Modeling the long-term dynamics of nutrients and phytoplankton in the Gulf of Riga

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A B S T R A C T

The long term dynamics of nitrogen, phosphorus, and phytoplankton in the Gulf of Riga were simulated with a biogeochemical box model that resolved seasonal cycles. The model was calibrated using a numerical optimization procedure that adjusted 37 parameters to maximize the model data fit for field observations from 1973 to 2000 and validated with an independent dataset covering 2001–2007. Both the long-term increase and subsequent decline in winter nitrogen concentrations, as well as the continuous increase in winter phosphate levels were well reproduced by the model, which also gave reasonable representations of the seasonal dynamics of nutrients and phytoplankton. Starting from the mid-1990s, the model simulated an increase in cyanobacteria growth sustained by internal phosphorus loading. While nitrogen was efficiently removed by denitrification from the Gulf of Riga, comparatively slow export to the Baltic Proper was the main removal pathway of phosphorus. Modeled residence times were 5.4 years for nitrogen and 38 years for phosphorus. Scenario simulations indicated that the Gulf of Riga responds to phosphorus load reductions with a gradual decrease in primary production and cyanobacteria growth, while the effect of nitrogen load reductions is largely offset by nitrogen fixation.

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1. Introduction

Baltic Sea biogeochemical models are currently advancing from research instruments to decision support tools for combating eutrophication. When the riparian countries in 2007 agreed on nutrient load reduction targets in an ambitious HELCOM Baltic Sea Action Plan (HELCOM, 2007), they endorsed recovery scenarios based on simulations with the SANBALTS (Savchuk and Wulff, 2007) biogeochemical boxmodel. Together with the relevance of model predictions for management, progress in computing speed and modeling skills have triggered efforts to validate various Baltic ecosystem models by hindcasts of nutrient and phytoplankton concentrations. For example, Schernewski and Neumann (2005) have validated the ERGOM model with hindcasts of DIN concentrations for 1990–2000, Eilola et al. (2009) compared output from RCO-SCOBI to oxygen and phosphate concentrations in 1960–1999, and the SANBALTS model was validated by hindcasting nutrient concentrations in nine Baltic sub-basins in 1970–2003 (Savchuk and Wulff, 2009). Recently, Eilola et al. (2010) compared hindcasts by the three coupled physical–biogeochemical models BALSEM, ERGOM and RCO-SCOBI to nutrient and oxygen concentrations for 1970–2005 and concluded that uncertainties in nutrient loading and in the parameterizations of nitrogen and phosphorus fluxes from the bottom sediments contributed most to differences in model results.

Long-term hindcasts are sensitive tests of biogeochemical model performance because changes on decadal timescales are driven by the balance between nutrient inputs and losses and therefore indicate whether the magnitude of major biogeochemical fluxes is described adequately. In this context, the Gulf of Riga (Fig. 1), a subsystem of the Baltic Sea with restricted water exchange to the Baltic Proper, good coverage by marine monitoring data, and a history of increasing and decreasing eutrophication due to large and highly variable riverine nutrient inputs, provides an interesting test area for developing and validating biogeochemical models. A biogeochemical box model for the Gulf of Riga ecosystem has been developed earlier and calibrated to reproduce nutrient and chlorophyll a observations during a three-year time period (Savchuk 2002). To simulate the long-term changes in nutrients and phytoplankton in the Gulf of Riga ecosystem, we have adapted the model and then calibrated 37 model parameters to reproduce nutrient and phytoplankton observations in a 28-year time period (1973–2000). We have validated the model with data covering an additional seven year period (2001–2007). Based on the model results, we have established the driving factors of seasonal nutrient and phytoplankton dynamics, analyzed the processes determining the long-term nutrient budget of the Gulf of Riga and simulated the Gulf’s response to nutrient load reductions.

2. Materials and methods

2.1. Study area

The Gulf of Riga (Fig. 1) is a relatively shallow water body, with maximum and mean depths of 62 and 20 m (Carman et al., 1996),
separated from the Baltic Proper by Saaremaa and Hiumaa islands. The connecting Irbe Strait and Suur Strait are shallow (sill depths 20 m and 5 m, Leppäranta and Myrberg, 2009), restricting water exchange with the Baltic Proper to water masses above the Eastern Gotland Basin halocline. Since the salinity difference with the Gulf of Riga water mass is not sufficient to generate a persistent halocline the water circulation is monomictic, with a seasonal thermocline developing in the summer months. The Gulf of Riga catchment includes the Daugava River, which, according to runoff, is the 4th largest river entering the Baltic Sea (HELCOM, 2004). Riverine nutrient inputs to the Gulf of Riga increased continuously during the 1970s and 1980s, peaked in 1990, and declined afterwards (Yurkovskis, 2004). Eutrophication led to rising winter nutrient pools and increases in summer phytoplankton biomass, a loss of benthic invertebrate communities in the central Gulf and changes in their species composition in coastal areas (HELCOM, 2009). Decreasing loads during the 1990s reduced winter nitrate concentrations and caused a partial recovery of benthic communities (Aigars et al., 2008), but phosphate concentrations and summer phytoplankton biomass remained at high levels (ICES, 2009). These changes in nutrient and biota are documented by regular marine monitoring since 1973, following HELCOM COMBINE guidelines.

2.2. Biogeochemical model

We modified a biogeochemical box model (Savchuk, 2002) for simulating the long-term dynamics of nitrogen and phosphorus in the Gulf of Riga by reducing the number of state variables and by simplifying the parameterization of biogeochemical reactions. In the final model, three groups of phytoplankton, cyanobacteria, diatoms and other phytoplankton grow in the water column, dependent on

![Fig. 1. Map of the Gulf of Riga with major freshwater inputs and connections to the Baltic Proper. Crosshatched areas denote coastal and transitional waters.](image)

![Fig. 2. State variables and main biogeochemical reaction pathways in the Gulf of Riga biogeochemical model.](image)
light, NH₄, NO₃ and PO₄ concentrations (Fig. 2). Their growth is coupled to nutrient assimilation fluxes based on Redfield (Redfield, 1958, Redfield et al., 1963) ratios. Phytoplankton is further grazed by mesozooplankton, which instantaneously regenerate a fraction of their nutrient uptake by excretion. A detritus pool consisting of detritus nitrogen and phosphorus collects phytoplankton and zooplankton mortality fluxes, as well as unassimilated zooplankton food generated by “sloppy feeding” and defecation. Nutrients are slowly remineralized from the detritus pool while detritus sinks to the bottom. Nitrogen and phosphorus are further remineralized in the bottom sediments. In the bottom sediments, biogeochemical transformations of nitrogen are simulated by releasing a part of the generated nitrogen flux into the water column and removing the remainder through denitrification. Similarly, remineralized phosphorus is either released to the water column or adsorbed to the bottom sediments. The share of each pathway in the model depends on oxygen concentrations, which are included as a state variable in the model by coupling all biogeochemical reactions to their stoichiometric oxygen consumption or production. Model equations and parameter values are described in detail in Appendix A and B.

To reduce model execution time, which is important for applying numerical parameter estimation routines, we simplified the original model (Savchuk, 2002) primarily to reduce the number of state variables. Preliminary runs had shown that nutrient and biota concentrations in the coastal box of the original model were difficult to calibrate. The coastal box spans a very inhomogeneous region, including the transitional waters in the Southern Gulf of Riga which receive more than 80% of the freshwater runoff to the gulf (Andrushaitis et al., 1995), together with remote coastal areas along the Western shore of the gulf which lack significant riverine inputs. In addition, water exchange between coastal areas and the central Gulf was expected to be large along the undifferentiated linear coastline. Since also the number of state variables in a box model is proportional to the number of model boxes, we decided to remove the coastal box from the original model. This simplified the physical structure of the model (Fig. 3) to two homogenous boxes representing the upper mixed layer (0–10 m) and the demersal water layer (10–50 m). Analysis of the long-term nutrient pools in the Gulf of Riga indicated that phosphorus and nitrogen were the main limiting nutrients for the gulf’s phytoplankton communities (Yurkovskis, 2004). To reduce the number of state variables further, we removed silica from the original model. Also, phytoplankton dynamics were simplified from the original model by describing cyanobacteria as obligatory nitrogen fixers. To increase the stability of the model towards variations in parameters, we reduced the number of exponential functions in the original model. Observations (Tamminen and Seppälä, 1999, Seppälä et al., 1999, Maestrini et al., 1997, 1999) suggested that, at least during summer, phytoplankton growth was predominantly limited by the rate of nutrient delivery to the pelagic model box. Because the three groups of phytoplankton in the model were described by differing maximum growth rates, the maximum growth rate of each group as well as their specific mortality were treated as a temperature invariant. This restricts temperature dependency of biological rates in the model to processes that describe pelagic and benthic nutrient mineralization (zooplankton grazing, mineralization of detritus and benthic organic matter). Sinking of living autotrophs, a small flux in the original model, was neglected. We also did not include a light dependency on particulate matter content in the pelagic model box because nutrient limitation was sufficient to prevent excessive growth of phytoplankton. Further, the phytoplankton growth rates in the demersal box were set to zero to account for the low average light conditions in the 10–50 m water layer. Detritus sedimentation was simplified by using a constant sinking velocity. Because pelagic oxygen concentrations in the Gulf of Riga are generally above the threshold for denitrification, pelagic denitrification was not taken into account.

2.3. Model forcing

Continuous forcing functions were interpolated from monthly time series covering the time period 1973–2007. River runoff and associated nutrient loads (NO₃, NH₄, PO₄, organic nitrogen and phosphorus) to the Gulf of Riga were taken from Laznik et al. (1999) for the time period 1977–1995. For 1996–2007 nutrient loads were calculated from monitoring data obtained from the Latvian Environment, Geology and Meteorology Centre, multiplied by a regression factor based on 1991–1995 data to achieve consistency between both data sources. Riverine nutrient concentrations were unavailable in 1973–1976 and were replaced by average monthly concentrations in 1977–1980. 30% of the organic nitrogen load and 100% of the organic phosphorus load were considered to be bioavailable and included into the model detritus pools. Monthly water exchange with the Baltic Proper was interpolated from half-year values (Bērziņš et al., 1994, Bērziņš, personal communication) based on a salt and water budget of the Gulf of Riga in 1990 and 1995 as described in Savchuk (2002). Direct point source inputs and loads from unmonitored coastal areas to the Gulf of Riga in 1990 and 1995 were taken from HELCOM (1993, 1998, 2004) and for 2001–2007 from Kistikua (2008). For the time period prior to 1990, direct point source loads were assumed to follow the 1989 GDP growth rate of the USSR (1.4% per year with respect to 1990 values, US CIA 1990). Phytoplankton growth was forced with solar radiation from Töravere/Estonia (V. Russak, personal communication). Sea-ice cover of the gulf was estimated from a numerical model of the heat budget in the Gulf of Riga (Seņnikovs and Bethers, 2000). Wind data to force the atmosphere–water exchange of oxygen were taken from a station in Sõrve, Estonia (Soomere, 2003, A. Toompaa, personal communication). Missing data were replaced by monthly averages for the three preceding years. Water density in each model box, which drives the vertical water exchange in the model, was

Fig. 3. Physical structure of the Gulf of Riga biogeochemical model.
calculated from Latvian marine monitoring data as monthly averages of all observations in the pelagic model box. For the demersal box, average water density was calculated in 10 m intervals, and the averages for each slice were weighted according to the hypsographic curve (Bērziņš et al., 1994) of the Gulf of Riga.

2.4. Model calibration and validation

The model was calibrated with and validated against observations of dissolved nutrients (NO$_3$, NH$_4$, PO$_4$), oxygen, phytoplankton (chlorophyll $a$, biomass of cyanobacteria, diatoms and other species) and mesozooplankton from the central Gulf of Riga, i.e. the area outside coastal and transitional waters (see Fig. 1). Savchuk (2002) had estimated 5.8 and 30.2 years residence time of nitrogen and phosphorus in the Gulf of Riga. To capture the long-term dynamics of nutrients in the Gulf, we used a time series of similar length as the phosphorus residence time for model calibration. Calibration data therefore span the time period 1973–2000 except for the biomass of diatoms (1976–2000), cyanobacteria and other phytoplankton (1993–2000, using only data from samples fixed by acid lugol). The model was validated by extending the simulations to the time period 2001–2007, thus including a seven year period of observations that had not been used during the model calibration. Nutrient and phytoplankton data for calibration and validation were provided by the Latvian Institute of Aquatic Ecology from the Latvian national marine monitoring program (www.bior.gov.lv). The seasons winter (January–March), spring (April–May), summer (June–September) and autumn (October–December) were covered on average by 1.9, 2.7, 4.4 and 2.9 monitoring surveys each year during the calibration period. Zooplankton data are part of the Latvian national fish resources monitoring and were available from quarterly surveys in February, May, August, and October (www.bior.gov.lv). Sampling frequency during calibration and validation periods was similar.

We used a simulated annealing algorithm (Wah et al., 2007) to adjust 37 biological and geochemical parameters until the model represented the interannual fluctuations in the winter nutrient pools and the seasonal dynamics of nutrients, phytoplankton, and zooplankton reasonably well, giving at the same time realistic estimates of primary and secondary production. A penalty function based on the weighted sum of squared model-data deviations measured the misfit between the modeled and observed values of chlorophyll $a$, the biomasses of cyanobacteria, diatoms, other phytoplankton, and mesozooplankton, as well as the concentrations of pelagic and demersal oxygen, ammonium, nitrate and phosphate. Additional terms were included to penalize parameter sets that predicted unrealistically low (<130 g C m$^{-2}$ year$^{-1}$) levels of primary production, as well as excessive changes in sediment nitrogen and phosphorus pools. The choice of weights in optimization problems is non-trivial (Evans, 2003) and ideally assures the scaling of variables to similar magnitude and, at the same time, accounts for the uncertainty associated with field observations, assigning less weight to variables with large observation error. Here, we initially accounted only for differences in the range and number of observations, using the squared 75th percentile of the observed values multiplied by the number of observations available for each variable as the inverse of its weight. During the course of the optimization these weights were manually adjusted to improve the model-data fit and the optimization procedure was restarted. Model-data correlations for the individual state variables were then used to identify a parameter set among the 50 best solutions of the optimization routine that gave a good representation of both nutrient and phytoplankton dynamics.

The 37 parameters included into the calibration procedure were allowed to vary between preset minimum and maximum values. New parameter values were generated from their previous values by drawing from Cauchy distributions with variable search radii. The search radius for each parameter was periodically adjusted to maintain an efficient ratio between accepted and rejected parameter sets. A detailed description of the algorithm can be found in Wah et al. (2007), and the optimized model parameter set generated during the model calibration is listed in Annex B.

A simple sensitivity analysis was performed by decreasing and increasing each calibrated model parameter by 10% of its value to further explore the model response to variations in the final parameter set.

2.5. Scenario simulations

The HELCOM Baltic Sea Action Plan (HELCOM, 2007) proposes reducing the phosphorus load to the Gulf of Riga by 750 t per year, equal to a 34% decrease from the observed riverine and point source load during 1997–2003. No nitrogen load reductions were suggested for the gulf. We have simulated the response of the Gulf of Riga ecosystem to these load reductions in a 100 year scenario simulation, where the first 30 years of the simulation were forced by observed nutrient loads for 1973–2003. Reaching the eutrophied status quo of the Gulf of Riga ecosystem after this spin-up period, phosphorus load reductions were fully implemented starting from year 31 of the simulation. Roughly following HELCOM scenarios (HELCOM, 2007) which advocate improving sewage treatment, we set the direct point source load of phosphorus to zero, resulting in a load reduction of 200 t year$^{-1}$ and reduced the river load by 25% to achieve the same decrease in point source and river load as proposed in the Baltic Sea Action Plan. We applied the load reduction to the observed loads during the Baltic Sea Action Plan reference years 1997–2003 and repeated the resulting seven year phosphorus load time series until the end of the simulation to mimic natural variability in the reduced phosphorus load. A status-quo reference scenario was generated by repeating the observed 1997–2003 phosphorus loads during years 31–100 of the simulation. Except direct point source inputs, which were kept at reference year values, all other model forcing, including nitrogen loads, repeated the observed 1973–2007 cycle during the entire simulation period to capture long-term periodic variations in runoff and climate forcing. Based on the reference scenario, we also constructed a nitrogen reduction simulation by setting the direct point source load of nitrogen to zero and reducing the riverine inputs by 25%.

3. Results

3.1. Modeled seasonal dynamics of phytoplankton, nutrients and oxygen

The simulated seasonal succession of phytoplankton (Fig. 4, top) started with a spring bloom composed of the other species and diatom model groups. Significant development of cyanobacteria (>5% of annual phytoplankton biomass) was simulated at the beginning of the simulation period, in 1974, 1976 and 1977, and starting from 1996, when blooms were modeled for all years except 1999 (validation period) and 2005 and 2007 (validation period).

Simulated pelagic nitrate and phosphate dynamics (Fig. 4, middle panels) followed the seasonal pattern typical for Baltic Sea surface waters. The spring bloom caused a sharp drop in nitrate and phosphate concentration, summer values remained at low levels, followed by a concentration increase during winter. The model occasionally overestimated summer phosphate and nitrate concentrations in the pelagic box, in particular for the nutrient not limiting phytoplankton growth at that time. Seasonal dynamics of nitrate and phosphate in the demersal box generally showed declining concentrations during the spring bloom and a build-up in winter. Especially nitrate showed large inter-annual variations in demersal summer concentrations, which were well represented by the model. The model also depicted the seasonal dynamics of oxygen in the Gulf of Riga (Fig. 4, bottom). Pelagic oxygen concentrations followed the temperature-dependent oxygen solubility in water with minimum values during summer. The model simulates lower demersal oxygen concentrations during summer, but values are overestimated and inter-annual variations are not fully captured.
3.2. Long-term changes in the Gulf of Riga nutrient status

Nutrient concentrations in winter, when biological uptake is negligible, are a widely accepted indicator of nutrient status in Baltic Sea sub-basins (HELCOM 2007, 2009, Fleming-Lehtinen et al., 2008b, 2009). In the Gulf of Riga, winter nitrate concentrations in surface waters increased up to 1991, declined afterwards and only after 2000 have started to increase again. In contrast, winter phosphate concentrations have increased steadily during the model calibration and validation periods. These

Fig. 4. Dynamics of phytoplankton, nutrients and oxygen in pelagic and demersal model box during 1975 (1), 1980 (2), 1990 (3), 1996 (4), and 2000 (5). Markers denote average values observed during monitoring cruises, with error bars corresponding to the standard deviation of the measurements. Lines are model results.
features were well represented in the model simulations (Fig. 5) although the model tended to smooth inter-annual fluctuations and underestimated peak nutrient concentrations.

3.3. Model performance

We have used the correlation coefficient (Pearson r) to measure the level of agreement between field data and the biogeochemical model output. This simple performance index has the advantage that the influence of field-data uncertainty on the correlation coefficient can be estimated empirically (Monte et al., 1996). Field measurements describe the true state of the environment by their – hopefully unbiased – mean and an error term, which is normally distributed. The magnitude of the error term can be measured by the field observation data variance. The uncertainty in the field data decreases the model-data correlation because, for a given set of input data, a perfect model would represent the data mean from which the actual field observations as one realization of the field data distribution deviate depending on their variance. Monte et al. (1996) suggested using the empirical correlation between realizations of the field data set generated by Monte-Carlo simulations to estimate the upper limit of the model-data correlation (rmax). The larger the measurement uncertainty, the smaller the rmax.

The maximum achievable correlation coefficient rmax (Table 1) was larger for nutrients (0.53–0.90) than for biotic state variables (0.41–0.86), reflecting the variability in the observational data. Correlation coefficients between model output and observations for the calibration period were largest for pelagic and demersal oxygen concentrations (0.92 and 0.89), and ranged from 0.59 to 0.75 for all nutrient concentrations except NH4, and between 0.33 and 0.53 for biotic state variables. The upper 95% confidence limit of the model-data correlation coefficient was in all cases smaller than rmax. Because the model-data correlation was usually close to rmax the model was thought to give a reasonable fit for the simulated state variables.

By visual comparison, winter nutrient concentrations correspond well to observations (Fig. 5), but the model-data correlation was significant only for winter NO3. However, for winter nutrients the comparison is based on a single data point per year and had, therefore, less degrees of freedom than in the case of continuously measured parameters.

For phosphate, dissolved oxygen concentrations, chlorophyll a and biomass of other phytoplankton, the model performed equally well

![Fig. 5. Observed (dots) and simulated (line) winter nutrient concentrations in the surface layer (0–10 m) of the central Gulf of Riga (left panel: nitrate, right panel: phosphate), high observed NO23 in 2002 were considered an outlier. The stippled gray line marks the beginning of the model validation period 2001–2007.](image)

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Pearson r</th>
<th>Calibration</th>
<th>Validation</th>
<th>rmax</th>
<th>Pearson r</th>
<th>Calibration</th>
<th>Validation</th>
<th>rmax</th>
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<tr>
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<tr>
<td>Chlorophyll a</td>
<td>0.53</td>
<td>0.43 [0.43, 0.61]</td>
<td>0.45 [0.28, 0.60]</td>
<td>0.86</td>
<td></td>
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<tr>
<td>Cyanobacteria</td>
<td>0.48</td>
<td>0.30 [0.30, 0.60]</td>
<td>0.21 [0.01, 0.40]</td>
<td>0.42</td>
<td></td>
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<td>Diatoms</td>
<td>0.38</td>
<td>0.25 [0.25, 0.50]</td>
<td>n.s.</td>
<td>0.48</td>
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<td>Other phytoplankton</td>
<td>0.33</td>
<td>0.12 [0.12, 0.51]</td>
<td>0.37 [0.18, 0.54]</td>
<td>0.41</td>
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<td>Mesozooplankton</td>
<td>0.48</td>
<td>0.29 [0.29, 0.63]</td>
<td>n.s.</td>
<td>n.d.</td>
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<tr>
<td>NO3</td>
<td>0.75</td>
<td>0.42 [0.42, 0.90]</td>
<td>n.s.</td>
<td>0.70</td>
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<td>PO4</td>
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<td>n.s.</td>
<td>n.s.</td>
<td>0.53</td>
<td></td>
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<td><strong>Nutrients and oxygen</strong></td>
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<td>n.s.</td>
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<td>0.54</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
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<tr>
<td>NO3</td>
<td>0.70</td>
<td>0.64 [0.64, 0.76]</td>
<td>0.55 [0.40, 0.68]</td>
<td>0.75</td>
<td>0.59 [0.51, 0.67]</td>
<td>0.59 [0.11, 0.48]</td>
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<tr>
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<td>0.77 [0.67, 0.84]</td>
<td>0.90</td>
<td>0.66 [0.59, 0.72]</td>
<td>0.66 [0.50, 0.74]</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.92</td>
<td>0.90 [0.90, 0.94]</td>
<td>0.91 [0.87, 0.94]</td>
<td>0.90</td>
<td>0.89 [0.87, 0.91]</td>
<td>0.92 [0.88, 0.95]</td>
<td>0.84</td>
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</tbody>
</table>

1: significant at p = 0.10.
n.s: p > 0.10.
n.d.: not determined due to lack of data standard deviations.
during the validation and the calibration period. For all other parameters, correlation coefficients decreased by 0.2–0.3 units. For winter nutrients, diatoms and mesozooplankton, the model-data correlation became insignificant in the validation period.

Sensitivity analysis showed that the model retained its stability at moderate changes in the calibrated parameter set. Varying the 37 parameters that caused a variation of 1–4% (Table 2). The model responded most sensitively to parameters governing the remineralization rates of phosphorus and nitrogen from detritus and bottom sediments. Also, the specific growth rates and mortalities for phytoplankton species, as well as their half-saturation constant for phosphate were important model parameters. Further, model sensitivity was also relatively large towards parameter \( q\text{BN} \) that governs denitrification and nitrate release from bottom sediments.

### 3.4. Nutrient turnover

Simulated primary production increased from 176 g C m\(^{-2}\) year\(^{-1}\) in 1973–1980 to 220 g C m\(^{-2}\) year\(^{-1}\) in the 1980s and declined again slightly to 206 g C m\(^{-2}\) in the 1990s. Phytoplankton consequently assimilated an average of 578 000 t of nitrogen (including 5120 t of nitrogen provided by nitrogen fixation) and 80 000 t of phosphorus annually. Despite the large riverine and point sources inputs of organic matter, which provided 14 400 t of bioavailable organic nitrogen and 705 t of bioavailable organic phosphorus annually, phytoplankton production was by far the biggest source of organic nitrogen (97.6%) and phosphorus (99.1%) for the Gulf of Riga foodweb. Phytoplankton uptake of nitrogen and phosphorus from the water column also widely exceeded the external inputs to the Gulf of Riga. Riverine, point sources, atmospheric inputs and the water exchange with the Baltic Proper provided on average 87 590 t of inorganic and bioavailable organic nitrogen, and 37 55 t of phosphorus annually, i.e. 16% and 4.7% of the phytoplankton demand. The remainder was covered by nutrient mineralization, with detritus degradation strongly dominating the remineralization flux.

Average simulated DIN and DIP fluxes in the water column during the model calibration period 1973–2000 (Fig. 6) showed that the share of remineralization in providing nutrients to phytoplankton was largest during summer. Then remineralized nutrient fluxes, which were modeled as excretion by zooplankton and degradation of detritus, covered 70% of the phytoplankton nitrogen demand and 69% of its phosphorus assimilation (June–August averages). During the spring bloom (April–May) nutrient regeneration in the pelagic box covered approximately one third of the phytoplankton nutrient demand. Nutrient fluxes from the demersal box, i.e. the sum of net entrainment and upwelling of bottom water, were the largest source of nitrogen and phosphorus to the spring bloom, ensuring slightly more than half of the phytoplankton production. External inputs, i.e. mainly river loads, covered 10% of the spring bloom nitrogen budget, but only 2% of its phosphorus requirement. Consumption of nutrients accumulated during winter in the pelagic water layer accounted for 9% of the phytoplankton nitrogen uptake (phosphorus: 10%). From September to mid-October the pycnocline gradually weakened and the simulated mixing between pelagic and demersal box increased,
creating a growing nutrient flux into the productive surface layer. In the model, nutrient regeneration contributed roughly 60% and inputs from the demersal layer about 40% of the phytoplankton nitrogen and phosphorus demand during autumn. However, especially during the decline phase of the bloom, phytoplankton became light-limited and the nutrient supply started to exceed the phytoplankton uptake, leaving nitrogen and phosphorus to accumulate in the surface layer.

In the model, the demersal waters in the Gulf of Riga served as a nutrient regeneration “bioreactor” which efficiently regenerated sedimenting detritus. In fact, of 592,000 t of predominantly autochthonous organic nitrogen (P: 80,700 t) processed in the Gulf each year, 52% (P: 53%) were remineralized in the pelagic part of the water column, 29% (P: 29%) in the demersal layer, and only 18% (P: 16%) reached the bottom sediments.

### 3.5. Gulf of Riga nutrient budget

The largest external source of both nitrogen and phosphorus to the Gulf of Riga are riverine inputs. During the model calibration period 1973–2000, rivers provided 83% of the total nitrogen load, atmospheric inputs accounted for 13%, while direct point sources and the inflow of water from the Baltic Proper contributed each 3% to the nitrogen input to the Gulf. In comparison, inflow from the Baltic Proper and direct point sources were more important to the phosphorus budget of the Gulf, contributing 27% and 14% of the total phosphorus load, while atmospheric deposition provided 9%. Rivers, though also the most important source of phosphorus, provided only 50% of the total phosphorus load.

Depending mainly on river runoff, nutrient inputs have fluctuated widely during the model calibration period. Nutrient inputs generally increased between 1973 and 1990 and declined afterwards. For the model calibration period 1973–2000, rivers delivered on average 100,000 t year$^{-1}$ of bioavailable nitrogen and 1900 t year$^{-1}$ of phosphorus to the Gulf of Riga. Maximum nitrogen and phosphorus inputs during the model calibration period were observed in 1990 and were 2.8 and 2.2 times larger than their minimum in 1996. However, even the minimum nutrient loads from land, point sources and atmosphere (N: 63,100 t year$^{-1}$, P: 1520 t year$^{-1}$) were about twice as large as the pre-industrial nutrient inputs into the Gulf of Riga (N: 34,600 t year$^{-1}$, P: 750 t year$^{-1}$, Savchuk et al., 2008 based on Scherniewski and Neumann, 2005).

Nutrient sinks differed substantially for nitrogen and phosphorus (Fig. 7). Most of the nitrogen, on average 81% of the annual input, left the Gulf of Riga by denitrification, 19% were exported to the Baltic Proper and only 3% were buried in the bottom sediments. In contrast, export to the Baltic Proper was the largest phosphorus sink (76% of phosphorus inputs), making the Gulf a net exporter of phosphorus to the Baltic Proper, followed by sediment burial (23%). During the calibration period, the modeled nutrient budgets were not completely balanced. In the 28 year calibration period the Gulf of Riga lost 77,200 t of nitrogen and gained 9880 t of phosphorus. Almost half of the nitrogen loss occurred during the first year of the simulation, presumably as a model spin-up effect.

The nitrogen budget of the Gulf of Riga showed large interannual variability, with net gains and losses following each other. During 1973–1990 more nitrogen was received than lost and, disregarding the spin-up year 1973, the Gulf accumulated 2800 t of nitrogen annually. Later nitrogen losses mostly exceeded inputs and, on average, 8920 t of nitrogen was removed from the Gulf each year. In contrast to nitrogen, the phosphorus pool changed steadily, with increasing gains until 1990. After 1990, phosphorus accumulation slowed and, starting from 1994, turned into net loss. Both nitrogen and phosphorus pool changes occurred predominantly in the bottom sediments, accounting for 71% of the modeled nitrogen loss and 76% of the phosphorus gain.

Compared to the nutrient pools contained in the water column and bottom sediments, the annual nutrient input to the Gulf of Riga was relatively small (Table 3). Annually, only 19% of the nitrogen and 2.6% of the phosphorus pool were renewed, equivalent to residence times of 5.4 years for nitrogen and 38 years for phosphorus. For both nutrients, bottom sediments stored more than 90% of the total pool.

### 3.6. Response to nutrient load reductions

Reducing the phosphorus load to the Gulf of Riga as proposed in the Baltic Sea Action Plan gradually changed nutrient and phytoplankton concentrations in the Gulf of Riga, whereas in the reference run nutrient pools and primary production remained at the 1997–2003 level (Fig. 8). Neither winter DIN, winter DIP nor primary production had significant (p < 0.10) temporal trends during years 31–100 of the reference simulation, showing that the model reproduces stable nutrient and phytoplankton concentrations in the absence of temporal trends in forcing. In contrast, winter DIP concentrations as well as simulated primary production showed a significant (p < 0.05) temporal decrease after phosphorus load reductions were implemented, i.e. during years 31–100 of the phosphorus reduction scenario. Comparing the final seven years of the simulation to the 1997–2003 reference period, winter DIP
concentrations dropped by 27% from 0.83 mmol m$^{-3}$ to 0.61 mmol m$^{-3}$ after 70 years of reduced phosphorus loading. Primary production simultaneously declined by 23% from 218 g C m$^{-2}$ year$^{-1}$ to 167 g C m$^{-2}$ year$^{-1}$. Phosphorus load reductions also had a pronounced impact on phytoplankton species composition. As shown by the contribution of nitrogen fixing phytoplankton to primary production, cyanobacteria blooms were pronounced during low riverine nitrogen input to the Gulf, but the intensity of the blooms strongly declined in the reduced phosphorus load scenario. Already in the bloom period in the simulation years 59–65, which had the same low nitrogen load as the reference period, cyanobacteria primary production was reduced by 60%, and the share of cyanobacteria in the summer phytoplankton biomass dropped from 17% to 6%. Phosphorus load reductions also had a noticeable effect on nitrogen dynamics in the Gulf of Riga. While winter nitrate concentrations during periods of low riverine input are roughly the same in the reference and reduced phosphorus load scenarios, winter DIN values exceed the reference scenario values during periods of high DIN load.

Under nitrogen load reductions, winter DIN concentrations in the Gulf of Riga are predicted to decline, while DIP pools remain on a high level. Primary production was equal to the reference run when runoff was low and was slightly lower than during the status quo at high runoff, but nitrogen fixation increased in the nitrogen load reduction scenario.

4. Discussion

4.1. Model-data fit

Models with many poorly known parameters that are tuned to a specific situation might lose predictive potential, i.e. not work in different situations (Fennel and Neumann, 2004). However, the reasonable model-data correlations and the correctly predicted winter nutrient trends found for the validation period indicate that the model is suitable to predict the future ecosystem state of the Gulf of Riga. However, the calibrated model parameters might not be applicable for different marine ecosystems or extremely different nutrient loads and climatic forcing.

Other than in the case of winter nutrients and mesozooplankton, where the lack of model-data correlation during the validation period is likely due to the low number of observations (one and three observations annually), the large drop in model-data correlation for diatoms during the validation period is a weakness in the model parameterization. Because diatoms are little affected by different sample fixatives (Klein Breteler, 1985), all available diatom observations have been included into the calibration dataset, resulting in a time series starting in 1976. Non-diatoms, where small cells might be lost by formalin preservation, have been considered only starting from the end of 1993, when the Latvian marine monitoring program replaced formalin fixation with acid Lugol’s solution. Most of the calibration dataset, therefore, does not include the mixed summer phytoplankton communities in the Gulf of Riga (see for example Kalveka, 1996, Yurkovskis et al., 1999) and exaggerates the importance of diatoms in the ecosystem. In addition, silica consumption, which might have constrained diatom growth, was not included into the model. As a result, the model generally overestimated diatom biomass in summer, while other species, in particular, cyanobacteria were represented more reliably.

4.2. Phytoplankton species composition

The modeled nutrient budgets (Fig. 7) suggest that with declining loads in the 1990s nitrogen was quickly removed from the ecosystem, whereas the still increasing winter phosphate concentrations (Fig. 5) confirmed that phosphorus was efficiently retained in the Gulf of Riga. As in the Baltic Proper, where high availability of DIP at a simultaneous nitrogen shortage leads to the development of cyanobacteria blooms (Naussch et al., 2008, Vahreta et al., 2007, Stal et al., 2003), the biogeochemical model also depicted an increase in nitrogen fixing phytoplankton in the Gulf of Riga after 1993. The modeled increase in cyanobacteria growth during the 1990s agrees well with satellite observations (Kahru et al., 1994, 2007), which found virtually no cyanobacteria surface blooms in the Gulf of Riga before 1992, while later blooms occurred regularly.

The modeled cyanobacteria blooms are generated at high phosphorus pools in the water column (Fig. 4). Cyanobacteria blooms in the Baltic Sea are related to the availability of DIP when DIN is exhausted, although the actual triggering of blooms is not understood well (Naussch et al., 2008). Varying proportions of cyanobacteria, predominantly Aphamizonomon sp., are a characteristic feature of the summer phytoplankton communities in the Gulf of Riga (Kalveka, 1996, Yurkovskis et al., 1999), though surface blooms of cyanobacteria are more commonly reported in the adjacent Baltic Proper and the Gulf of Finland (HELCOM, 2009). The maximum annual nitrogen fixation input during the model calibration period was 29.5 t year$^{-1}$ (average: 5120 t year$^{-1}$), corresponding to 1.82 g N m$^{-2}$ year$^{-1}$ (average: 0.32 g N m$^{-2}$ year$^{-1}$). The simple parameterization of cyanobacteria as obligatory nitrogen fixers will tend to produce higher nitrogen fixation rates than life-cycle representation, where only heterocysts fix nitrogen (Hense and Burchard, 2010). However, the modeled values are still at the lower end of the range of nitrogen fixation rates reported for the Baltic Proper since the end of the 1990s (0.2–3.0 g N m$^{-2}$ year$^{-1}$; Larsson et al., 2001, Wasmund et al., 2001, Rahm et al., 2000, Schneider et al., 2002, Rolf et al., 2007), probably because of a lower share of years with cyanobacteria summer blooms in the Gulf of Riga.

4.3. Nutrient regeneration

The remineralization of detritus was the major pathway of nutrient regeneration in the Gulf of Riga model, whereas nutrient excretion by zooplankton provided only 3.0% of the regenerated nitrogen and 2.8% of the regenerated phosphorus flux. Modeled zooplankton grazing equaled on average 8.5% of the simulated primary production, indicating overall weak mesozooplankton grazing pressure on phytoplankton. In the model, grazing control was only important during the second half of August, when the simulated zooplankton biomass was large and primary production strongly nutrient limited. Grazing on phytoplankton then reached up to 64% of simulated primary production. The low importance of zooplankton grazing for phytoplankton mortality simulated is in contrast to the perception of grazing control of summer phytoplankton communities (Banse, 1982). However, studies in the Baltic Sea have shown that grazing control was important mainly for large zooplankton species, while grazing removed only about 10–20% of the total summer phytoplankton production (Kiørboe and Nielsen, 1994). In the model, the calibrated specific maximum ingestion rate for mesozooplankton (1.2 d$^{-1}$ at 20 °C) was in a realistic range, being slightly lower than rates typically reported for small copepods (Hansen et al., 1997), but larger than rates characteristic for large copepods (Sommer et al., 2005). This agrees well with the
mesozooplankton composition in the Gulf of Riga, which is dominated by comparatively small species (Acartia sp., Eurytemora affinis, ICES, 2009, Yurkovskis et al., 1999).

The actual mechanism of nutrient regeneration from non-living suspended organic matter in marine ecosystems is far more complex than the simple first-order mineralization of detritus incorporated in the Gulf of Riga biogeochemical model. Nutrient regeneration is mainly connected to the microbial loop, which is a grazing chain involving bacteria, heterotroph nanoflagellates and ciliates (Azam et al., 1983). The microbial loop processes the majority of primary production in the open oceans (Steele, 1998). In the Kattegat, ciliates, the top predators in the microbial loop remineralized 40–60% of the annual primary production (Nielsen and Kierboe, 1994), supporting substantial nutrient regeneration rates outside the classical phytoplankton grazing chain.

4.4. Gulf of Riga nutrient budget

The modeled long-term dynamics of nutrients and phytoplankton in the Gulf of Riga are driven by the balance between inputs of bioavailable nutrients and their major sinks. Denitrification removed on average 80% of the bioavailable nitrogen inputs to the Gulf, while export to the Baltic Proper was the dominating phosphorus loss process, covering 76% of the phosphorus inputs. The simulated denitrification rates, on average 4.6 g N m⁻² year⁻¹ in 1973–2000, were within the range of rates observed in the Eastern Gotland Basin (2.7–11 g N m⁻² year⁻¹, Schneider et al., 2002). However, they were larger than observations in the Northern Baltic Proper and the Gulf of Finland (0.08–1.54 g N m⁻² year⁻¹, Tuominen et al., 1998 and 0.5–3.32 g N m⁻² year⁻¹, Gran and Pitkänen, 1999). This is surprising because field measurements mostly cover fine-grained, organic rich accumulation sediments (Hietanen and Kuparinen, 2008), which make up only 28% of the Gulf of Riga bottom area (Carman et al., 1996), but denitrification rates outside accumulation areas are potentially significantly smaller (Stockenberg and Johnstone, 1997). However, the modeled denitrification flux, on average 75 000 t year⁻¹ during 1973–2000, ranges between the Gulf of Riga denitrification flux calculated in steady state budgets (55 000 t year⁻¹ in 1997–2003, Savchuk and Wulff, 2007) and transient budget simulations (84 000 t year⁻¹ for 1970–2003, Savchuk and Wulff, 2009). It also agrees well with the denitrification estimate derived from short-term simulations (74 100 t year⁻¹ in 1993–1995, Savchuk, 2002) and budget calculations for 1991–1999 (84 000 t year⁻¹ including burial, Savchuk, 2005).

Because of the estuarine nature of the Baltic Sea, which transports nitrogen rich riverine inputs towards a, in relative terms, nitrogen poor North Sea, all sub-basins of the Baltic are net exporters of nitrogen (see for example flows between basins in Savchuk and Wulff, 2007 and Savchuk, 2005). The nutrient exchange between the Gulf of Riga and the Baltic Proper cannot be measured directly on long time scales, but models and budget calculations give a range of estimates of the net nitrogen export from the Gulf of Riga. In our model, the net export of 17500 t year⁻¹ is slightly lower than 19200 t year⁻¹ estimated by Savchuk (2002), 20700 t year⁻¹ for DIN in Yurkovskis et al. (1993) and 44000 t year⁻¹ according to Savchuk (2005). Because the simulated nitrogen export to the Baltic Proper follows the riverine input signal (see Fig. 7), part of the variation in net nitrogen export between different models might be attributable to the different time periods covered in the simulations. The modeled net phosphorus export from the Gulf of Riga, 2530 t year⁻¹, is slightly larger than estimates from other published budget models (800 t year⁻¹–2200 t year⁻¹, Savchuk, 2002, 2005, Savchuk and Wulff, 2009). Only the phosphorus mass balance model constructed by Håkanson (2009) gives a significantly larger export flux (6160 t year⁻¹) because phosphorus sources in that model also include significant input from land uplift.

According to the simulated nutrient budget, sediment burial is the smallest phosphorus sink in the Gulf of Riga, removing 870 t year⁻¹ of phosphorus, or 23% of the annual phosphorus inputs. The magnitude of the burial flux is within the range of recent budget model estimates (0–1500 t year⁻¹, Savchuk, 2002, 2005, Savchuk and Wulff, 2007) and only slightly lower than the phosphorus storage of 1100 t year⁻¹ estimated based on measurements of phosphorus content in bottom sediments (Carman et al., 1996). Compared to the magnitude of the phosphorus budget components (see Fig. 7), the differences between the model estimates are considerable, indicating large uncertainty in both net phosphorus export and the phosphorus burial flux. In particular, the phosphorus export can be expected to be sensitive to changes in N/P ratios and phytoplankton community structure in the gulf, but also to DIP concentrations in the surface layer of the Baltic Proper, since the net phosphorus flux depends on the phosphate concentration gradient between both basins.

In contrast to the nutrient export flux to the Baltic Proper, which is controlled by the model-data fit to observed nutrient concentrations and the salt-budget based water exchange between the gulf and the Baltic Proper, denitrification and sediment burial are only weakly constrained by the plausible range of fluxes found in field observations and model experiments in the Baltic Sea. In our model, remineralization rates of nutrients in the bottom sediments and the split of nitrogen into release and denitrification are among the most sensitive model parameters. As a result, the parameter calibration procedure adjusts the efficiency of nitrogen and phosphorus sinks and therefore compensates bias in the nutrient inputs. In particular, the uncertainty in the bioavailable fraction of the riverine organic nitrogen and phosphorus is large. Experimental studies are mostly available on time scales of days to weeks and have found between 8 and 72% (average 31%) and 4 and 131% (average 75%) of dissolved organic nitrogen and phosphorus in Baltic rivers to be bioavailable (Stepanauskas et al., 2002). Contrary to nitrogen, a substantial part of the non-dissolved reactive phosphorus load in rivers can be particle bound (Meybeck, 1982, Stålarrison et al., 1999) with environmental mobility depending on its speciation (James and Larson, 2008). For the rivers draining into the Gulf of Riga, phosphate accounted for a comparatively high share (73%, Stålarrison et al., 1999) of the load, making the model less sensitive to the assumed bioavailability of non-DIP phosphorus.

4.5. Response to changes in nutrient loads

Winter nutrient concentrations (Fig. 5) indicated that nitrogen pools in the Gulf of Riga respond quickly to changes in nutrient loads, while phosphate concentrations continued to increase also after declining inputs in the 1990s. The slow response of the phosphorus pool is caused by its long residence time (see Table 3) and large internal loading. Simulated internal loading, i.e. modeled phosphate outflows from the bottom sediments reached on average 4.7 times the annual riverine, point source and atmospheric input in the biogeochemical model. In contrast, nitrogen concentrations quickly followed the changes in riverine inputs, with internal loading equivalent to only 34% of the annual nitrogen input. Similar differences in internal loading and nitrogen and phosphorus residence time, caused by the magnitude of their biogeochemical sinks, have been found in earlier nutrient budgets of the Gulf of Riga (Savchuk, 2002) and nutrient budgets for the entire Baltic Sea (Wulff and Stigebrandt, 1989, Savchuk, 2005).

In accordance to the long residence time of phosphorus in the Gulf of Riga, our phosphorus load reduction scenario showed a gradual decrease of phosphorus pools and primary production that had not led to a steady state after 70 years of simulation. Similar response rates were observed in nutrient load reduction scenarios for the Baltic Sea (Savchuk and Wulff, 2007, 2009). Despite the slow overall response, the impact of phosphorus load reductions on cyanobacteria
was much more pronounced than on primary production in total. The cyanobacteria blooms simulated during low nitrogen input years declined almost instantaneously (Fig. 8) with increasing difference between the reference and phosphorus reduction scenario during the simulation period. Our model, therefore, does not respond in a “vicious cycle” (Vahtera et al., 2007), where internal phosphorus loading and nitrogen fixation compensate the effect of phosphorus load reductions. Rather, internal phosphorus loading sustains cyanobacteria blooms under lowered nitrogen loads. A similar initial increase in cyanobacteria development after reducing nitrogen loads was also indicated in scenario models for the entire Baltic Sea (Savchuk and Wulff, 2007).

5. Conclusions

The biogeochemical model presented is capable of simulating the response of the Gulf of Riga to changes in nutrient loads on decadal time-scales. Good model performance and stable model behavior under constant nutrient loads suggest that the model can be used to predict the future development of nutrient concentrations, phytoplankton biomass and primary production, assuming moderate changes in nutrient loads and climatic forcing. Because of the high freshwater impact and consequently large nitrogen load, cyanobacteria blooms in the gulf occur less frequently than in the Baltic Proper. The simulated increase in the share of cyanobacteria after declining nitrogen loads in the 1990s is sustained by high internal phosphorus loading from the bottom sediments which is not matched by nitrogen inputs. Under current nitrogen and phosphorus loads, cyanobacteria blooms can be expected to occur regularly. However, the model suggests that under reduced phosphorus loads cyanobacteria blooms decline faster than total primary production in the Gulf of Riga.

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Appendix A. Model description

The change in concentration of a state variable \( k \) in model box \( j \) is given by its rate of change due to internal biogeochemical processes, \( \Phi_k^j \) and its rate of change due to external inputs and water exchange between model boxes, \( \Pi_k^j \):

\[
\frac{dC_k^j}{dt} = \Phi_k^j + \Pi_k^j
\]

(1)

\( j \) and \( k \) are text placeholders that denote the model state variables and the respective model box. Values of \( j \) are \( p \), \( d \) and \( s \) to denote pelagic, demersal and sediment model boxes. Concentrations and fluxes are expressed per unit volume for pelagic and demersal boxes and per unit area for the sediment box.

Three groups of autotrophs — nitrogen fixing phytoplankton \( A1 \), diatoms \( A2 \) and other species \( A3 \), as well as mesozooplankton \( ZH \) represent primary and secondary producers in the Gulf of Riga. Their concentrations are expressed in nitrogen units (mmol N m\(^{-3}\)) and their phosphate content is assumed to follow constant phytoplankton N/P ratios \( \lambda_i \) and zooplankton N/P ratios \( \lambda_{ZH} \). Non-living organic
matter is simulated as detritus DN with variable N/P ratio. Concentrations of dissolved nutrients are represented as ammonium NH, nitrate NO and phosphate PO.

Changes in phytoplankton concentration due to internal processes for species groups A1–A3 are given by the rates of net primary production PP, natural mortality \(m_i\) and grazing by zooplankton \(G_i\):

\[
\psi_i^j = PP_i^j - M_i^j - G_i^j
\]

(2)

Net primary production PP is modeled as a first order processes with group specific, maximum growth rate \(\mu_i\) and limitation factor \(\Lambda_i\) that expresses the effect of light and dissolved nutrients:

\[
PP_i = \mu_i A_i
\]

(3)

The limitation factor \(\Lambda_i\) is the minimum of the light limitation effect \(\psi_{\text{LT}}\), the nitrogen limitation effect \(\psi_{\text{NO}}\) and the phosphorus limitation effect \(\psi_{\text{PO}}\):

\[
\Lambda_i = \min(\psi_{\text{LT}}, \psi_{\text{NO}}, \psi_{\text{PO}})
\]

(4)

The individual limitation effects depend according to hyperbolic functions on nutrient concentrations in each model box and light intensity \(I\) at its top with half-saturation constants \(h_{\text{NO}}, h_{\text{PO}}\) and \(h_L\):

\[
\psi_{\text{NO}} = \frac{N_{\text{NO}}}{N_{\text{NO}} + h_{\text{NO}}}
\]

(5)

\[
\psi_{\text{PO}} = \frac{PO}{PO + h_{\text{PO}}}
\]

(6)

\[
\psi_{\text{LT}} = \frac{L}{L + h_L}
\]

(7)

Dissolved nitrogen available to phytoplankton \(N_{\text{DN}}\) is a weighted sum of ammonium and nitrate concentrations, to account for preferential uptake of ammonium.

\[
N_{\text{DN}} = NH + \frac{NO}{1 + \left(\frac{NH}{C_{\text{DN}}}\right)^b}
\]

(8)

Nitrogen-fixing phytoplankton is modeled as obligatory nitrogen fixers and \(\psi_{\text{NO}} = 1\).

Natural mortality of each phytoplankton group was treated as a first-order loss process with constant specific mortality \(m_i\).

\[
M_i = m_i A_i
\]

(9)

The grazing loss \(G_i\) depends on the availability of phytoplankton group \(i\) as a food source \(\alpha_i\) and the feeding rate \(f_{\text{ZH}}\) of mesozooplankton in the respective model box.

\[
G_i = f_{\text{ZH}} \alpha_i A_i \text{ZH}
\]

(10)

The change in concentration of mesozooplankton due to internal processes \(\psi_{\text{ZH}}\) is determined by their growth rate \(S\) and a mortality term \(M_{\text{ZH}}\):

\[
\psi_{\text{ZH}}^j = S_{\text{ZH}}^j - M_{\text{ZH}}^j
\]

(11)

Mesozooplankton is assumed to feed on a mixture of phytoplankton and detritus particles \(F_{\text{ZH}}\) proportional to their concentrations in the respective model box, weighted by an availability factor \(\alpha\) for each food source to account for food preferences.

\[
F_{\text{ZH}} = \sum_{i=1}^{3} \alpha_i A_i + \alpha_{\text{ZH}} \text{DN}
\]

(12)

The specific mesozooplankton feeding rate \(f_{\text{ZH}}\) increases linearly towards a temperature dependent maximum rate \(f_{\text{ZH}\text{max}}\) as the available food concentration \(F_{\text{ZH}\text{sat}}\) approaches its saturation value \(F_{\text{ZH}\text{sat}}\).

\[
f_{\text{ZH}\text{max}} = a_f \exp(b_f T)
\]

(13)

\[
f_{\text{ZH}} = \begin{cases} 
  f_{\text{ZH}\text{max}} F_{\text{ZH}} / F_{\text{ZH}\text{sat}} & F_{\text{ZH}} < F_{\text{ZH}\text{sat}} \\
  f_{\text{ZH}\text{max}} & F_{\text{ZH}} \geq F_{\text{ZH}\text{sat}}
\end{cases}
\]

(14)

Thus, the grazing loss of each phytoplankton group \(G_i\) and detritus \(G_{\text{DN}}\) is given by

\[
G_i = ZH f_{\text{ZH}} \alpha_i A_i
\]

(15)

\[
G_{\text{DN}} = ZH f_{\text{ZH}} \alpha_{\text{ZH}} \text{DN}
\]

(16)

Further, the grazed food is split into unassimilated food lost by e.g. “sloppy feeding” \(U_{\text{ZH}}\) and the actual food intake \(K_{\text{ZH}}\).

\[
U_{\text{ZH}} = \sum_{i=1}^{3} u_i G_i + u_{\text{DN}} G_{\text{DN}}
\]

(17)

\[
K_{\text{ZH}} = \sum_{i=1}^{3} (1-u_i) G_i + (1-u_{\text{DN}}) G_{\text{DN}}
\]

(18)

The corresponding phosphorus fluxes \(U_{\text{ZH}}\) and \(K_{\text{ZH}}\) are calculated based on the fixed N/P ratios for phytoplankton, \(\lambda_p\) and the variable detritus N/P ratio \(\lambda_D\).

\[
U_{\text{ZH}} = \sum_{i=1}^{3} u_i G_i / \lambda_p + u_{\text{DN}} G_{\text{DN}} / \lambda_D
\]

(19)

\[
K_{\text{ZH}} = \sum_{i=1}^{3} (1-u_i) G_i / \lambda_p + (1-u_{\text{DN}}) G_{\text{DN}} / \lambda_D
\]

(20)

The food intake is further divided into assimilated food \(S_{\text{ZH}}\) equivalent to mesozooplankton growth, and excretion loss \(E_{\text{ZH}}\). Assimilated food is determined by the intake of limiting nutrient, i.e. the nutrient which is, compared to the zooplankton N/P ratio \(\lambda_{\text{ZH}}\) in short supply. A constant fraction \(\varepsilon_{\text{ZH}}\) of the limiting nutrient intake is lost by excretion. The nutrient supplied in excess is assimilated corresponding to the zooplankton N/P ratio \(\lambda_{\text{ZH}}\) and the surplus is excreted leading to

\[
S_{\text{ZH}} = \begin{cases} 
  (1-\varepsilon_{\text{ZH}}) K_{\text{ZH}} / K_{\text{ZH}\text{max}} & K_{\text{ZH}} / K_{\text{ZH}\text{max}} \leq \lambda_{\text{ZH}} \\
  \lambda_{\text{ZH}} (1-\varepsilon_{\text{ZH}}) K_{\text{ZH}} / K_{\text{ZH}\text{max}} > \lambda_{\text{ZH}}
\end{cases}
\]

(21)

\[
E_{\text{ZH}} = \begin{cases} 
  \varepsilon_{\text{ZH}} K_{\text{ZH}} / K_{\text{ZH}\text{max}} & K_{\text{ZH}} / K_{\text{ZH}\text{max}} \leq \lambda_{\text{ZH}} \\
  K_{\text{ZH}} - \lambda_{\text{ZH}} K_{\text{ZH}} / K_{\text{ZH}\text{max}} > \lambda_{\text{ZH}}
\end{cases}
\]

(22)

with corresponding phosphorus assimilation \(S_{\text{ZH}}\) and phosphorus excretion

\[
S_{\text{ZH}} = S_{\text{ZH}} / \lambda_{\text{ZH}}
\]

\[
E_{\text{ZH}} = E_{\text{ZH}} / \lambda_{\text{ZH}}
\]

(23)
Zooplankton mortality $M_{2H}$ is a density dependent quadratic closure term in the model with specific mortality $m_{2H}$:

$$M_{2H} = m_{2H}Z^2$$  \(24\)

Detritus, i.e. non-living organic matter, collects all losses of living organic matter that occur in particulate form and is generated by the mortality fluxes of phyto- and zooplankton $M_I$ and $M_{2H}$, as well as unassimilated zooplankton food $U_{2H}$. The bioavailable fraction of riverine organic nutrient inputs is also assigned to the detritus pool. Detritus is lost from each model box by remineralisation $W_D$ and a sinking flux $S_D$, as well as by grazing $G_D$. To account for unequal N/P ratios in the detritus sources and different nitrogen and phosphorus mineralisation rates, detritus nitrogen and phosphorus, $\Phi_{2N}$ and $\Phi_{2P}$, were each treated as a model state variables. Changes in detritus nitrogen and phosphorus due to internal processes are then described by

$$\Phi_{2N} = \sum_{i=1}^{3} M_i' + M_{2H}' + U_{2H}' - W_{2N}' - G_{2N}' - S_{2N}'$$  \(25\)

$$\Phi_{2P} = \sum_{i=1}^{3} M_i' / \lambda_i + M_{2H}' / \lambda_{2H} + U_{2H}' - W_{2P}' - (G_{2P}' + S_{2P}') / \lambda_P$$  \(26\)

with variable detritus N/P ratio $\lambda_D$.

$$\lambda_D = \frac{DN}{DP}$$  \(27\)

Detritus sinks with constant velocity $w_D$ and consequently

$$S_{2N} = w_D DN S_{2N}^i / \Omega_P$$  \(28\)

Mineralisation of detritus is a temperature dependent process with different first-order kinetics of nitrogen and phosphorus.

$$W_{2N} = a_{2N} \exp(b_{2NT}) DN$$  \(29\)

$$W_{2P} = a_{2P} \exp(b_{2PT}) DP$$  \(30\)

Inorganic nutrients are represented by ammonium $NN$, nitrate $NO$, and phosphate $PO$. Their biogeochemical dynamics are described by uptake during phytoplankton growth $V_{PN}$, $V_{PO}$ and $V_{PN}$, release to the water column by zooplankton excretion $E_{2P}$ and $E_{2NP}$, ammonium and phosphate fluxes from the mineralization of detritus $W_{2N}$ and $W_{2P}$ as well as by nitrification of ammonium $W_O$.

$$\Phi_{1N} = - \sum_{i=1}^{3} \Phi_{2N}^i + E_{2N} + W_{2N} - W'_O$$  \(31\)

$$\Phi_{1O} = - \sum_{i=1}^{3} \Phi_{2O}^i + W'_O$$  \(32\)

$$\Phi_{1P} = - \sum_{i=1}^{3} \Phi_{2P}^i + E_{2NP} + W_{2P}$$  \(33\)

Nitrogen fixing phytoplankton $A_1$ were modeled as obligatory nitrogen fixers and consequently $V_{NN1} = V_{N01} = 0$. Spring and summer phytoplankton assimilate inorganic nitrogen with preference for ammonium. Phosphate is assimilated according to phytoplankton N/P ratios $\lambda_P$.

$$V_{NN} = \sum_{i=1}^{3} \frac{3}{2} PP_i N_{NN}$$  \(34\)

$$V_{NO} = \sum_{i=1}^{3} \frac{3}{2} PP_i N_{NO} - N_{NH}$$  \(35\)

Nitrification rates depend on temperature and ammonium concentrations and are suppressed at low oxygen conditions:

$$W_0 = a_\Phi \exp(b_\Phi T) \frac{O_2}{\eta_{WO} + O_2}$$  \(37\)

In the pelagic and demersal box oxygen is produced by photosynthesis and consumed by the zooplankton respiration, the oxidation of detritus, as well as by the nitrification of NH$_4$.

$$\Phi_{O2} = \sum_{i=1}^{3} 1 + x_{1P} PP_i^0 - x_{2P} E_{2N} - x_{2P} W_{2N} - \beta_{2P} W_0$$  \(38\)

Three state variables, sediment organic nitrogen $BN$ and fertilizing organic phosphorus $BP$ and a pool of highly redox sensitive adsorbed phosphorus $BPads$, are used to simulate the dynamics of nutrients in the bottom sediments. Changes in benthic organic nitrogen and phosphorus are the result of sedimenting detritus inputs, mineralization of benthic nitrogen and phosphorus $W_{BN}$ and $W_{BP}$, and the permanent burial of nitrogen and phosphorus in the bottom sediments, $B_{BN}$ and $B_{BP}$. The dynamics of adsorbed phosphorus is determined by the rates of phosphorus adsorption and desorption, $X_{ads}$ and $X_{des}$, as well as by the burial flux of adsorbed phosphorus, $BPads$.

$$\Phi_{BN} = S_{BN} x_{ads} - X_{ads} - B_{BN}$$  \(39\)

$$\Phi_{BP} = S_{BP} / \lambda_D x_{des} - X_{des} - B_{BP}$$.  \(40\)

$$\Phi_{BPads} = X_{ads} - X_{des} - B_{BPads}$$  \(41\)

The mineralisation of nutrients in the bottom sediments follows first-order, temperature dependent kinetics.

$$W_{BN} = a_{BN} \exp(b_{BN} T) BN$$  \(42\)

$$W_{BP} = a_{BP} \exp(b_{BP} T) BP$$  \(43\)

The fate of the mineralized benthic nitrogen and phosphorus is split into several pathways, depending on the oxygen concentration experienced by the bottom sediments $O_b$, which is determined by oxygen concentrations in the demersal model box.

$$O_b = O^P - \omega$$  \(44\)

A fraction of remineralized nitrogen $\theta$ is released as NH$_4$, whereas the remaining proportion $(1 - \theta)$ is oxidized to NO$_3$ and subsequently either denitrified or released to the demersal box.

$$\theta = \left(1 + \frac{O_b}{O_b^+ + (0.1)}\right)^{-1}$$  \(45\)

The share of NO$_3$ that escapes denitrification $\eta_{NO}$ increases with bottom water oxygen concentration, whereas the fraction of NO$_3$ denitrified, $1 - \eta_{NO}$, decreases.

$$\eta_{NO} = \frac{q_{NO}}{1 + \exp(a_{NO} - b_{NO} O_b)}$$  \(46\)

Similarly, the share of PO$_4$ generated that is subsequently adsorbed to the sediments $\eta_{PO}$ increases with oxygen concentration $O_b$, whereas
the fraction immediately released to the demersal water, $1 - \gamma_p$, increases.

$$\gamma_p = \frac{q_{BP}}{1 + \exp(a_{BP} - b_{BP}q_B)} \quad \text{with} \quad q_{BP} \leq 1 \quad (47)$$

Consequently, the release of NH$_4$ and NO$_3$ to the demersal model box $Y_{NN}$ and $Y_{NO}$, as well as the denitrification flux $Y_{DEN}$ are given by

$$Y_{NN} = \delta \omega_{BN} \quad (48)$$

$$Y_{NO} = (1 - \gamma_p)\nu_p \omega_{BN} \quad (49)$$

$$Y_{DEN} = (1 - \gamma_p)(1 - \eta_V)\omega_{BN} \quad (50)$$

Phosphate adsorbs to the bottom sediments with rate $X_{ads}$

$$X_{ads} = \eta_p \omega_{BP} \quad (51)$$

whereas desorption rate $X_{des}$ is modeled to approach its maximum rate $q_{BPdes}$ with declining oxygen conditions.

$$X_{des} = BP_{ads}q_{BPdes}(1 - \gamma_p) \quad (52)$$

Consequently, remineralized phosphorus is released to the water column at rate

$$Y_{PO} = W_{BP} - X_{ads} + X_{des} \quad (53)$$

Permanent burial of sediment organic nitrogen, phosphorus and adsorbed phosphorus occur with burial velocity $b_{ur}$.

$$B_{BN} = b_{ur}BN \quad (54)$$

$$B_{BP} = b_{ur}BP \quad (55)$$

$$B_{BPads} = b_{ur}BP_{ads} \quad (56)$$

Sediment oxygen consumption is caused by the mineralization of organic matter not covered by denitrification, as well as by the nitrification of remineralized nitrogen:

$$Y_{O2} = -\delta \omega_{BN}(\omega_{BN} - \omega_{DEN}) - \delta \omega_{BN}(\omega_{NO} + \omega_{DEN}) \quad (57)$$

Both the pelagic and the demersal model box receive external nutrient inputs. Because the inflowing water $Q_{BG}$ from the Baltic Proper is slightly more saline and therefore denser, it is allocated to the demersal model box, whereas river water $Q_{R}$ enters the pelagic box, together with point source and atmospheric inputs $L$. The outflowing water $Q_{BG} + Q_{R}$ leaves the Gulf of Riga from the pelagic model box. The exchange of water between pelagic and demersal box is modeled as the results of a vertical mixing flux $\nu Q_{mix}$ and an advective upwelling flux component that is equal to the inflow from the Baltic Proper $Q_{BG}$.

$$\nabla^p \cdot \nabla^p = \nu Q_{mix}(\nabla^p \cdot \nabla^p) - S^p \cdot \nabla^p + Q_{BG}(\nabla^p \cdot \nabla^p) + Q_{k}(\nabla^p \cdot \nabla^p) + L_k \quad (58)$$

$$\nabla^d \cdot \nabla^d = \nu Q_{mix}(\nabla^d \cdot \nabla^d) - S^d \cdot \nabla^d + S^d \cdot \nabla^d + \gamma_k \cdot S_k + Q_{BG}(\nabla^d \cdot \nabla^d) \quad (59)$$

The vertical mixing flux decreases, when stratification of the water column, as expressed by the density difference between demersal and pelagic box, $\rho_d - \rho_p$, increases. For dissolved states variables, phytoplankton and detritus $V_k = 1$, whereas zooplankton is able to actively migrate between both boxes and therefore a larger coefficient was used ($V_{Zw} = 2$).

$$Q_{pd} = \frac{\rho_p \omega_p}{1 + \rho_p(\rho_d - \rho_p)^2}$$

The air–water exchange of oxygen at the surface of the pelagic box, $L_{O2}$, depends on the observed wind speed $w$ and the temperature-dependent oxygen saturation $O_2$, in the pelagic model box (Sergeev et al., 1979):

$$L_{O2} = \frac{\gamma_1(O_2 - \omega_{OP})}{\gamma_2 \omega_{OP} - \gamma_1 \omega_{O2} + \gamma_4} \quad (61)$$

### Appendix B. Model parameters

#### Table B1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Pelagic box</th>
<th>Demersal box</th>
<th>Sediment box</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>Volume</td>
<td>km$^3$</td>
<td>155</td>
<td>268</td>
</tr>
<tr>
<td>$c$</td>
<td>Surface area</td>
<td>km$^2$</td>
<td>16 200</td>
<td>14 300</td>
</tr>
<tr>
<td>NH</td>
<td>Ammonium</td>
<td>mmol m$^{-3}$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>NO</td>
<td>Nitrate</td>
<td>mmol m$^{-3}$</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>PO</td>
<td>Phosphate</td>
<td>mmol m$^{-3}$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>O2</td>
<td>Oxygen</td>
<td>mmol m$^{-3}$</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>A1</td>
<td>Cyanobacteria</td>
<td>mmol N m$^{-3}$</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>A2</td>
<td>Diatoms</td>
<td>mmol N m$^{-3}$</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>A3</td>
<td>Other phytoplankton</td>
<td>mmol N m$^{-3}$</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>ZH</td>
<td>Mesozooplankton</td>
<td>mmol N m$^{-3}$</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td>DN</td>
<td>Detritus nitrogen</td>
<td>mmol m$^{-3}$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>DP</td>
<td>Detritus phosphorus</td>
<td>mmol m$^{-3}$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>BEN</td>
<td>Benthic organic nitrogen</td>
<td>mmol m$^{-2}$</td>
<td>2357</td>
<td></td>
</tr>
<tr>
<td>BEP</td>
<td>Benthic organic phosphorus</td>
<td>mmol m$^{-2}$</td>
<td>285</td>
<td></td>
</tr>
<tr>
<td>BP$_{ads}$</td>
<td>Benthic adsorbed phosphorus</td>
<td>mmol m$^{-2}$</td>
<td>5</td>
<td></td>
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#### Table B2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>A1 Cyanobacteria</th>
<th>A2 Diatoms</th>
<th>A3 Other phytoplankton</th>
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</thead>
<tbody>
<tr>
<td>$k_i$</td>
<td>N/P ratio</td>
<td>day$^{-1}$</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Maximum specific growth rate</td>
<td>day$^{-1}$</td>
<td>1.90 (1.00)</td>
<td>1.90 (1.00)</td>
</tr>
<tr>
<td>$k_{i}$</td>
<td>Half-saturation constant for light</td>
<td>W m$^{-2}$</td>
<td>362 (150)</td>
<td>285 (150)</td>
</tr>
<tr>
<td>$k_{i}$</td>
<td>Half-saturation constant for inorganic nitrogen</td>
<td>mmol N m$^{-3}$</td>
<td>3.97 (3.00)</td>
<td>2.93 (1.00)</td>
</tr>
<tr>
<td>$k_{i}$</td>
<td>Half-saturation constant for phosphate</td>
<td>mmol P m$^{-3}$</td>
<td>0.50 (0.05)</td>
<td>0.23 (0.10)</td>
</tr>
<tr>
<td>$m_i$</td>
<td>Specific mortality rate</td>
<td>day$^{-1}$</td>
<td>0.25 (0.20)</td>
<td>1.40 (1.00)</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Availability as food source</td>
<td></td>
<td>0.5</td>
<td>1.0</td>
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</tbody>
</table>
**Table B3**

Mesozooplankton parameters. Parameters included in the model calibration routine are marked by * and their initial values are given in brackets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>λ&lt;sub&gt;ZH&lt;/sub&gt;</td>
<td>N/P ratio</td>
<td></td>
</tr>
<tr>
<td>α&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Availability as food source</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>a&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>* Mineralization rate of detritus nitrogen at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>Temperature constant for detritus nitrogen mineralization</td>
<td>°C&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>a&lt;sub&gt;NP&lt;/sub&gt;</td>
<td>* Mineralization rate of detritus phosphorus at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;NP&lt;/sub&gt;</td>
<td>Temperature constant for detritus phosphorus mineralization</td>
<td>°C&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>w&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Sinking velocity</td>
<td>m day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>m&lt;sub&gt;ZH&lt;/sub&gt;</td>
<td>* Specific mortality rate</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;mmol N&lt;sup&gt;-1&lt;/sup&gt; day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
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**Table B4**

Detritus parameters. Parameters included in the model calibration routine are marked by * and their initial values are given in brackets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>α&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Availability as food source</td>
<td></td>
</tr>
<tr>
<td>α&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>* Mineralization rate of detritus nitrogen at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>Temperature constant for detritus nitrogen mineralization</td>
<td>°C&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>α&lt;sub&gt;NP&lt;/sub&gt;</td>
<td>* Mineralization rate of detritus phosphorus at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;NP&lt;/sub&gt;</td>
<td>Temperature constant for detritus phosphorus mineralization</td>
<td>°C&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>w&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Sinking velocity</td>
<td>m day&lt;sup&gt;-1&lt;/sup&gt;</td>
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</table>

**Table B5**

Pelagic biochemical processes and dissolved oxygen parameters. Parameters included in the model calibration routine are marked by * and their initial values are given in brackets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
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<tr>
<td>f&lt;sub&gt;IN&lt;/sub&gt;</td>
<td>Threshold ammonium concentration</td>
<td>m&lt;sup&gt;-1&lt;/sup&gt;mmol N</td>
</tr>
<tr>
<td>α&lt;sub&gt;N&lt;/sub&gt;</td>
<td>* Maximum specific nitrification rate at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;N&lt;/sub&gt;</td>
<td>Temperature constant for nitrification</td>
<td>°C&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>f&lt;sub&gt;VD&lt;/sub&gt;</td>
<td>Oxygen half-saturation constant of nitrification</td>
<td>ml O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>β&lt;sub&gt;A&lt;/sub&gt;</td>
<td>Oxygen equivalent for photosynthesis</td>
<td>ml O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>β&lt;sub&gt;DH&lt;/sub&gt;</td>
<td>Oxygen equivalent for zooplankton excretion</td>
<td>ml O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>β&lt;sub&gt;DN&lt;/sub&gt;</td>
<td>Oxygen equivalent for detritus mineralization</td>
<td>ml O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>β&lt;sub&gt;BN&lt;/sub&gt;</td>
<td>Oxygen equivalent for benthic nitrogen mineralization</td>
<td>ml O&lt;sub&gt;2&lt;/sub&gt;</td>
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</table>

**Table B6**

Sediment biogeochemical process parameters. Parameters included in the model calibration routine are marked by * and their initial values are given in brackets.

<table>
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<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>* Mineralization rate of benthic nitrogen at 0 °C</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;NN&lt;/sub&gt;</td>
<td>Turnover rate density coefficient</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt; day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>γ&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Coefficient for oxygen water exchange</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>γ&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Coefficient for oxygen water exchange</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>γ&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Coefficient for oxygen water exchange</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

**References**


