Sea area (Schneider, 2011).

By default, the BFM model assumes that the air-sea gas exchange decreases linearly with increasing sea-ice concentration, until totally blocking any gas exchange when the ice concentration reaches 100%. However,

Table 1
Experimental Setup for the REF and FIX Simulations

Experiment	Note	Stoichiometry	Maximum C:N	Maximum C:P	Simulation period
REF	Reference run	Variable	33	742	1980–2010
FIX	Sensitivity run	Fixed			1990–2010

in reality sea-ice never completely prevents gas exchange (e.g., Tison et al., 2017), especially when the sea-ice is thin as the one found in the Gulf of Bothnia. Sensitivity studies (not shown here) indicated that damping gas-exchange linearly up to a sea-ice concentration of 80% gave the most realistic $p\text{CO}_2$ values during the ice-covered season, without affecting the development of $p\text{CO}_2$ during the productive season. Thus, a cap of 80% was chosen for this model configuration.

2.3. Simulations

Two simulations were performed (Table 1); (i) a reference simulation (REF) with flexible C:N:P ratios, and (ii) a simulation (FIX) with fixed Redfield ratios. REF was run for 31 years, from 1980 to 2010, where the first 10 years were used to spin-up the model. The FIX experiment was started from restarts for year 1990 from REF and was run for 21 years until 2010. Model data were stored with a monthly output frequency.

2.3.1. REF

The REF simulation was done with the original BFM with added parameterizations for the benthic nutrient fluxes, terrestrial DOM, and the light climate as described in section 2.2. To cope with the strong nutrient limitations, especially in the Bothnian Bay, the maximum C:N and C:P ratios were set to 33 and 742, respectively (Table 1), which are among the more extreme values from the Baltic Sea found in the literature (Spilling et al., 2015). All BFM settings used in REF are presented in Tables S1–S7 in the supporting information.

2.3.2. FIX

To investigate the importance of variable stoichiometry, a sensitivity experiment (FIX) was performed where the internal C:N:P ratios of the phytoplankton were fixed to the Redfield ratio (106:16:1; Table 1). The phytoplankton module was reformulated to express the phytoplankton dynamics in one single currency, chosen to be nitrogen. The uptake and release of carbon and phosphorus are directly related to the nitrogen through the Redfield ratio. Because the nutrient limitation can no longer be related to the internal phytoplankton C:nutrient ratios, a Michaelis-Menten function (Michaelis & Menten, 1913) was instead used to represent an external nutrient limitation. The half-saturation constant for P and N-limitation was set to 0.01 mmol P m^{-3} and 0.25 mmol N m^{-3} , respectively. For a mathematical description, the reader is referred to Appendix A6. All model settings not related to the phytoplankton internal stoichiometry (maximum growth rate, light sensitivity, etc.) were kept identical to the REF experiment.

2.4. Validation Data

Observational data of salinity, temperature, nutrients, chlorophyll-a, TA, pH, primary production, DOC, and PAR were obtained from the Swedish marine database SHARK (Svenskt HavsARKiv, <http://sharkweb.smhi.se/>). Monthly measurements from the stations in Figure 1 between 1990 and 2010 were extracted. The primary production data, measured with the ^{14}C method, contain the total carbon fixation, and therefore the production of both particulate and dissolved organic carbon. For validation of the $p\text{CO}_2$, data from Löffler et al. (2012) have been used. After normalizing the model output of $p\text{CO}_2$ to the year of 2010 (taking into account the increase in atmospheric $p\text{CO}_2$), climatological means of the seasonal $p\text{CO}_2$ cycle in the Bothnian Sea, the Northern Quark, and the Bothnian Bay (Figure 1) were created. As the data collected by Löffler et al. (2012) mainly come from off-shore waters with only a few measurements from the coastal zone, model data from areas shallower than 30 m (Figure 1) were not used in the comparison.

3. Results

In the following subsections, monthly climatological means (covering the period 1990–2010) for simulations REF and FIX (cf., section 2.3) are presented and validated against observations. For salinity, temperature, nutrients, and chlorophyll, model results have been extracted at positions of the F9-A13 and C3 stations,

which are the stations with the most available measurements, and that have physical and biogeochemical properties representative of the Bothnian Bay and Bothnian Sea, respectively. For the thermohaline structure, vertical profiles from the REF simulation are shown. The two simulations use the same physical parameters, and therefore do not differ from each other in physical properties. The sea-ice dynamics are validated in Pemberton et al. (2017). For the biogeochemical variables, we focus on the seasonal cycle in surface waters because of our specific aim to study plankton and nutrient dynamics as well as CO₂ fluxes between air and sea. Longer time series, and deepwater values of temperature, salinity, and biogeochemical properties, are presented supporting information Figure S1–S18. For primary production rates, the model is compared with measured rates at the F9-A13, B3, and C1 stations, to represent the Bothnian Bay, the Northern Quark, and the Bothnian Sea, respectively. No measurements of primary production exist at the C3 station.

3.1. Modeled Temperature and Salinity Fields

The observed temporal and spatial variability in temperature and salinity is generally well reproduced by the model (Figures 2 and 3), indicating that the model simulates realistic estuarine circulation. As in the observational data, the seasonal thermocline starts forming in May and breaks down in October at the F9-A13 station in the Bothnian Bay. At the C3 station in the Bothnian Sea, the seasonal thermocline starts developing already in April and lasts until November (Figure 2). There is a small positive salinity bias in the Bothnian Sea, while it is slightly negative in the Bothnian Bay (Figure 3), suggesting that the exchange between the two basins might be too low in the model. The observed halocline at about 50 m of depth is reproduced by the model, both in the Bothnian Sea and in the Bothnian Bay. The model also captures the weak freshening of the surface waters observed during summer.

3.2. Macro Nutrients

In the REF simulation, the surface winter concentrations of DIN ($NH_4^+ + NO_3^- + NO_2^-$), with higher concentrations in the Bothnian Bay and lower concentrations in the Bothnian Sea, correspond well to measured concentrations (Figure 4), although the concentration of DIN in the Bothnian Sea is about 2 mmol N m⁻³ too high. Similarly, for dissolved inorganic phosphorus (DIP, PO_4^{3-}), the model reproduces the very low observed concentrations in the Bothnian Bay and the higher concentrations in the Bothnian Sea, although there is a positive bias of 0.05 mmol P m⁻³ in the Bothnian Sea. These nutrient distributions result in high N:P ratios in the Bothnian Bay, well above 100, while the N:P ratios in the Bothnian Sea are quite close to the Redfield ratio (Figures 4c and 4d). The N:P ratios in the model agree well with the observations, although the deviations are larger in the Bothnian Bay. The very low DIP concentration in this basin means that a small bias in the concentration gives a large bias in N:P ratios.

The decrease of DIP and DIN at the F9-A13 and the C3 stations during the productive season is in general well reproduced in the REF run (Figure 5), although it tends to start earlier in the model than in the observations. At the F9-A13 station in the Bothnian Bay, the most limiting nutrient, phosphate, has been consumed in May. From Figure 5, it appears as if the model overestimates the DIP drawdown at this station. However, the detection limit for phosphate is approximately 0.01–0.02 mmol m⁻³ (Hansen & Koroleff, 1999), meaning that observed concentrations around these values cannot be distinguished from zero. As the winter concentrations of phosphate at this station lies around 0.04–0.05 mmol m⁻³, which is at the least twice as big as the detection limit, there is an uncertainty of about a factor of two in the DIP uptake. A lower DIP consumption, as would be the case if the actual phosphate concentration would be higher than 0.00 in summer, would require higher C:P and N:P uptake ratios of phytoplankton (up to the double as predicted by the model). Nevertheless, it does not affect the conclusions of this paper, which is discussed in section 4.3. The simulated uptake of DIN at the F9-A13 station continues until July, even though the phosphate is depleted, but it is not large enough to bring the simulated DIN concentrations down to the observed values. The difference between the winter and summer DIN concentrations at this station is 4 mmol N m⁻³ in the REF simulation, compared to the observed 6 mmol N m⁻³. At the C3 station in the Bothnian Sea, all nutrients in the surface water have been consumed in April. The low summer concentrations are maintained until October, when the autumn mixing sets in at both the C3 and the F9-A13 stations.

In the FIX experiment, the consumption of DIN is not large enough to bring the modeled concentrations down to observed levels (Figure 5), at any station. At the F9-A13 station in the Bothnian Bay the difference between the winter and summer DIN concentrations is less than 2 mmol N m⁻³ in the FIX experiment, compared to 6 mmol N m⁻³ difference in the observations. At the C3 station in the Bothnian Sea, the

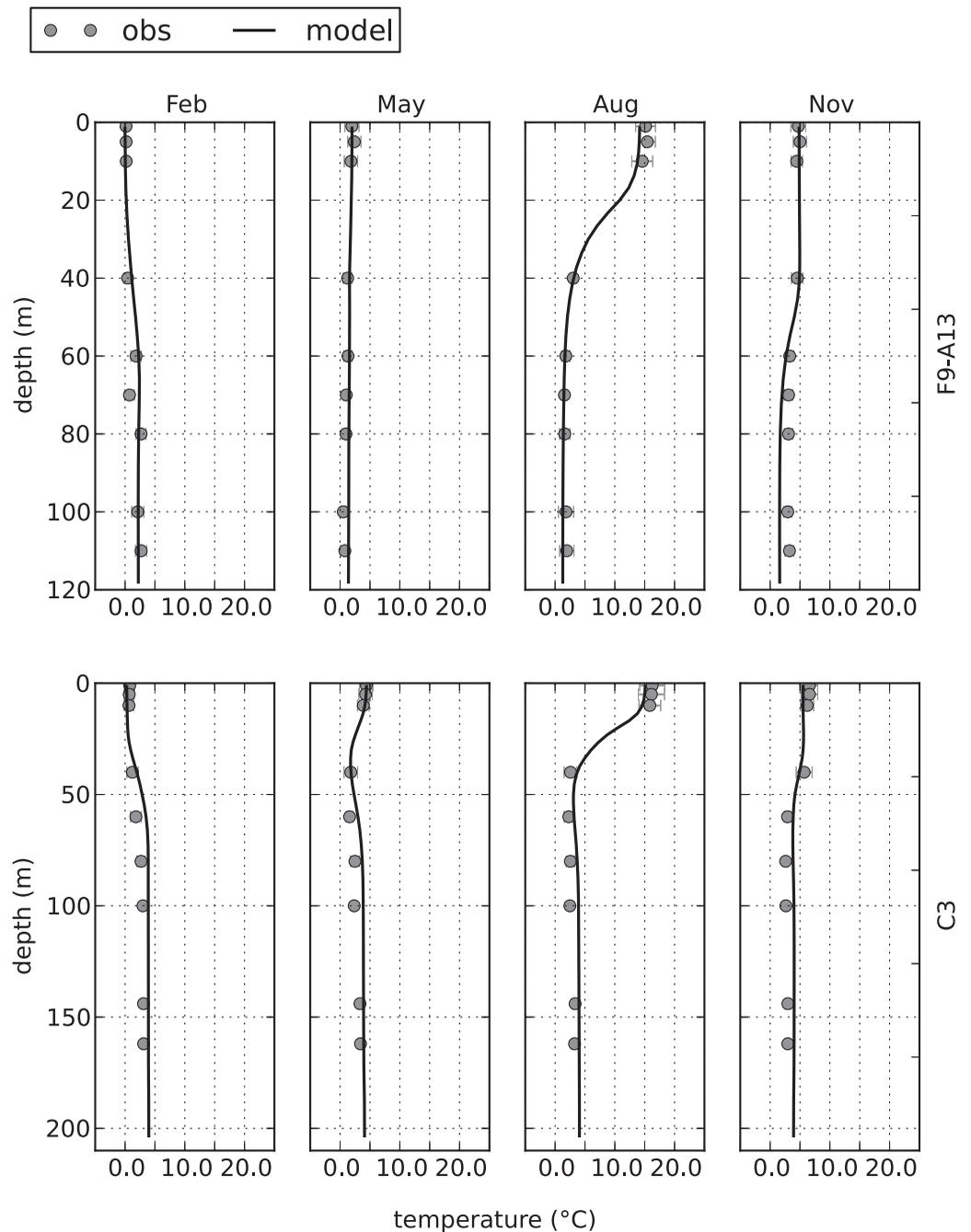


Figure 2. Monthly climatologies (1990–2010) of measured (grey circles) and modeled (black line) temperature profiles at the F9-A13 station in the Bothnian Bay (upper plot) and the C3 station in the Bothnian Sea (lower plot) for February, May, August, and November, respectively.

discrepancy with the observations is not as large as at F9-A13. Here the decrease in the DIN concentration during the spring bloom is of the same magnitude as in the observations. There is, however, an increase in the DIN concentrations during summer, in contrast to the observed concentrations that stay depleted until October. The heavily reduced nitrogen assimilation in the Bothnian Bay, and therefore reduced burial of nitrogen in the sediments, leads to an increase in the DIN concentration on a longer time scale (supporting information Figure S10 in the). This increase is also noticed in the Bothnian Sea as there is a large transport of DIN southward from the Bothnian Bay.

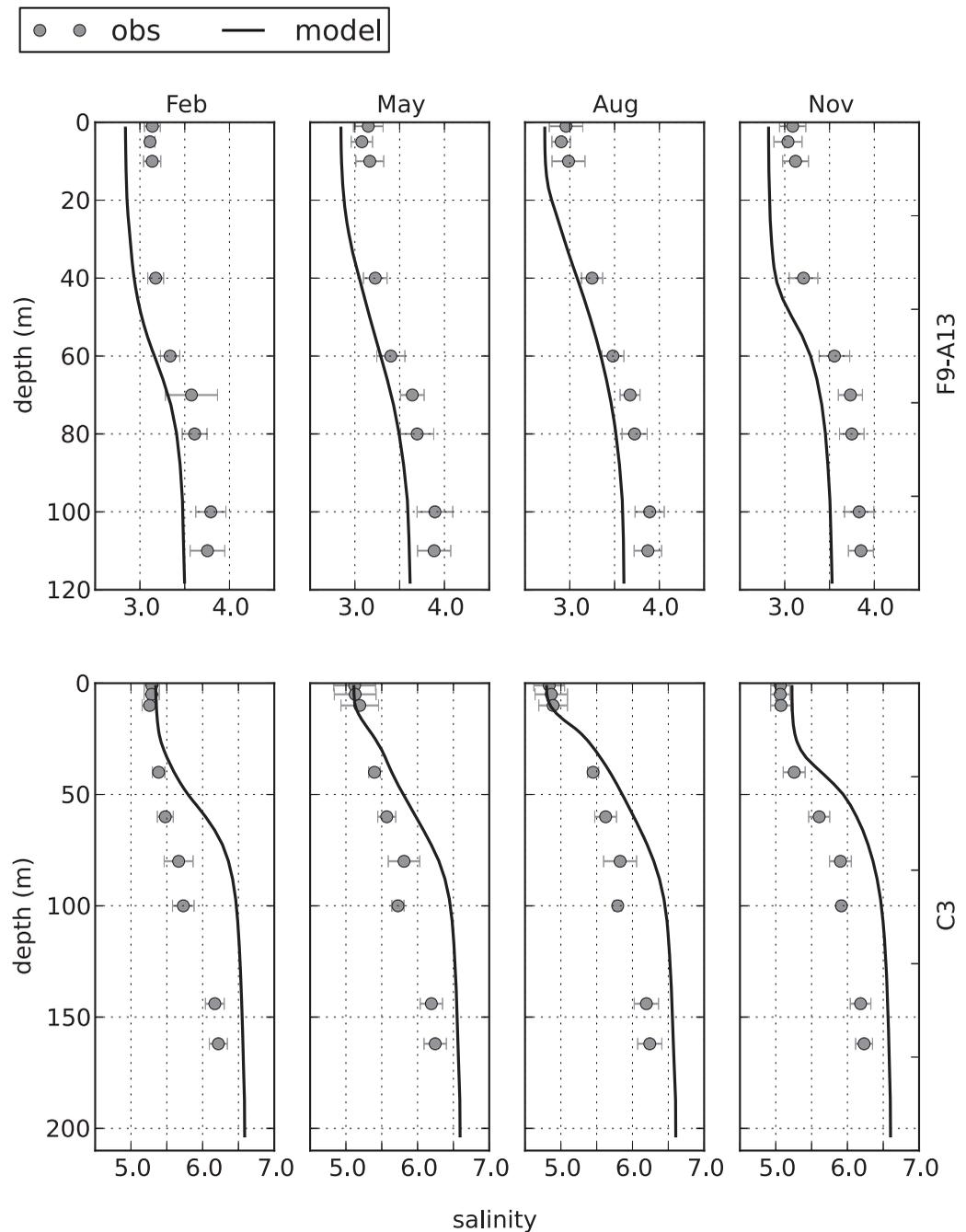


Figure 3. Monthly climatologies (1990–2010) of measured (grey circles) and modeled (black line) salinity profiles at the F9-A13 station in the Bothnian Bay (upper plot) and the C3 station in the Bothnian Sea (lower plot) for February, May, August, and November, respectively.

3.3. Chlorophyll

The modeled surface chlorophyll in the REF simulation is overall comparable with observations at the F9–13 and the C3 stations (Figure 5), indicating that the model satisfactorily reproduces the general phytoplankton cycle. As in the observations at the C3 station, the model simulates a spring bloom that reaches its peak in April. An autumn bloom can be observed with its modeled maximum between September and October, compared to the observed maximum in October. The model fails to reproduce the high chlorophyll values during the spring bloom at the C3 station. At the F9-A13 station, no distinctive spring bloom is simulated, consistent with the observations. Here the model overestimates the chlorophyll concentration in April.

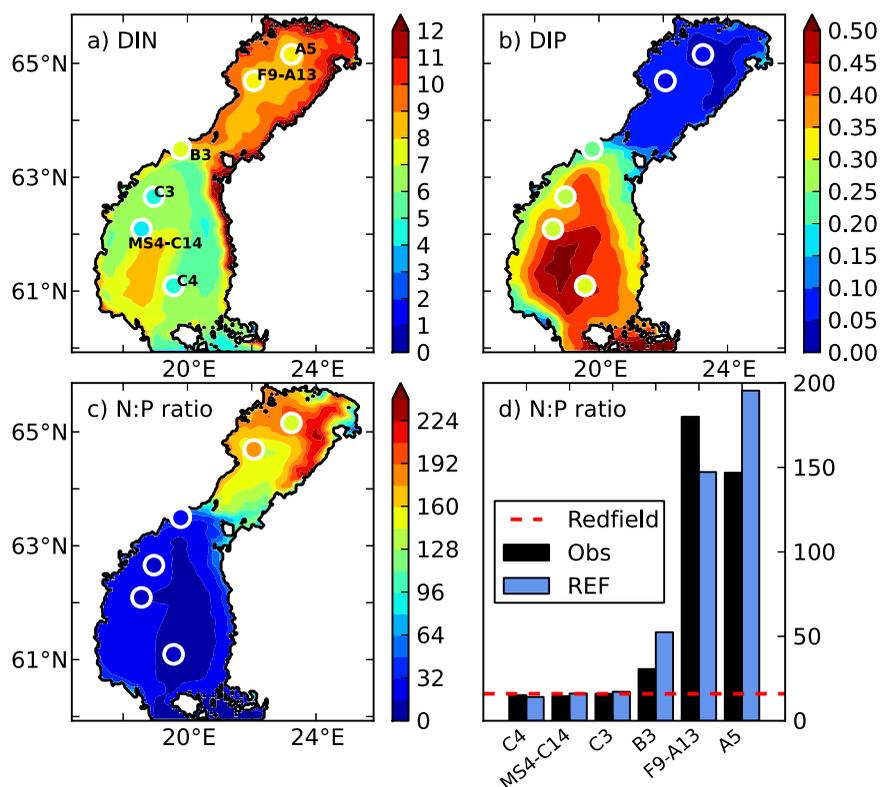


Figure 4. Surface water (0–10 m), (a) DIN (mmol N m^{-3}), (b) DIP (mmol P m^{-3}), and (c, d) N:P ratio, climatology (1990–2010) for February. Filled contours in Figures 4a–4c are modeled fields from the REF simulation, and filled circles are observed values. In Figure 4d modeled N:P ratios from the REF simulation (blue bars) are compared to observed N:P ratios (black bars) at each station. Dashed red line indicates the Redfield ratio (N:P = 16).

In the FIX experiment the chlorophyll concentrations are in general similar to those in the REF simulation and the observations (Figure 5). The productive season is somewhat longer in the FIX experiment compared to the REF experiment, which is probably a result of the reduction of loss terms in the fixed stoichiometry approach compared to variable stoichiometry approach (Appendix A6).

3.4. pCO_2 Dynamics

The modeled seasonal cycle of pCO_2 in the REF run compares in general well with the observations from Löffler et al. (2012), both regarding timing and amplitude (Figure 6), except for a too early start of the pCO_2 drawdown in the Bothnian Sea. In the Bothnian Bay the modeled pCO_2 values are higher than the observed ones during January, February, and March. This could result from a too strong blocking effect of the modeled sea-ice on the air-sea exchange of CO_2 , and that too much CO_2 from remineralized organic matter, therefore is accumulated under the sea-ice. Another possible explanation is that the observations are biased toward open waters, while the results include areas with both thick and thin ice. In addition, there could be a too large degradation of the excreted semilabile DOC in surface waters due to the absence of aggregation and sinking of this material in the model. In all basins the modeled pCO_2 values drop to values around 200–250 μatm in summer, and are slightly higher than the observed values in the Bothnian Bay and in the Bothnian Sea.

In the FIX experiment, the DIC assimilation is not large enough for the pCO_2 to reach the observed values (Figure 6). In the Bothnian Sea and the Northern Quark, there is a pCO_2 drawdown during the spring bloom, which is of similar magnitude as in REF, while there is barely any pCO_2 drawdown in the Bothnian Bay. During summer there is an increase in the pCO_2 in all subbasins, in contrast to the continuous drawdown in the REF run and the observations, as the modeled primary production is not large enough to counteract the effects of, for example, increasing temperatures, remineralization, and air-sea CO_2 exchange that thrives to equalize the pCO_2 in the sea and the atmosphere.

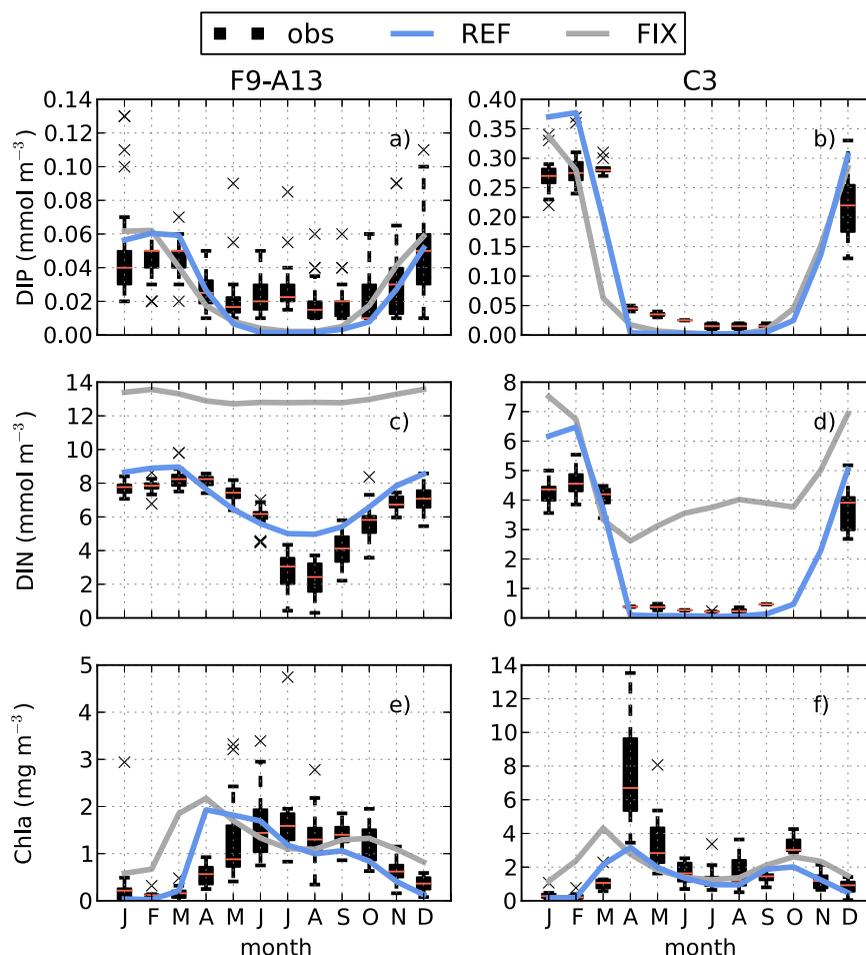


Figure 5. Modeled and observed seasonal cycle of (a, b) DIP, (c, d) DIN, and (e, f) chlorophyll a in surface waters (0–10 m) at the F9-A13 (left column) and the C3 station (right column). The modeled data are monthly means for the years 1990–2010. The observations are shown as box plots, showing the medians (red line), upper and lower quartiles (extent of box), range (extent of whiskers), and outliers (crosses), for each month.

3.5. Primary Production

The annual depth-integrated carbon fixation, or production of total organic carbon (DOC and POC), in the REF run is 90, 152, and 236 g C m⁻² y⁻¹ for the Bothnian Bay, the Quark, and the Bothnian Sea, respectively (Table 2). In the POC, we include both living (algal biomass) and nonliving particulate organic carbon. A substantial part of the fixed carbon is directly exuded as semilabile extracellular DOC due to carbon overflow (52, 37, and 26% for the BB, the NQ, and the BS, respectively, not shown). The relative extracellular release is higher in the Bothnian Bay due to the more nutrient limiting conditions. When comparing the modeled total organic carbon production to rates measured by the ¹⁴C method, which contains the production of both DOC and POC, it appears as if the REF simulation overestimates the primary production (Figure 7), despite the good agreement between the modeled and observed pCO₂. However, when looking closer into the seasonal variations in the primary production and only comparing the modeled production of POC to the observed production, the modeled production in REF agrees remarkably well with the measured rates at the F9-A13 and B3 stations (Figure 7), even though the observed production should contain the production of both POC and DOC. At the C1 station the modeled productive season seems to be too long compared to observations, although the modeled chlorophyll dynamics in REF at the nearby station, C3, agrees well with observations regarding the timing, and the spring bloom peak at this station is even underestimated. During summer (from May to September), on the other hand, the pattern is similar as at the other two stations in the Bothnian Bay and the Northern Quark: if only the production of POC is considered, the modeled production of organic carbon in REF agrees well with observed production rates.

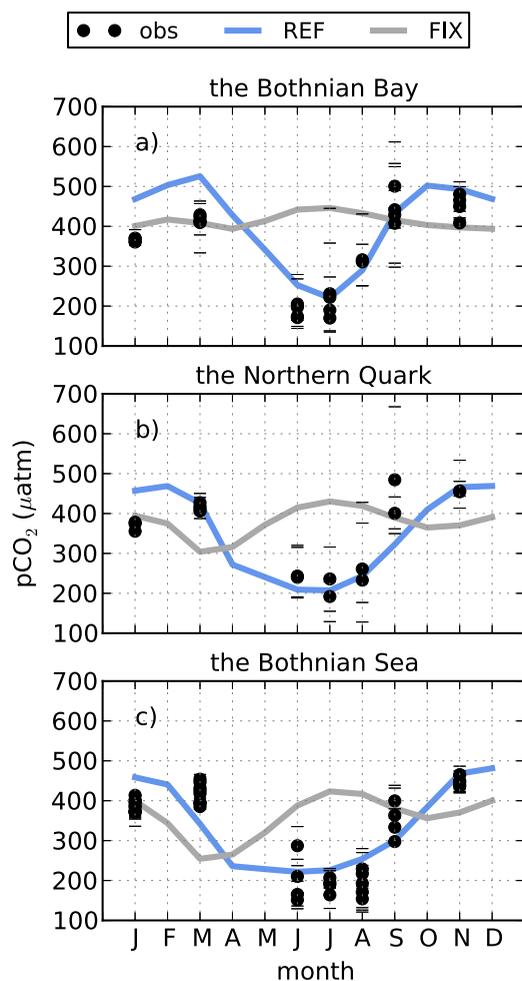


Figure 6. Modeled and observed seasonal cycle of $p\text{CO}_2$ in (a) the Bothnian Bay, (b) the Northern Quark, and (c) the Bothnian Sea. The modeled data are a climatology for each subbasin for the upper 0–6 m between 1990 and 2010. The observations come from Löffler et al. (2012) and were collected between 1998 and 2010 at 4–6 m of depth. The black dots show the observed means, and the black lines show the observed maximum and minimums.

and nutrient assimilation, as well as physiological plasticity of nutrient storage, must be taken into account to adequately simulate nutrient and $p\text{CO}_2$ dynamics in the Gulf of Bothnia. While a flexible N:P ratio is more important for simulating the nutrient dynamics, flexible C:nutrient ratios and production of extracellular DOC are more important for the carbon fixation and $p\text{CO}_2$ dynamics.

Regarding the nutrient dynamics, the model with fixed stoichiometry underestimates the drawdown of nitrogen in the Bothnian Bay (Figure 5), where the observed winter N:P ratio deviates far from the Redfield ratio (Figure 4). This gives rise to unrealistically high concentrations of DIN in the basin and too large export

of it from the Bothnian Bay to the Bothnian Sea. Edman and Andersson (2014) demonstrated a similar problem in the Bothnian Bay in their model with fixed phytoplankton stoichiometry. A behavior like this is to be expected, as the internal N:P ratios in phytoplankton tend to deviate from the Redfield ratios during nutrient limitation, as pointed out and discussed thoroughly by e.g., Flynn (2003, 2010). In the simulation with variable stoichiometry, the internal N:P ratio of the phytoplankton reaches values as high as 140 at the F9 station in the Bothnian Bay (Figure 8), enabling higher uptake of DIN than in

In the FIX experiment the total organic carbon production is considerably lower than in REF (Table 2), which can be expected from the weaker $p\text{CO}_2$ drawdown during the productive season (Figure 6). The primary production in the FIX simulation agrees on the other hand better with the observed one (Figure 7).

3.6. Stoichiometry

The results presented in this section, and the conflicting mismatch between the $p\text{CO}_2$ and primary production, will be further discussed in section 4.2.

In the REF simulation, the assimilation of carbon and the lesser-limiting nutrients do not stop when the most limiting nutrient is depleted, which enables a higher nitrogen and carbon assimilation than in the FIX experiment. The uncoupling of nutrient assimilation results in seasonal deviations in the phytoplankton N:P stoichiometry (Figure 8), while the uncoupling of nutrient and carbon assimilation results in variations in the C:nutrient ratios, and the production of extracellular DOC.

At the F9-A13 station, where phosphate is the most limiting nutrient, the internal N:P and C:P ratios increase during the productive season as a response to the low phosphate concentration and the continuous DIN and DIC assimilation, and reach their maximum values of 140 and 530, respectively, in July. The internal C:N ratio at the F9-A13 station shows almost no seasonality and is always below the optimal C:N ratio, indicating that DIN exists in excess and that there is a luxury consumption of this nutrient.

At the C3 station the N:P ratio slightly increases during summer, showing that DIP is more limiting than DIN. In contrast to the F9-C3 station, the N:P ratio stays quite close to the Redfield ratio of 16, which indicates that also DIN is limiting the phytoplankton. The limiting effect of both DIN and DIP is also mirrored in the C:P and C:N ratios, which both increase during the summer due to the continuous carbon fixation in absence of DIP and DIN, to reach values of 470 and 20, respectively.

4. Discussion

4.1. The Importance of Phytoplankton Stoichiometric Plasticity

The results presented above, demonstrate that uncoupling of carbon and nutrient assimilation, as well as physiological plasticity of nutrient storage, must be taken into account to adequately simulate nutrient and $p\text{CO}_2$ dynamics in the Gulf of Bothnia. While a flexible N:P ratio is more important for simulating the nutrient dynamics, flexible C:nutrient ratios and production of extracellular DOC are more important for the carbon fixation and $p\text{CO}_2$ dynamics.

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Table 2

Total Organic Carbon Production (1990–2010) in $\text{g C m}^{-2} \text{y}^{-1}$ in the REF and FIX Experiments

Basin	BB	NQ	BS	Total
REF	90	152	236	180
FIX	16	54	136	87

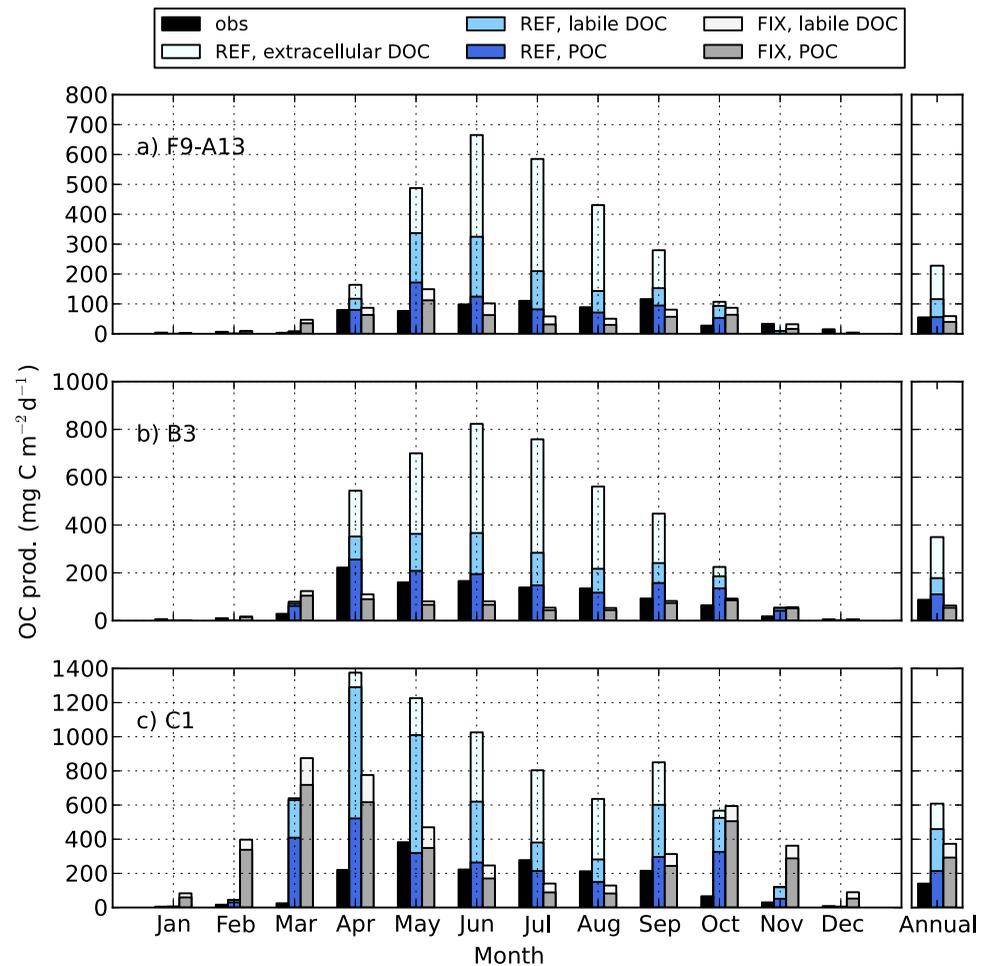


Figure 7. Modeled (for experiments REF and FIX, climatology for 1990–2010), and observed (all available data between 1990 and 2010) depth integrated annual primary production. The column to the left shows monthly values, and the column to the right annual means. For the REF experiment, the modeled primary production has been divided into the production of POC (including algal biomass and nonliving POC), labile and semilabile (extracellular) DOC. For the FIX experiment, where there is no production of extracellular DOC, the modeled production has been divided into the production of POC and labile DOC.

FIX, which results in better agreement with observations. However, this is in the extreme upper end of phytoplankton N:P ratios that have been observed in experimental studies. Goldman et al. (1979) grew phytoplankton in media with various N:P ratios, and they measured N:P ratio of 115, during P-limitation. It is possible that a part of the fixed nitrogen is released in the phytoplankton exudates (Pujo-Pay et al., 1997), which would lower the internal N:P ratios needed to reproduce the nitrogen drawdown. Sensitivity simulations (not shown) have further shown that the use of organic P can lower the simulated phytoplankton N:P ratios considerably. To our knowledge, there are no measurements of phytoplankton stoichiometry in the Gulf of Bothnia that could be used to validate the model. Pertola et al. (2002) reported an N:P ratio of 21 in the POM from three measurements around midsummer 1999 in the Gulf of Bothnia, which is much lower than the N:P ratios of our modeled phytoplankton. The N:P ratio in POM is, however, also influenced by other factors such as preferential remineralization, the stoichiometry of zooplankton, and aggregating allochthonous DOM.

Not surprisingly, the fixed-stoichiometry approach manages to simulate well the drawdown of nitrogen during the spring bloom in the Bothnian Sea, where the winter N:P ratio is close to the Redfield ratio (Figures 4 and 5). In the variable-stoichiometry approach, the internal N:P ratio of the phytoplankton stays quite close to the Redfield ratio at the C3 station (Figure 4), indicating that phosphorus and nitrogen both have a limiting effect on the modeled phytoplankton in the Bothnian Sea, and that the variable internal N:P ratio does

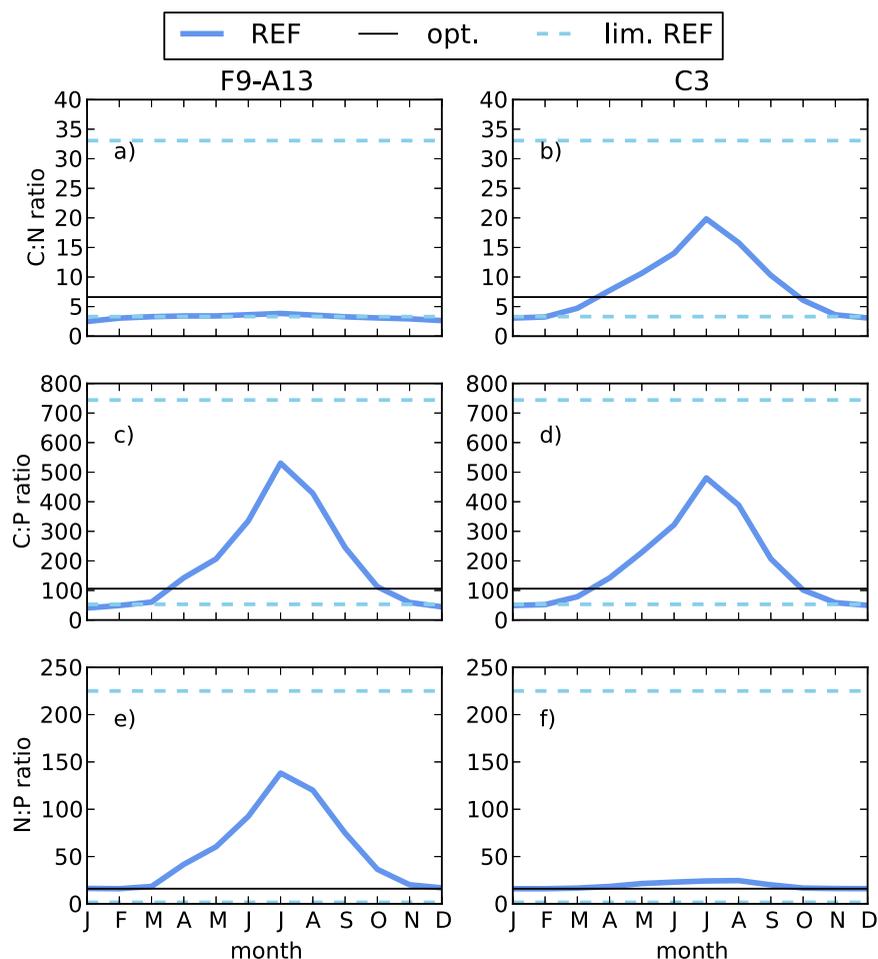


Figure 8. Modeled 20 year mean (1990–2010) of the seasonal evolution of phytoplankton C:N, C:P, and N:P ratios at the F9-A13 and C3 station, respectively, in the REF experiment. The dashed blue lines indicate the limits in REF, respectively, and the black line shows the optimal ratio (Redfield).

not play a crucial role for the nutrient dynamics in this subbasin. A problem in the fixed-stoichiometry approach arises during the summer months, under nutrient limiting conditions, when FIX cannot keep DIN concentrations at the lower levels (Figure 5) due to an apparent underestimation of the summer production.

The variable-stoichiometry approach reproduces well the observed drawdown of the $p\text{CO}_2$ during the productive season, due to the continuous DIC assimilation also in absence of nutrients. The fixed-stoichiometry approach, on the other hand, only manages to simulate the $p\text{CO}_2$ dynamics during the spring bloom in the Bothnian Sea and the Northern Quark, i.e., during nutrient replete conditions. During summer, it shows an unrealistic increase of the $p\text{CO}_2$ (Figure 6) as the carbon fixation is not large enough to counteract the effects of increasing temperatures, remineralization, and air-sea exchange on the $p\text{CO}_2$. In the variable-stoichiometry approach, the internal C:N and C:P ratios of the phytoplankton reach values several times higher than the Redfield ratio; up to 22 and 550, respectively (Figure 8), contributing to the higher primary production and DIC assimilation than in the FIX experiment. Pertola et al. (2002) measured C:N and C:P ratios in POM in the Gulf of Bothnia reaching up to 14 and 338, respectively, suggesting that the phytoplankton internal ratios could deviate far from the Redfield ratios. It is, however, not only the flexible internal ratio of carbon to nutrients that plays an important role for the $p\text{CO}_2$ drawdown in the REF simulation; a substantial part, 26, 37, and 52% of the fixed carbon, is released as extracellular carbohydrates (semilabile DOC) in the Bothnian Sea, the Northern Quark, and the Bothnian Bay, respectively. This is comparable to the observed extracellular release that comprised 48, 45, and 50% of the primary production at stations in

Table 3
Modeled Air-Sea CO₂ Exchange (1990–2010) in g C m⁻² y⁻¹ in Simulations REF and FIX, and Calculated Air-Sea Exchange in Löffler et al. (2012) (Obs.)

Basin	BB	NQ	BS	Total
REF	-6.5	16.2	22.7	13.3
FIX	-11.9	3.6	17.9	7.0
Obs.	-1.4 to -2.5		5.9–17.05	

and its functioning as a sink of atmospheric CO₂ (Table 3). The net CO₂ uptake for the whole Gulf of Bothnia is reduced by 47% compared to the variable-stoichiometry approach. The difference in the net uptake of atmospheric CO₂ between the two simulations could increase, if there is any aggregation and sedimentation of the extracellular DOC. Schartau et al. (2007) suggested that up to 63% of the excreted extracellular DOC can become subject of aggregation into particulate material.

4.2. Missing Link in the Carbon Cycle

The modeled primary production needed to reproduce the pCO₂ dynamics exceeds the measured values by up to 400% at stations F9-A13, B3, and C1 (Figure 7), which at a first glance seems contradictory. Could this discrepancy be due to biases or poorly constrained/missing processes in the model? Biases in alkalinity could for example affect the simulated pCO₂. Unfortunately, there are not enough measurements from the

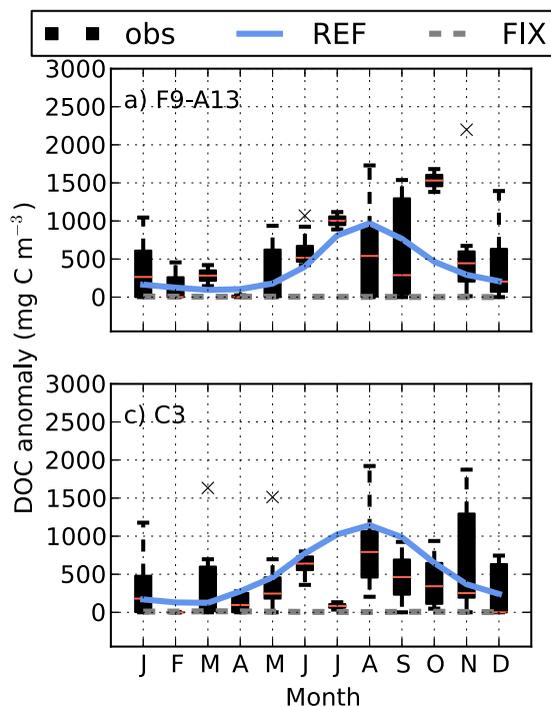


Figure 9. Modeled and observed seasonal cycle of DOC in surface waters (0–10 m) at the (a) F9-A13, and (b) C3 stations. We have chosen to compare with DOC comparisons at offshore stations where seasonal variations in terrestrially derived DOC are negligible. The modeled DOC consists of monthly means (1990–2010) of the labile and semilabile marine produced DOC (the terrestrial DOC has been removed). The observed DOC is shown as a box plot, showing the anomaly from a background concentration (calculated as the minimum DOC concentration in each year containing observations). The red lines show the medians, the extent of the boxes show the upper and lower quartiles, the extent of the whiskers show the range of the data, and the crosses show the outliers.

the three different subbasins (Sandberg et al., 2004). Other model experiments simulating carbon dynamics in mesocosm experiments and in the North Sea, some of them including the production of extracellular DOC, have likewise pointed out that C:nutrient ratios higher than the Redfield ratio are needed in order to accurately model the carbon fixation and the buildup of organic carbon (Ayata et al., 2013; Flynn, 2003, 2010; Prowe et al., 2009; Schartau et al., 2007).

The lower primary production with the fixed-stoichiometry formulation, compared to the variable-stoichiometry formulation, has a considerable effect on the air-sea CO₂ exchange in the Gulf of Bothnia

and its functioning as a sink of atmospheric CO₂ (Table 3). The net CO₂ uptake for the whole Gulf of Bothnia is reduced by 47% compared to the variable-stoichiometry approach. The difference in the net uptake of atmospheric CO₂ between the two simulations could increase, if there is any aggregation and sedimentation of the extracellular DOC. Schartau et al. (2007) suggested that up to 63% of the excreted extracellular DOC can become subject of aggregation into particulate material.

The modeled primary production needed to reproduce the pCO₂ dynamics exceeds the measured values by up to 400% at stations F9-A13, B3, and C1 (Figure 7), which at a first glance seems contradictory. Could this discrepancy be due to biases or poorly constrained/missing processes in the model? Biases in alkalinity could for example affect the simulated pCO₂. Unfortunately, there are not enough measurements from the entire time period to validate its behavior on a longer time scale (supporting information Figures S7 and S16). Further, if the model for example simulates a too fast recycling of recently fixed carbon in the surface waters (meaning that a large part of the recently fixed carbon is returned to its inorganic form), compared to the recycling of nutrients, it would give the appearance that a larger primary production is needed to simulate the pCO₂ drawdown. In the model the labile DOM have a turnover time of 1 day and is recycled fast in the surface waters, but the production of it and its C:nutrient ratios are difficult to validate. However, even if not considering the production of labile DOC, the organic carbon production predicted by the model exceeds the observed one by up to 300% (Figure 7).

When comparing the modeled DOC in the experiments with the few existing DOC measurements in the Gulf of Bothnia, it is apparent that the modeled seasonal evolution of semilabile DOC in the REF experiment lies within the observed ranges of DOC, suggesting that the modeled production of semilabile DOC through carbon overflow is reasonable (Figure 9). Due to the fast turnover time of labile DOC, it is mainly the semilabile DOC that contributes to this seasonal DOC accumulation. Because the production of semilabile DOC in the REF simulation is higher than the observed total carbon production in the Bothnian Bay, and of similar magnitude as the observed production in the Bothnian Sea (Figure 7), this suggests that the observed primary production not only is too low to explain the seasonal pCO₂ cycle, but also is too low to explain the observed seasonal evolution of DOC. In the FIX experiment, where there is no production of semilabile DOC (due to the absence of carbon overflow) and only a production of labile DOC, the modeled DOC concentrations are much lower the observed ones (Figure 9).

While comparing modeled pCO₂ and DOC with measured pCO₂ and DOC in the surface water is more direct, there are several complicating factors associated with comparisons between simulated and measured

rates of primary production. The interpretation of results produced with the ^{14}C method is not straightforward, and the results depends on e.g. the length of the incubation, if the samples are filtered or not, light source (Andreasson et al., 2009; Elmgren, 1984; Larsson et al., 2010; Shulenberger & Reid, 1981). An intercalibration study from the Baltic Sea has revealed that measured rates of primary production can differ at least by a factor of three depending on method, and by a factor of two between different laboratories using the same method (Andreasson et al., 2009). The data, we use come from the protocol producing the lowest primary production in this intercalibration study, suggesting that they might underestimate the actual primary production. Another possible explanation to the higher production in the model compared to the observations can be found in Yacobi et al. (2007), who observed that a large production of extracellular DOC resulted in underestimations of the primary productivity measured with the ^{14}C method. They suggested that the extracellular DOC forms a coat on phytoplankton cells, slowing down the diffusion of ^{14}C into the cells. Indeed, it is especially during nutrient limitation when the largest production of extracellular DOC takes place in the model, that the differences between the observed and modeled organic carbon production is the largest.

Interestingly, the modeled pelagic primary production agrees better with the one measured with the ^{14}C method if only considering the production of POC (Figure 7). Vichi and Masina (2009) got similar results in a study with a BFM setup for the global ocean: when they excluded the modeled production of extracellular DOC, their modeled primary production agreed better with the measured one. They found a mechanistic explanation for it as the primary production data they compared to had been filtered, and thus only contained the production of POC. However, the primary production data we use have not been filtered and should contain the production of both POC and DOC, making the good agreement between the modeled POC production and observed production intriguing. Tedesco et al. (2017) obtained similar results with BFM when modeling sea-ice primary production in the Bothnian Bay. Their modeled production of POC agreed well with the total organic carbon production, measured with the same method as the primary production data used in this study. In the inter-calibration study from the Baltic Sea, where different ^{14}C methods were compared (Andreasson et al., 2009), it was shown that the method used to measure the TOC production rates, which are used in this study and in Tedesco et al. (2017), produced similar, or even lower primary production rates, compared to another method measuring POC production rates. No clear explanation for this inconsistency was given, and it was suggested that more investigations in this matter is needed. Nevertheless, it hints that the measured rates that we compare to could be closer to POC production rates than TOC production rates.

Our results suggest that there is a substantial part of the organic carbon production, and thus an important link in the carbon cycling in the pelagic Gulf of Bothnia, that is not captured with the ^{14}C method, nor with fix-stoichiometry models. Tuning models to fit primary production measured with the ^{14}C method, or using the Redfield ratio to determine carbon assimilation, can therefore lead to large underestimations of the organic carbon production, and would also lead to misleading results when modeling higher tropics levels and bacterial production.

4.3. Uncertainty Analysis

Comparing different model parameterizations is not straightforward. There are many parameters that can be tuned in order to improve/change the results of a simulation. For the REF and the FIX experiments, we kept the same parameters unless otherwise indicated. We additionally performed some sensitivity experiments where we varied the parameters specific for the FIX simulation (half-saturation constants for nutrient limitation and partitioning into dissolved and particulate organic matter). The partitioning into dissolved and particulate organic matter had negligible effects on the simulated results. The half-saturation constant for nutrient limitation was regulated to minimize the difference in the assimilation of the most limiting nutrient (DIP) between the FIX and the REF experiments. Because the uptake of carbon and lesser limiting nutrients is dependent on the uptake of the most limiting nutrient in fixed-stoichiometry formulations, it is important that the assimilation of P is similar in the FIX and REF experiments to get a reliable comparison of the C-assimilation and the air-sea CO_2 exchange. With the half-saturation constant of P-limitation set to $0.01 \text{ mmol P m}^{-3}$, the DIP assimilation differs by only 2% from the REF experiment, if computing for the whole domain. In the Bothnian Bay, on the other hand, the DIP assimilation is 11% lower than in REF. The sensitivity experiments did however show that this has minor effects on the pCO_2 dynamics and the air-sea CO_2 exchange in this area, which can be related to the larger remineralization of terrestrial DOC in the North (Fransner et al., 2016). The high C:P and N:P ratios needed to simulate the pCO_2 and nutrient dynamics in the Bothnian Bay, and the C:nutrient

ratios to simulate the $p\text{CO}_2$ in the Bothnian Sea, strongly suggest the need for variable stoichiometry models in order to adequately simulate the biogeochemical cycles in this region.

Because the detection limit of phosphate is 0.02, we cannot be sure that the phosphate is consumed down to 0.00 as predicted by the model; the summer phosphate concentrations can lie anywhere between 0.00 and 0.02. If the summer phosphate concentrations only are at 0.02, this would imply that a lower phosphate consumption take place, which would require even higher internal N:P and C:P ratios in the phytoplankton to reproduce the observed $p\text{CO}_2$ and macronutrient dynamics, and that the underestimation of DIC and DIN assimilation by fix-stoichiometry models would be even larger. More precise measurement techniques for phosphate are needed to go further into the stoichiometric dynamics in the Bothnian Bay.

Preferential remineralization and uptake of organic nutrients by phytoplankton are often presented as alternative explanations to consumption of nutrients and carbon in non-Redfieldian ratios. By allowing phytoplankton to use organic nutrients in a Baltic Sea model, Edman and Andersson (2014) obtained a slight improvement in the modeled $p\text{CO}_2$ and nutrient seasonal cycles in the Bothnian Bay, but it was not enough to explain the observed dynamics. Additional experiments with the model setup used in this study have, on the other hand, shown that organic nutrients can have a substantial effect on the modeled phytoplankton stoichiometry (not shown). However, the stoichiometry still deviates far from the Redfield ratio. This illustrates that organic matter dynamics alone is insufficient to resolve the seasonal nutrient cycles. The influence of organic nutrients on phytoplankton dynamics and their stoichiometry is subject that needs more research.

4.4. Future Perspectives

In this process study, we have focused on the importance of the decoupling of nutrient and carbon assimilation for seasonal nutrient and $p\text{CO}_2$ dynamics in the Northern Baltic Sea. The variable stoichiometry comes as a result of this decoupling, but we are not attempting to give a precise description of the phytoplankton stoichiometry in the area. There are also other factors that can influence the cellular C:N:P ratios, such as temperature and light conditions, as well as the growth phase and the growth strategy of phytoplankton, which are not included in BFM. For example, the intracellular content of P is known to be influenced by the concentration of P-rich ribosomes with their associated rRNA (Elser et al., 2003; Hillebrand et al., 2013). The optimal N:P ratio (meaning the optimal for maximum growth), which in our simulations is set to the Redfield ratio for all four phytoplankton groups, is known to depend on the growth strategy of phytoplankton and to vary between species. Fast growing phytoplankton tend to have a lower optimal N:P ratio than the canonical N:P of 16 (Arrigo, 2005), which is addressed in the model of Klausmeier et al. (2004). Temperature has been demonstrated to affect the concentration of ribosomes; at a constant protein synthesis, relatively more ribosomes are needed at low temperature which is reflected in the stoichiometry (Toseland et al., 2013), and results in changing stoichiometry ratios at different latitudes (Martiny et al., 2013). More micro and mesocosm studies along with other methods to measure organic carbon production, and model development, are needed to determine the relative effects of each factor on the phytoplankton, nutrient, and carbon dynamics in the Gulf of Bothnia. Further, sensitivity experiments on the specific parameters of the nutrient uptake should also be considered (in particular, the maximum allowed quota as well as the relaxation terms).

5. Conclusions

The objectives of this study were to present a new coupled physical-biogeochemical model with variable stoichiometry for the Gulf of Bothnia, to explore how phytoplankton stoichiometric flexibility could explain seasonal cycles in $p\text{CO}_2$ and macronutrients in the area, and how important it is for the organic carbon production and atmospheric CO_2 uptake. Our conclusions are:

1. By simulating a phytoplankton stoichiometry deviating far from the Redfield ratio, and the production of extracellular DOC, the model adequately reproduces seasonal variations in nutrient concentrations and $p\text{CO}_2$ in the Gulf of Bothnia.
2. The primary production needed to reproduce the observed drop in $p\text{CO}_2$ exceeds the measured primary production by up to 400%, suggesting that the organic carbon production in the Gulf of Bothnia may be higher than previous estimates.
3. Not accounting for the stoichiometric flexibility of phytoplankton results in a large underestimation of the atmospheric CO_2 uptake.

Appendix A: Model Equations

Here, the model equations relevant for this work are presented. For more details the reader is referred to Vichi et al. (2015b).

A1. Parameterization of Terrestrial Organic Matter

The terrestrial organic matter is introduced as a new state variable $R_{c,n,p}^{(7)}$. It is subject to a linear decay rate λ with a time scale of 1 year (Fransner et al., 2016). The decayed material ends up in the inorganic carbon, and the ammonium and phosphate pools:

$$\left. \frac{dR_c^{(7)}}{dt} \right|_{O^{(3)}}^{dec} = \lambda R_c^{(7)} \quad (A1)$$

$$\left. \frac{dR_n^{(7)}}{dt} \right|_{N^{(4)}}^{dec} = \lambda R_n^{(7)} \quad (A2)$$

$$\left. \frac{dR_p^{(7)}}{dt} \right|_{N^{(1)}}^{dec} = \lambda R_p^{(7)}. \quad (A3)$$

A2. Light Parameterization

The influence of CDOM on the light extinction is modulated through the specific attenuation coefficient for CDOM (k_{CDOM}) which is parameterized as a function of salinity:

$$k_{CDOM} = \text{MAX}(0.1, 0.5 - 0.06 \cdot S), \quad (A4)$$

where S is the modeled salinity.

A3. Carbon Fixation in the REF Experiment

The gross primary production (gpp), i.e., the carbon fixation, is calculated as follows:

$$\left. \frac{dP_c}{dt} \right|_{O^{(3)}}^{gpp} = f_p^T f_p^E f_p^{PP} r_p^0 P_c, \quad (A5)$$

where f_p^T , f_p^E , and f_p^{PP} are functions of temperature, light, and the concentrations of nonstorable nutrients (silica in this configuration), respectively, r_p^0 is the maximum specific phytoplankton growth rate, and P_c is the phytoplankton carbon biomass.

The net primary production, G_p , is calculated as the gross primary production minus the carbon loss terms:

$$G_p = \max \left(0, \left. \frac{dP_c}{dt} \right|_{O^{(3)}}^{gpp} - \left. \frac{dP_c}{dt} \right|_{R_c^{(7)}}^{exu} - \left. \frac{dP_c}{dt} \right|_{O^{(3)}}^{rsp} - \left. \frac{dP_c}{dt} \right|_{R_c^{(7)}}^{lys} \right), \quad (A6)$$

where the first term on the left-hand side is the gross primary production (gpp), the second term is losses due to exudation (exu), the third term is losses due to respiration (rsp), and the last term represent losses due to lysis (lys).

A4. Nutrient Uptake for the REF Experiment

The uptake of phosphorus is calculated as the minimum of the maximum potential uptake of available phosphorus in the water, and the maximum amount of phosphorus that can be assimilated without exceeding the maximum P:C ratio in the cell:

$$\left. \frac{dP_p}{dt} \right|_{N^{(1)}}^{upt} = \min \left(a_p N^{(1)} P_c, p_p^{\max} G_p + v_p \left(p_p^{\max} - \frac{P_p}{P_c} \right) P_c \right), \quad (A7)$$

where a_p is the affinity for phosphate and $N^{(1)}$ is the phosphate concentration in the surrounding water, p_p^{\max} is the maximum internal P : C ratio, G_p is the net primary production (equation (A6)), v_p is a restoration term to replenish the missing quota, and P_p/P_c is the current phytoplankton P : C ratio. The first expression on the right-hand side represents the available phosphorus in the water, the second term the amount of phosphorus that can be bound to replenishment of recently fixed carbon, and the third term on the right-hand side represents the amount of phosphorus that can be used to replenish missing cellular phosphorus, or that has to be

released due to excess luxury assimilation. This third term is analogous to the Droop (Droop, 1973) formulation in its dependence of a physiological rate on nutrient quota. In our case it regulates the rate of replenishment/release of missing/excess cellular nutrients, while in the Droop model it regulates the rate of growth of phytoplankton.

The formulation of the nitrogen uptake is the same as for phosphorus, except for the presence of two species; nitrate and ammonium, and the maximum potential uptake of inorganic nitrogen is calculated as the sum of the available ammonium and nitrate:

$$\sum_{j=3,4} \frac{dP_n}{dt} \Big|_{N^{(j)}}^{upt} = \min \left(\left(\frac{h_p^n}{h_p^n + N^{(4)}} + N^{(4)} \right) a_N P_c, n_p^{\max} G_p + v_p \left(n_p^{\max} - \frac{P_n}{P_c} \right) P_c \right), \quad (A8)$$

where a_N is the affinity for inorganic nitrogen and $N^{(4)}$ and $N^{(3)}$ are the ammonium and nitrate concentrations in the surrounding water, respectively. In BFM the state variable for nitrate $N^{(3)}$ is assumed to also include nitrite. The affinity for nitrate decreases with increasing ammonium concentrations, which is regulated with a saturation function (Vichi et al., 2015b). n_p^{\max} and P_n/P_c is the maximum and current internal phytoplankton $N : C$ ratio, respectively.

A5. Nutrient Limitation in the REF Experiment

In BFM, the nutrient status (or nutrient limitation) of phytoplankton is expressed on a quota form:

$$f_p^p = \min \left(1, \max \left(0, \frac{P_p/P_c - p_p^{\min}}{p_p^{\text{opt}} - p_p^{\min}} \right) \right) \quad (A9)$$

$$f_p^n = \min \left(1, \max \left(0, \frac{P_n/P_c - n_p^{\min}}{n_p^{\text{opt}} - n_p^{\min}} \right) \right), \quad (A10)$$

where f_p^p , f_p^n , and $f_p^{n,p}$ are the phosphorus and nitrogen limitation terms, respectively, ranging from close to 0 at nutrient limitation and 1 at nutrient replete conditions. P_p/P_c , p_p^{opt} , and p_p^{\min} are the simulated, optimal, and minimum phytoplankton C:P quota, and P_n/P_c , n_p^{opt} , and n_p^{\min} is the simulated, optimal, and minimum phytoplankton C:P quota, respectively. The nutrient status of the phytoplankton affects the lysis of the phytoplankton cells (fourth term in equation (A6)), the exudation of carbohydrates (which is contained in the second term in equations (A6)), sinking, and the chlorophyll synthesis. Nutrient limitation is in other words affecting the phytoplankton gross production indirectly by reducing the phytoplankton carbon biomass (P_c) and therefore the carbon fixation term in equation (A5).

For the postbloom phytoplankton functional groups, another parameterization for carbohydrate exudation (carbexu) is used, which is formulated as a function of the N:C and P:C ratios of the recently assimilated material, and also partially on the nutrient status of the cell (Vichi et al., 2004):

$$\frac{dP_c}{dt} \Big|_{R_c^{(j)}}^{\text{carbexu}} = G_p - G_p^{\text{bal}}, \quad (A11)$$

where

$$G_p^{\text{bal}} = \max \left(0, \min \left(G_p, \frac{1}{n_p^{\min}} \sum_{j=3,4} \frac{dP_n}{dt} \Big|_{N^{(j)}}^{upt} + \text{rest}_n, \frac{1}{p_p^{\min}} \frac{dP_p}{dt} \Big|_{N^{(1)}}^{upt} + \text{rest}_p \right) \right), \quad (A12)$$

where rest_n and rest_p are terms where the internal storage of nutrients are used to bind recently fixed carbon:

$$\text{rest}_n = \max \left(0, 0.05 \frac{1}{n_p^{\min}} \frac{dP_c}{dt} \Big|_{O^{(3)}}^{\text{gpp}} (P_n/P_c - n_p^{\min}) \right) \quad (A13)$$

$$\text{rest}_p = \max \left(0, 0.05 \frac{1}{p_p^{\min}} \frac{dP_c}{dt} \Big|_{O^{(3)}}^{\text{gpp}} (P_p/P_c - p_p^{\min}) \right). \quad (A14)$$

A6. FIX Experiment

To investigate the importance of variable stoichiometry, one simulation was done where the C:N:P ratios in the phytoplankton were fixed to Redfield (106:16:1). The phytoplankton dynamics is now expressed in one

single currency, chosen to be nitrogen. The nutrient and carbon assimilation are no longer decoupled. The uptake of nitrogen is expressed as the following:

$$\frac{dP_n}{dt} = f_p^T f_p^E f_p^{PP} f_p^{n,P} r_p^0 P_n, \quad (A15)$$

where $f_p^{n,P}$ is a Michaelis-Menten formula (Michaelis & Menten, 1913):

$$f_p^P = \frac{N^{(1)}}{\kappa_p + N^{(1)}} \quad (A16)$$

$$f_p^n = \frac{N^{(3)} + N^{(4)}}{\kappa_n + N^{(3)} + N^{(4)}} \quad (A17)$$

$$f_p^{n,P} = \min(f_p^P, f_p^n) \quad (A18)$$

ranging from close to one at nutrient replete conditions and zero at nutrient limiting conditions. κ_p and κ_n are half-saturation constants for nitrogen and phosphorus limitation that were set to 0.25 mmolN m⁻³ (Eilola et al., 2009) and 0.01 mmolP m⁻³, respectively.

The uptake of carbon and phosphorus are directly related to the nitrogen through the Redfield relation 106:16:1.

$$\frac{dPp}{dt} = \frac{dPn}{dt} \cdot \frac{1}{16} \quad (A19)$$

$$\frac{dPc}{dt} = \frac{dPn}{dt} \cdot \frac{106}{16} \quad (A20)$$

All processes (nutrient stress lysis rate, chlorophyll synthesis, equations (2.2.9), (2.2.10), and (2.2.37d) in Vichi et al., 2015b) dependent on the internal nutrient status of the phytoplankton in the original BFM code (equations (A9) and (A10)), have been reformulated to include the external nutrient limitation term (equations (A16) and (A17)). The partitioning of the organic matter, excreted through nutrient stress lysis, into DOM and POM is in the original BFM code dependent on the intracellular nutrient ratio (equations (2.2.9), (2.2.10), (2.2.11) in Vichi et al., 2015b). The more nutrient limited the phytoplankton are the more organic matter goes into the particulate phase. In FIX the partitioning was assumed to be 50–50%. A sensitivity experiment showed that this had little effect on the model results. The loss terms only affecting carbon in the original BFM code (respiration and release of extracellular DOC) have been removed, as these are not compatible with a fixed-stoichiometry formulation.

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