

NPZSD pH Template

MIKE ECO Lab template

A simple Nutrient, Phytoplankton, Zooplankton,

Sediment, Detritus and pH Model

– Scientific Documentation



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1 A simple NPZ model with pH

This documentation describes a simple **Nutrient-Phytoplankton-Zooplankton (NPZ)** model (see /1/) implemented as a MIKE ECO Lab template that includes also pH calculations. The main purpose of the template is to demonstrate how to include realistic pH calculations in an ECO Lab model.

The model contains zooplankton and phytoplankton components and coupled nutrient cycles. Additional compartments are sediment and detritus components. The model is a simple fixed stoichiometry model (see /2/), i.e. the simulated phytoplankton growth depends on the external/ambient concentrations rather than on an internal storage pool to keep complexity low. As the phytoplankton representation already contains the main nutrients, it can relatively simply be transformed into a variable stoichiometry model by introducing separate uptake and growth formulations (compare to the Eutrophication type family of ECO Lab templates and discussion in /2/).

Biomass or matter flow is modelled in terms of nitrogen, phosphorus and carbon. Chlorophyll content is derived from the phytoplankton biomass based on a fixed stoichiometric relation.

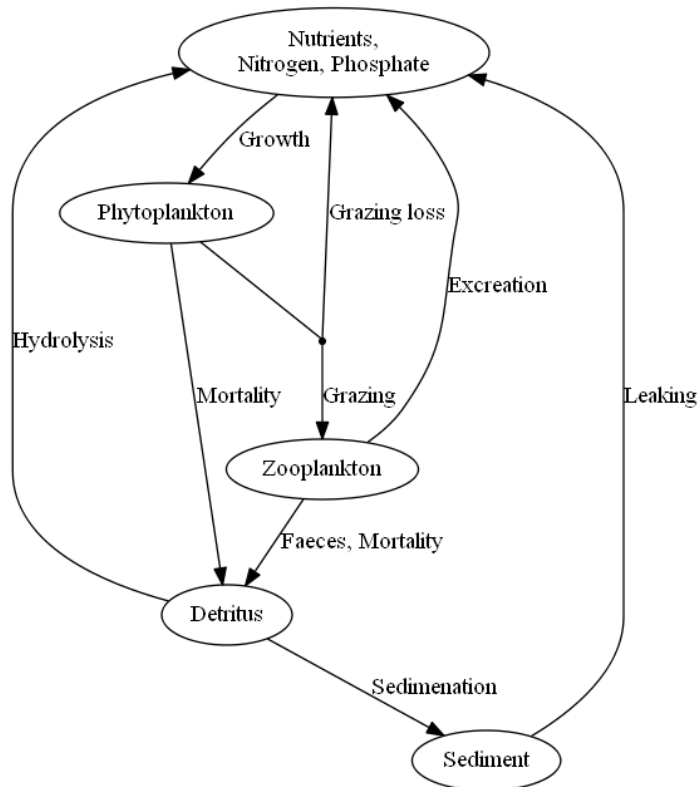
The model also includes the calculation of pH, i.e. the pH values are calculated on the base of the total dissolved inorganic carbon (DIC) and total alkalinity (ALK). Both change due to biological process, i.e. phytoplankton growth and process of the nutrient cycles. CO₂ exchange with the atmosphere can be included as well.

As the last important water quality component the template also contains an oxygen balance description, coupled to the different biological, bio-chemical and physical processes.

2 Model structure

The following chapter gives an overview of the model structure. First, a general diagram of the flow path is shown. Then a detailed flow path for the nitrogen, phosphorus and carbon cycles are included.

2.1 General structure



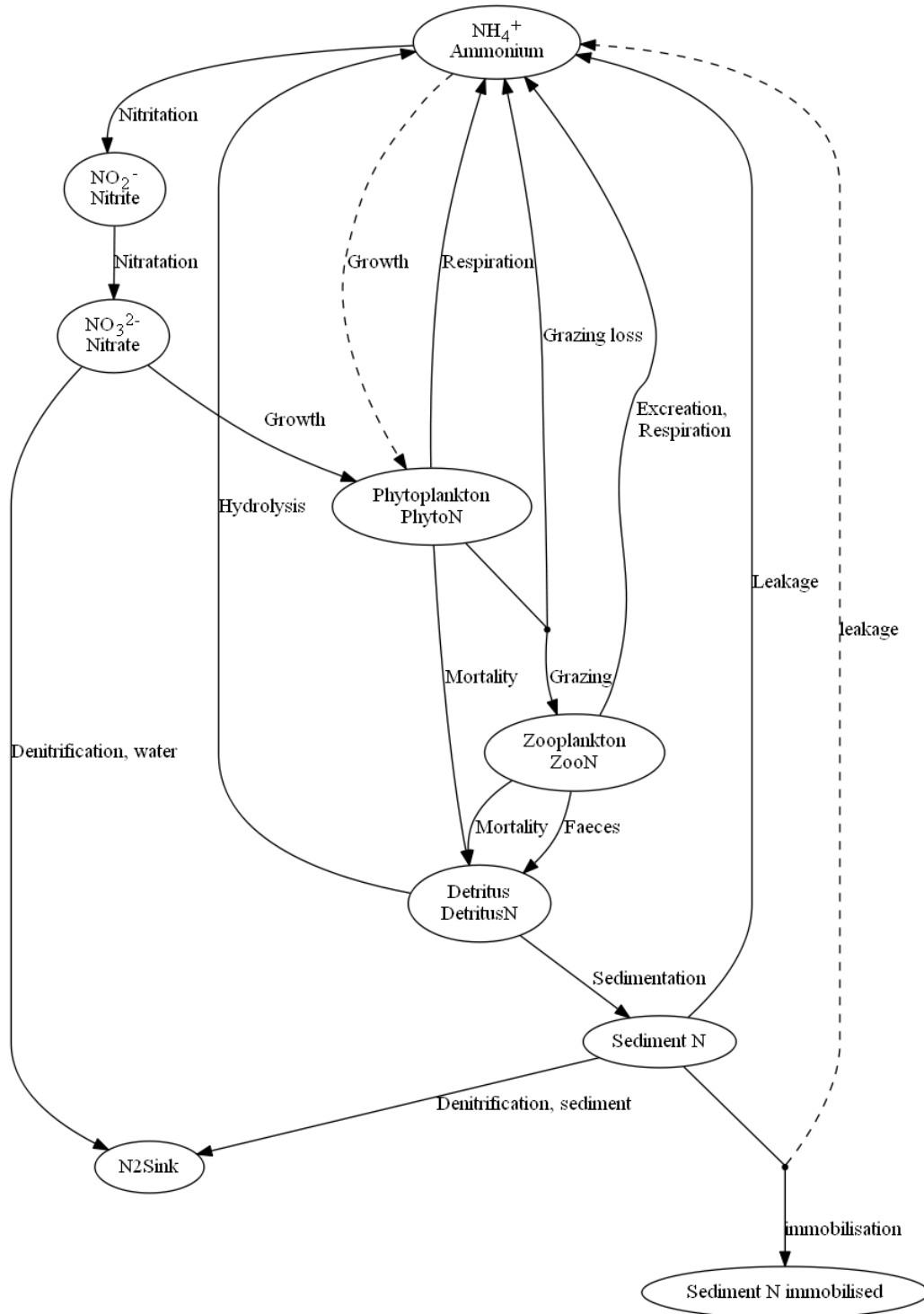
Dissolved nutrients (nitrogen, phosphorus) are being taken up by phytoplankton during growth. From the phytoplankton the flow goes into the detritus pool, either directly due to mortality or via the zooplankton that grazes on the phytoplankton. A part of the nutrients may be recycled into the dissolved nutrient pool as grazing loss, excretion or hydrolysis. Another part of the detritus sediments into the sediment pool. The sediment pool is linked to the dissolved nutrient pool via leakage but mainly acts as a kind of sink for most nutrients.

2.1.1 Detailed nutrient cycles

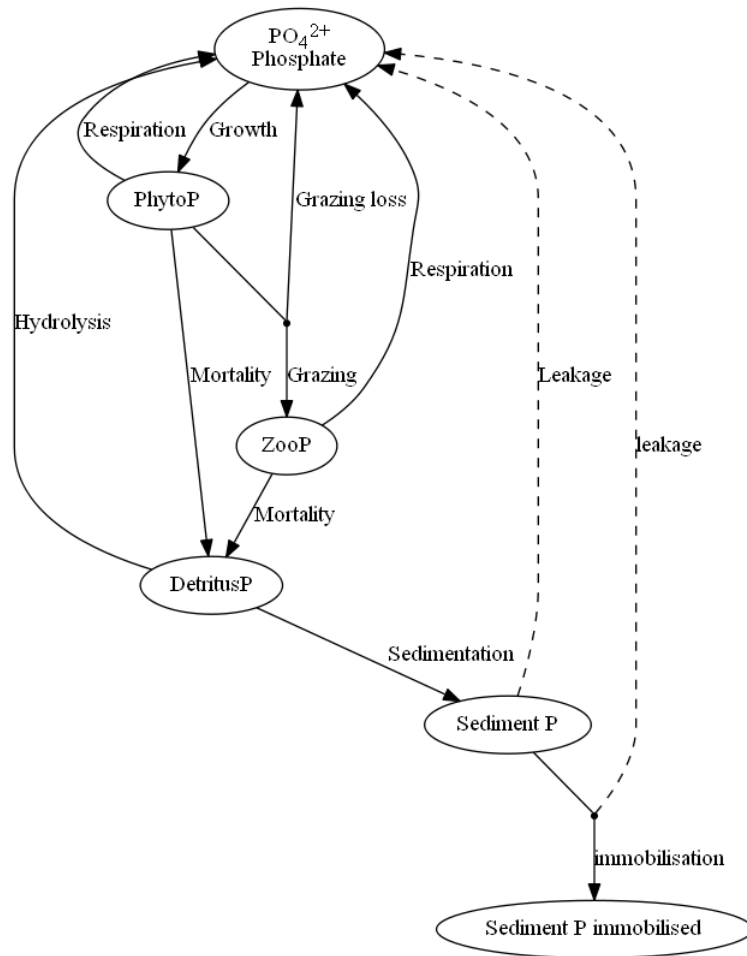
The following figures show the cycles of nitrogen, phosphorus and carbon in more details. In the figures, dotted lines /rectangular shapes indicate derived values (based on a fixed stoichiometry). The nitrogen cycle shows two alternative paths for phytoplankton uptake of dissolved nitrogen. Generally, phytoplankton can take up nitrogen as ammonium or as nitrate. The default path in the current model is via nitrate. Alternatively, an uptake as ammonium can be selected. For easy mass balance checks a state variable acting as nitrogen sink has been added. This variable collects all N₂ produced by denitrification in the water or sediment.

The phosphorus cycle corresponds to the general model description. Here the sediment pool usually acts as a sink but can also leak some phosphorus back into the water column.

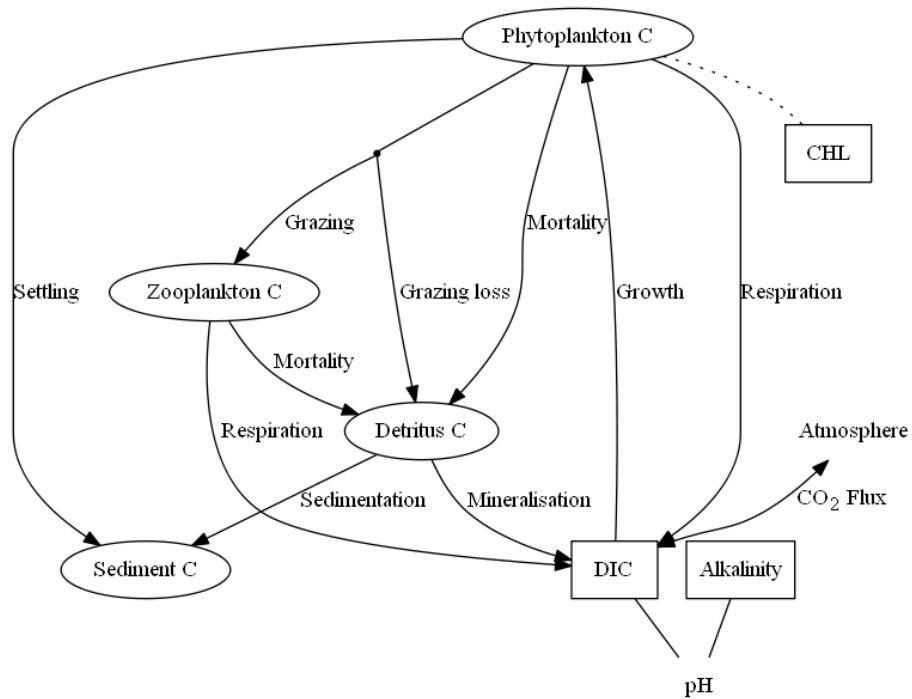
Nitrogen cycle



Phosphate cycle



Carbon cycle



Please note that the DIC is not considered as a limiting factor for the phytoplankton growth. DIC and alkalinity are used to determine pH.

3 Phytoplankton

This chapter describes the phytoplankton component in more details.

Phytoplankton is modelled using its nitrogen, phosphorus and carbon components. The chlorophyll is derived from the biomass via fixed stoichiometry.

$$\begin{aligned} \frac{d\text{PhytoplanktonN}}{dt} = & + \text{PhytoplanktonNGrowth} \\ & - \text{PhytoplanktonNMortality} \\ & - \text{PhytoplanktonNRespiration} \\ & - \text{ZooplanktonNGrazing} \\ & - \text{PhytoplanktonNSettling} \end{aligned} \quad (3.1)$$

$$\begin{aligned} \frac{d\text{PhytoplanktonP}}{dt} = & + \text{PhytoplanktonPGrowth} \\ & - \text{PhytoplanktonPMortality} \\ & - \text{PhytoplanktonPRespiration} \\ & - \text{ZooplanktonPGrazing} \\ & - \text{PhytoplanktonPSettling} \end{aligned} \quad (3.2)$$

$$\begin{aligned} \frac{d\text{PhytoplanktonC}}{dt} = & + \text{PhytoplanktonCGrowth} \\ & - \text{PhytoplanktonCMortality} \\ & - \text{PhytoplanktonCRespiration} \\ & - \text{ZooplanktonCGrazing} \\ & - \text{PhytoplanktonCSettling} \end{aligned} \quad (3.3)$$

$$\begin{aligned} \text{PhytoplanktonNGrowth} &= \text{PhytoplanktonGrowth} * \text{PhytoplanktonN} \\ \text{PhytoplanktonPGrowth} &= \text{PhytoplanktonGrowth} * \text{PhytoplanktonP} \\ \text{PhytoplanktonCGrowth} &= \text{PhytoplanktonGrowth} * \text{PhytoplanktonC} \end{aligned}$$

$$\begin{aligned} \text{PhytoplanktonNMortality} &= \text{PhytoplanktonMortality} * \text{PhytoplanktonN} \\ \text{PhytoplanktonPMortality} &= \text{PhytoplanktonMortality} * \text{PhytoplanktonP} \\ \text{PhytoplanktonCMortality} &= \text{PhytoplanktonMortality} * \text{PhytoplanktonC} \end{aligned}$$

$$\begin{aligned} \text{PhytoplanktonNRespiration} &= \text{PhytoplanktonRespiration} * \text{PhytoplanktonN} \\ \text{PhytoplanktonPRespiration} &= \text{PhytoplanktonRespiration} * \text{PhytoplanktonP} \\ \text{PhytoplanktonCRespiration} &= \text{PhytoplanktonRespiration} * \text{PhytoplanktonC} \end{aligned}$$

$$\begin{aligned} \text{ZooplanktonNGrazing} &= \text{ZooplanktonGrazing} * \text{ZooplanktonN} \\ \text{ZooplanktonPGrazing} &= \text{ZooplanktonGrazing} * \text{ZooplanktonP} \\ \text{ZooplanktonCGrazing} &= \text{ZooplanktonGrazing} * \text{ZooplanktonC} \end{aligned}$$

$$\begin{aligned} \text{PhytoplanktonNSettling} &= k_{sp} * \text{PhytoplanktonN} \\ \text{PhytoplanktonPSettling} &= k_{sp} * \text{PhytoplanktonP} \\ \text{PhytoplanktonCSettling} &= k_{sp} * \text{PhytoplanktonC} \end{aligned}$$

Further a derived variable exists, describing the chlorophyll based on the carbon biomass:

$$\text{CHL} = \frac{\text{PhytoplanktonC}}{\text{PhytoCtCHL}} \quad (3.4)$$

Where

PhytoCtCHL = Phytoplankton carbon to chlorophyll ratio
(default 50:1, can be 20:1-70:1 dependent on light adaption)

3.1 Phytoplankton growth

The phytoplankton growth is dependent on temperature, light and available nutrients.

$$PhytoplanktonGrowth = \mu * f_{p,temperature} * f_{light} * f_{nutrient} \quad (3.5)$$

Where

μ = Max. growth rate at 20°C
 $f_{p,temperature}$ = Phytoplankton temperature limitation
 f_{light} = Light limitation
 $f_{nutrient}$ = Nutrient limitation

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{p,temperature} = rho_p * e^{Temperature - 20.0} \quad (3.6)$$

Where

rho_p = Phytoplankton temperature coefficient
 Temperature = (ambient) Temperature in °C
 20.0 = Reference temperature (20.0 °C)

Light limitation

The light limitation follows a simple Monod-kinetic

$$f_{light} = \frac{light}{(light + ks_{light})} \quad (3.7)$$

Where

$light$ = Average light intensity in current layer [μE/m²/s]
 ks_{light} = Light half saturation intensity [μE/m²/s]

The average light intensity in the current layer is calculated as

$$light = I_z \frac{1 - e^{-\eta * dz}}{\eta * dz} \quad (3.8)$$

Where

I_z = Light intensity at current layer top [μE/m²/s]
 η = eta, attenuations coefficient [1/m]
 dz = Current layer thickness [m]

Light intensity at current layer top is calculated using a Lambert-Beer expression. The special ECO Lab function tracks the intensity of the above layers:

$$I_z = I_0 * e^{-\eta * dz} \quad (3.9)$$

Where

I_0 = Surface light intensity [$\mu\text{E}/\text{m}/\text{s}$]

The attenuations coefficient eta is a linear combination of the background attenuation and the attenuation caused by the phytoplankton

$$\eta = \eta_B + \eta_C * CHL \quad (3.10)$$

Where

η_B = Background attenuations coefficient [$1/\text{m}$]
 η_C = Chlorophyll attenuations coefficient [$\text{m}^2/\text{g CHL}$]
 CHL = Chlorophyll concentration [mg/l]

Nutrient limitation

The nutrient limitation is a minimum limitation of both modelled nutrients, nitrogen and phosphorus.

$$f_{\text{nutrient}} = \min(f_{\text{Nitrogen}}, f_{\text{Phosphorus}}) \quad (3.11)$$

The single nitrogen and phosphorus limitations follow a simple Monod-kinetic.

$$f_X = \frac{X}{(X + k_{S_X})} \quad (3.12)$$

Where

X = Nutrient concentration (NH_4 , NO_3 , PO_4)
 k_{S_X} = Half saturation concentration of the nutrient

By default, the model uses a preference uptake of ammonium over nitrate based on the availability of ammonium (limit concentration about $\sim 0.004 \text{ mg}/\text{l}$). From an energetically point of view, the uptake of ammonium is preferable over nitrate and is thus the dominant uptake path (see /8/). It is also possible to set a limitation for nitrate or ammonium alone or (for testing) to have no nitrogen limitation at all.

3.2 Phytoplankton mortality

$$\text{PhytoplanktonMortality} = r_p * f_{P,\text{temperature}} \quad (3.13)$$

Where

r_p = Max. mortality rate at 20°C
 $f_{P,\text{temperature}}$ = Temperature limitation (see growth description)

3.3 Phytoplankton loss due to zooplankton grazing

Zooplankton grazes on phytoplankton, causing a loss. For a closer description, see the zooplankton component.

3.4 Phytoplankton respiration

The phytoplankton respiration is dependent on temperature and the oxygen concentration.

$$\text{PhytoplanktonRespiration} = \text{resp}_P * f_{\text{Oxygen}} * f_{P, \text{Temperature}} \quad (3.14)$$

Where

- resp_P = Max. phytoplankton respiration rate at 20°C
- f_{Oxygen} = Oxygen limitation
- $f_{P, \text{Temperature}}$ = Phytoplankton temperature limitation

3.5 Phytoplankton settling

The phytoplankton settling is based on a fixed settling velocity

$$k_{sp} = \min \left(\frac{v_s}{dz}, \frac{0.99 * dz * 86400}{dt} \right) \quad (3.15)$$

Where

- v_s = Phytoplankton settling velocity [m/d]
- dz = Current layer thickness [m]
- dt = Current time step [sec]

The term ensures that the settling rate does not exceed a critical value and thus prevents excessive mass balance errors. However, especially in case of very small layers (fx. in shallow model locations in a 3D model with a vertical σ or σ -z coordinate system) it is advised to test the model for vertical mass preserving/Currant errors.

4 Zooplankton

This chapter describes the zooplankton component in more details.

Zooplankton is modelled using its nitrogen and phosphorus components.

$$\begin{aligned} \frac{dZooplanktonN}{dt} = & + ZooplanktonNGrowth \\ & - ZooplanktonNFaeces \\ & - ZooplanktonNExcretion \\ & - ZooplanktonNMortality \\ & - ZooplanktonNRespiration \end{aligned} \quad (4.1)$$

$$\begin{aligned} \frac{dZooplanktonP}{dt} = & + ZooplanktonPGrowth \\ & - ZooplanktonPFaeces \\ & - ZooplanktonPExcretion \\ & - ZooplanktonPMortality \\ & - ZooplanktonPRespiration \end{aligned} \quad (4.2)$$

$$\begin{aligned} \frac{dZooplanktonC}{dt} = & + ZooplanktonCGrowth \\ & - ZooplanktonCFaeces \\ & - ZooplanktonCMortality \\ & - ZooplanktonCRespiration \end{aligned} \quad (4.3)$$

$$\begin{aligned} ZooplanktonNGrowth &= aEf * ZooplanktonNGrazing \\ ZooplanktonPGrowth &= aEf * ZooplanktonPGrazing \\ ZooplanktonCGrowth &= aEf * ZooplanktonCGrazing \end{aligned}$$

$$\begin{aligned} ZooplanktonNFaeces &= (1 - aEf) * ZooplanktonNGrazing \\ ZooplanktonPFaeces &= (1 - aEf) * ZooplanktonPGrazing \\ ZooplanktonCFaeces &= (1 - aEf) * ZooplanktonCGrazing \end{aligned}$$

$$\begin{aligned} ZooplanktonNGrazing &= ZooplanktonGrazin * ZooplanktonN \\ ZooplanktonPGrazing &= ZooplanktonGrazing * ZooplanktonP \\ ZooplanktonCGrazing &= ZooplanktonGrazing * ZooplanktonC \end{aligned}$$

$$\begin{aligned} ZooplanktonNExcretion &= ZooplanktonExcretion * ZooplanktonN \\ ZooplanktonPExcretion &= ZooplanktonExcretion * ZooplanktonP \end{aligned}$$

$$\begin{aligned} ZooplanktonNMortality &= ZooplanktonMortality * ZooplanktonN \\ ZooplanktonPMortality &= ZooplanktonMortality * ZooplanktonP \\ ZooplanktonCMortality &= ZooplanktonMortality * ZooplanktonC \end{aligned}$$

$$\begin{aligned} ZooplanktonNRespiration &= ZooplanktonRespiration * ZooplanktonN \\ ZooplanktonPRespiration &= ZooplanktonRespiration * ZooplanktonP \\ ZooplanktonCRespiration &= ZooplanktonRespiration * ZooplanktonC \end{aligned}$$

Growth and faeces production are directly coupled to the grazing process

where

$$aEf = \text{Zooplankton assimilation/grazing efficiency (0.0-1.0)}$$

4.1 Zooplankton grazing

The zooplankton grazing rate is determined by the max filtration rate, the phytoplankton biomass (food concentration) and a temperature dependency. It also includes the effects of the food concentration on the filtration rate. The rate is defined as

$$\text{ZooplanktonGrazing} = g_z * \text{PhytoplanktonC} * f_{\text{Grazing}} * f_{z,\text{Temperature}} \quad (4.4)$$

Where

g_z	= Max. filtration rate at 20°C
PhytoplanktonC	= Phytoplankton/food concentration
f_{Grazing}	= Grazing limitation on phytoplankton concentration
$f_{z,\text{Temperature}}$	= Zooplankton temperature limitation

Grazing limitation

The zooplankton filtration is modulated by the available phytoplankton concentration (as phytoplankton C) in form of a simple Monod-kinetic:

$$f_{\text{Grazing}} = \frac{\text{PhytoplanktonC}}{(\text{PhytoplanktonC} + k_{S_{\text{grazing}}})} \quad (4.5)$$

Where

PhytoplanktonC	= Phytoplankton concentration (as carbon [mg/l])
$k_{S_{\text{grazing}}}$	= Grazing saturation concentration [mg/l]

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{z,\text{temperature}} = \text{rho}_z * e^{T_{\text{temperature}} - 20.0} \quad (4.6)$$

Where

rho_z	= Zooplankton temperature coefficient
Temperature	= (ambient) Temperature in °C
20.0	= Reference temperature (20.0 °C)

4.2 Zooplankton excretion

The zooplankton excretion is a simple 1st order process limited by the temperature. The rate is defined as

$$\text{ZooplanktonExcretion} = d_z * f_{z,\text{Temperature}} \quad (4.7)$$

Where

d_z	= Max. excretion rate at 20°C
-------	-------------------------------

4.3 Zooplankton mortality

$$\text{ZooplanktonMortality} = r_z * f_{Z, \text{Temperature}} \quad (4.8)$$

Where

r_z = Max. zooplankton mortality rate at 20°C
 $f_{Z, \text{Temperature}}$ = Temperature limitation (see growth description)

4.4 Zooplankton respiration

$$\text{ZooplanktonRespiration} = \text{resp}_z * f_{\text{Oxygen}} * f_{Z, \text{Temperature}} \quad (4.9)$$

Where

resp_z = Max. zooplankton respiration rate at 20°C
 f_{Oxygen} = Oxygen limitation
 $f_{P, \text{Temperature}}$ = Zooplankton temperature limitation

5 Detritus

This chapter describes the Detritus component in more details.

Detritus is modelled using its nitrogen and phosphorus components.

$$\begin{aligned} \frac{dDetritusN}{dt} = & + PhytoplanktonNMortality \\ & + ZooplanktonNMortality \\ & + ZooplanktonNFaces \\ & - DetritusNMineralisation \\ & - DetritusNSedimentation \end{aligned} \quad (5.1)$$

$$\begin{aligned} \frac{dDetritusP}{dt} = & + PhytoplanktonPMortality \\ & + ZooplanktonPMortality \\ & + ZooplanktonPFaces \\ & - DetritusPMineralisation \\ & - DetritusPSedimentation \end{aligned} \quad (5.2)$$

$$\begin{aligned} \frac{dDetritusC}{dt} = & + PhytoplanktonCMortality \\ & + ZooplanktonCMortality \\ & + ZooplanktonCFaces \\ & - DetritusCMineralisation \\ & - DetritusCSedimentation \end{aligned} \quad (5.3)$$

Where

$$\begin{aligned} DetritusNMineralisation &= DetritusMineralisation * DetritusN \\ DetritusPMineralisation &= DetritusMineralisation * DetritusP \\ DetritusCMineralisation &= DetritusMineralisation * DetritusC \end{aligned}$$

$$\begin{aligned} DetritusNSedimentation &= ksd * DetritusN \\ DetritusPSedimentation &= ksd * DetritusP \\ DetritusCSedimentation &= ksd * DetritusC \end{aligned}$$

Where

$$ksd = \text{Detritus sedimentation rate [/d]}$$

5.1 Detritus settling

Settling is a simple 1st order process with a settling rate defined as

$$ksd = \min \left(\frac{v_{settling}}{dz}, \frac{0.99 * dz * 86400}{dt} \right) \quad (5.4)$$

Where

- $v_{settlng}$ = Detritus settling velocity [m/d]
- dz = Current layer thickness [m]
- dt = Current time step [sec]

The term ensures that the settling rate does not exceed a critical value and thus prevents excessive mass balance errors. However, especially in case of very small layers (fx. in shallow model locations in a 3D model with a vertical σ or σ -z coordinate system) it is advised to test the model for vertical mass preserving/Currant errors.

5.2 Detritus mineralisation process

The detritus mineralisation is a simple 1st order process, dependent on ambient temperature and oxygen concentration. The rate is defined as

$$DetritusMineralisation = k_{Detritus} * f_{D,temperature} * f_{O_2} \quad (5.5)$$

Where

- $k_{Detritus}$ = Max. detritus materialisation rate at 20°C
- $f_{D,temperature}$ = Temperature limitation
- f_{O_2} = Oxygen limitation

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{D,temperature} = rho_D * e^{Temperature - 20.0} \quad (5.6)$$

Where

- rho_D = Detritus temperature coefficient
- Temperature = (ambient) Temperature in °C
- 20.0 = Reference temperature (20.0 °C)

Oxygen limitation

The mineralisation process is limited by the available oxygen concentration in form of a simple Monod-kinetic:

$$f_{O_2} = \frac{Oxygen}{(Oxygen + ks_{Oxygen})} \quad (5.7)$$

Where

- $Oxygen$ = Oxygen concentration [mg/l]
- ks_{Oxygen} = Oxygen half saturation concentration [mg/l]

6 Sediment

This chapter describes the sediment compartment in more details.

Sediment matter flow is determined by sedimentation and leakage and, for the nitrogen content, denitrification. As the sediment compartment represents an area concentration [g/m²], all open water column based processes (volume concentration) must be transformed.

$$\begin{aligned} \frac{dSedimentN}{dt} = & + DetritusNSedimentationArea \\ & - SedimentNLeakArea \\ & - SedimentDenitrificationArea \\ & - SedimentNMineralisationArea \end{aligned} \quad (6.1)$$

$$\begin{aligned} \frac{dSedimentP}{dt} = & + DetritusPSedimentationArea \\ & - SedimentPLeakArea \\ & - SedimentPMineralisationArea \end{aligned} \quad (6.2)$$

$$\begin{aligned} \frac{dSedimentC}{dt} = & + DetritusCSedimentationArea \\ & - SedimentCMineralisationArea \end{aligned} \quad (6.3)$$

6.1 Area sedimentation

The area sedimentation process simply transforms the volume based detritus sedimentation process into area based water bed process

$$DetritusNSedimentationArea = DetritusNSedimentation * dz \quad (6.4)$$

$$DetritusPSedimentationArea = DetritusPSedimentation * dz \quad (6.5)$$

$$DetritusCSedimentationArea = DetritusCSedimentation * dz \quad (6.6)$$

Where

$$dz = \text{(Bed) Layer height}$$

6.2 Leakage from sediment

Leakage from the sediment is a simple 1st order process:

$$SedimentNLeakArea = lr_N * SedimentN \quad (6.7)$$

$$SedimentPLeakArea = lr_P * SedimentP \quad (6.8)$$

Where

$$lr_N = \text{Nitrogen leakage rate, sediment [d]}$$

$$lr_P = \text{Phosphorus leakage rate, sediment [d]}$$

NOTE:

In this model the sediment acts as a phosphorus sink, i.e. there is no or very limited leakage of phosphorus! In nature phosphorus (PO_4^{3-}) and iron ions (Fe^{3+}) will form an insoluble complex ($FePO_4$) under aerobic conditions. Under anaerobic conditions, the iron will be reduced to Fe^{2+} and the bound phosphate will be released again. These processes are currently not covered by the model.

Area->volume conversion

Sediment leakage from the bed per area can be transformed to sediment leakage per volume [g mg/l/d] by dividing with the layer height above the bed:

$$SedimentNLeakVolume = \frac{SedimentNLeakArea}{dz} \quad (6.9)$$

$$SedimentPLeakVolume = \frac{SedimentPLeakArea}{dz} \quad (6.10)$$

Where

dz = (Bed) layer height [m]

6.3 Sediment-bound denitrification

Sediment-bound denitrification is a simple 1st order process that is dependent on ambient temperature:

$$SedimentDenitrificationAra = r_{Sed,denit} * f_{Sed,temperature} * SedimentN \quad (6.11)$$

Where

$r_{Sed,denit}$ = Max denitrification rate at 20°C

$f_{Sed,temperature}$ = Temperature limitation

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{Sed,temperature} = rho_{Sed} * e^{Temperature - 20.0} \quad (6.12)$$

Where

rho_{Sed} = Sediment temperature coefficient

Temperature = (ambient) Temperature in °C

20.0 = Reference temperature (20.0 °C)

6.4 Sediment-bound mineralisation

$$SedimentNMineralisationArea = resp_{Sed} * f_{Sed,temperature} * f_{Sed,O_2} * SedimentN \quad (6.13)$$

$$SedimentCMineralisationArea = resp_{Sed} * f_{Sed,temperature} * f_{Sed,O_2} * SedimentC \quad (6.14)$$

Where

$resp_{sed}$	= Sediment mineralisation rate [/d]
$f_{sed,temperature}$	= Sediment temperature limitation
f_{sed,o_2}	= Sediment oxygen limitation
$SedimentN$	= Sediment nitrogen
$SedimentC$	= Sediment carbon

Oxygen limitation

The mineralisation is limited by the available oxygen concentration in form of a simple Monod-kinetic. Here well-aerated sediments are considered, i.e. the oxygen concentration inside the sediment corresponds to the concentration above the sediment.

$$f_{sed,o_2} = \frac{Oxygen}{(Oxygen + k_{S_{sed,oxygen}})} \quad (6.15)$$

Where

$Oxygen$	= Oxygen concentration [mg/l]
$k_{S_{sed,oxygen}}$	= Sediment oxygen half saturation concentration [mg/l]

7 Nitrogen cycle

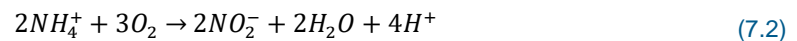
The nitrogen is the main modelled “currency”. Besides the already listed nitrogen compartments *PhytoplanktonN*, *ZooplanktonN*, *DetritusN* and *SedimentN*, the nitrogen cycle includes total dissolved ammonium (NH₄), nitrite (NO₂) and nitrate (NO₃). Based on the pH value the total ammonium can be further separated in its ionized (NH₄-N) and un-ionized (NH₃-N) form. Here, the un-ionized NH₃-N concentration is of particular interest, as this form is toxic for many aquatic organism (fish).

7.1 Total ammonium

$$\begin{aligned} \frac{dtNH_4}{dt} = & + ZooplanktonNExcretion \\ & + DetritusNMineralisation \\ & + SedimentNLeakVolume \\ & - Nitritation \\ & - PhytoplanktonAmmoniumUptake \\ & + PhytoplanktonNRespiration \\ & + ZooplanktonNRespiration \end{aligned} \quad (7.1)$$

Nitritation

Nitritation oxidizes ammonium to nitrite. The stoichiometric equation for this reaction is:



This leads to an O:N stoichiometry of

$$\frac{3 * 2 * M_O}{2 * M_N} = \frac{3 * 2 * 12.011}{2 * 14.007} = 2.5725 \frac{gO}{gN} \quad (7.3)$$

In the template, nitritation is simulated as a simple 1st order process dependent on temperature and oxygen:

$$Nitritation = r_{nitritation} * f_{Nit, Temperature} * f_{O_2} * NH_4 \quad (7.4)$$

Where

$r_{nitritation}$	= Max nitritation rate at 20°C
$f_{Nit, Temperature}$	= Temperature limitation
f_{O_2}	= Oxygen limitation

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{Nit, temperature} = rho_{Nit} * e^{Temperature - 20.0} \quad (7.5)$$

Where

rho_{Nit}	= Nitritation temperature coefficient
Temperature	= (ambient) Temperature in °C
20.0	= Reference temperature (20.0 °C)

Oxygen limitation

The nitritation is limited by the available oxygen concentration in form of a simple Monod-kinetic

$$f_{O_2} = \frac{Oxygen}{(Oxygen + ks_{Oxygen})} \quad (7.6)$$

Where

Oxygen = Oxygen concentration [mg/l]
ks_{Oxygen} = Oxygen half saturation concentration [mg/l]

Uptake of ammonium by phytoplankton

If the model is parameterised to include ammonium uptake by phytoplankton:

$$PhytoplanktonAmmoniumUptake = PhytoplanktonNGrowth \quad (7.7)$$

Ionized/un-ionized ammonium

The fractions of ionized and un-ionized ammonium depend on the pH value:

$$K_d = \frac{[NH_3]_{aq} * [H^+]}{[NH_4^+]} \quad (7.8)$$

Emerson (17) proposed an empirical value for the NH_4^+ ionization constant:

$$K_d = 10^{-\left(0.09018 + \frac{2729.92}{T_k}\right)} \quad (7.9)$$

T_k = Temperature in Kelvin

The fraction of the ionized form can be computed as

$$f_{tNH_4} = \frac{[H^+]}{([H^+] + K_d)} \quad (7.10)$$

Thus

$$[NH_4^+] = f_{NH_4} * tNH_4 \quad (7.11)$$

$$[NH_3]_{aq} = (1 - f_{NH_4}) * tNH_4 \quad (7.12)$$

Where

tNH_4 = total ammonium concentration

7.2 Nitrite

$$\frac{dNO_2}{dt} = \begin{matrix} + \text{Nitritation} \\ - \text{Nitrification} \end{matrix} \quad (7.13)$$

Nitration

Nitration oxidizes nitrite (NO₂) to nitrate (NO₃). In nature, this can occur on an aerobic and anaerobic pathway. The current template only considers the aerobic pathway. The stoichiometric equation for this aerobic reaction is:



This leads to an O:N stoichiometry of

$$\frac{2 * M_O}{2 * M_N} = \frac{2 * 12.011}{2 * 14.007} = 0.8575 \frac{gO}{gN} \quad (7.15)$$

In the template, nitration is simulated as a simple 1st order process dependent on temperature and oxygen:

$$Nitration = r_{nitration} * f_{Nit, Temperature} * f_{O_2} * NO_2 \quad (7.16)$$

Where

$r_{nitration}$	= Max nitration rate at 20°C
$f_{Nit, Temperature}$	= Temperature limitation (see above)
f_{O_2}	= Oxygen limitation (see above)

7.3 Nitrate

$$\begin{aligned} \frac{dNO_3}{dt} = & + Nitration \\ & - Denitrification_{Water} \\ & - PhytoplanktonNitrateUptake \end{aligned} \quad (7.17)$$

Denitrification

Denitrification reduces nitrate (NO₃) to molecular nitrogen (N₂). It is modelled as a simple 1st order reaction dependent on temperature

$$Denitrification_{Water} = r_{denitrification, water} * f_{DeNit, Temperature} * f_{InhO_2} * NO_3 \quad (7.18)$$

Where

$r_{denitrification, water}$	= Max denitrification rate at 20°C
$f_{DeNit, Temperature}$	= Temperature limitation
f_{InhO_2}	= Oxygen inhibition

Temperature limitation

The temperature limitation is a simple Arrhenius temperature correction:

$$f_{Nit, temperature} = rh_{ONit} * e^{Temperature - 20.0} \quad (7.19)$$

Where

ρ_{Nit} = Nitritation temperature coefficient
 Temperature = (ambient) Temperature in °C
 20.0 = Reference temperature (20.0 °C)

Oxygen inhibition

Denitrification is actually an anaerobic process. To overcome some limitations of the model (fx. subscale environmental variations) an oxygen inhibition has been added:

$$f_{InhO_2} = \frac{k_{S_{InhO_2}}}{(Oxygen + k_{S_{InhO_2}})} \quad (7.20)$$

Where

$Oxygen$ = Oxygen concentration [mg/l]
 $k_{S_{InhO_2}}$ = Oxygen inhibition half saturation concentration [mg/l]

Uptake of nitrate by phytoplankton

If the model is parameterised to include nitrate uptake by phytoplankton

$$PhytoplanktonNitrateUptake = PhytoplanktonNGrowth \quad (7.21)$$

7.3.1 Nitrogen Sink

The template contains a simple nitrogen sink component. This component facilitates mass balance checks:

$$\frac{dN2Sink}{dt} = Denitrification_{Water} + Denitrification_{Sediment} \quad (7.22)$$

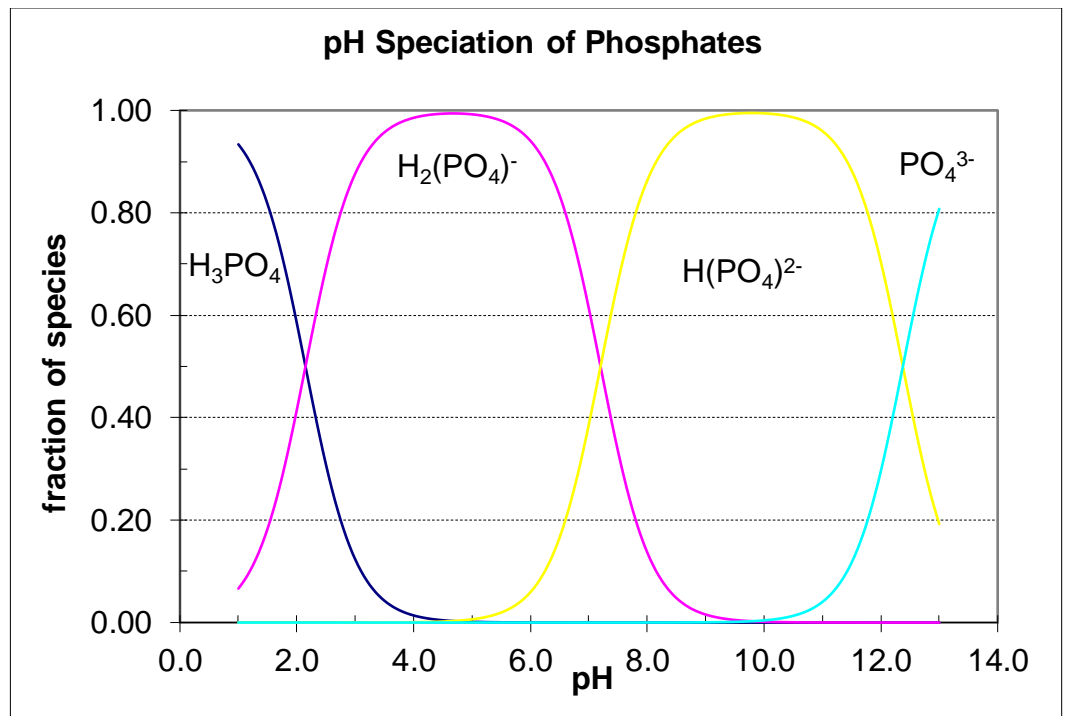
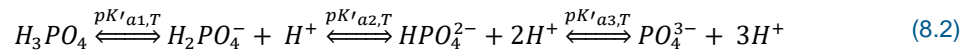
8 Phosphorus cycle

Besides the already listed phosphorus compartments *PhytoplanktonP*, *ZooplanktonP*, *DetritusP* and *SedimentP*, the phosphorus cycle includes total dissolved phosphorus (PO_4).

$$\begin{aligned} \frac{dPO_4}{dt} = & + \text{DetritusPMineralisation} \\ & + \text{ZooplanktonPExcretion} \\ & + \text{SedimentPLeakVolume} \\ & - \text{PhytoplanktonPGrowth} \\ & + \text{PhytoplanktonPRespiration} \\ & + \text{ZooplanktonPRespiration} \end{aligned} \quad (8.1)$$

Speciation of total phosphorus

In principle, dissolved phosphorus can be present in four different species, dependent on the pH.



The speciation α for the individual species can be calculated as

$$\begin{aligned} \alpha (H_3PO_4) &= \frac{[H^+]^3}{[H^+]^3 + [H^+]^2 * K'_{a1,T} + [H^+] * K'_{a1,T} * K'_{a2,T} + K'_{a1,T} * K'_{a2,T} * K'_{a3,T}} \end{aligned} \quad (8.3)$$

$$\begin{aligned} \alpha (H_2PO_4^-) &= \frac{[H^+]^2 * K'_{a1,T}}{[H^+]^3 + [H^+]^2 * K'_{a1,T} + [H^+] * K'_{a1,T} * K'_{a2,T} + K'_{a1,T} * K'_{a2,T} * K'_{a3,T}} \end{aligned} \quad (8.4)$$

$$\alpha (HPO_4^{2-}) = \frac{[H^+] * K'_{a1,T} * K'_{a2,T}}{[H^+]^3 + [H^+]^2 * K'_{a1,T} + [H^+] * K'_{a1,T} * K'_{a2,T} + K'_{a1,T} * K'_{a2,T} * K'_{a3,T}} \quad (8.5)$$

$$\alpha (PO_4^{3-}) = \frac{K'_{a1,T} * K'_{a2,T} * K'_{a3,T}}{[H^+]^3 + [H^+]^2 * K'_{a1,T} + [H^+] * K'_{a1,T} * K'_{a2,T} + K'_{a1,T} * K'_{a2,T} * K'_{a3,T}} \quad (8.6)$$

Where

- [H⁺] = Concentration of H⁺, i.e. 10^{-pH}
 K'_{a1,T} = (Temperature compensated) equilibrium constant 1st reaction
 K'_{a2,T} = (Temperature compensated) equilibrium constant 2nd reaction
 K'_{a3,T} = (Temperature compensated) equilibrium constant 3rd reaction

pK Equilibrium constant (25°C)	
pKa1	2.15
pKa2	7.21
pKa3	12.67

For the pH range pH ~4-10 occurring in most surface waters either H₂PO₄⁻ or HPO₄²⁻ will be the relevant specie. For simplicity, the speciation will be calculated at 25°C. In the pH range pH~4-10 the average charge of the PO₄ specie is thus:

$$aPO4 = 1 + \alpha (HPO_4^{2-}) \quad (8.7)$$

Calculation of the speciation $\alpha (HPO_4^{2-})$

Using the [H⁺]=10^{-pH} and K_x=10^{-pK_x} the calculation of $\alpha (HPO_4^{2-})$ can be simplified:

$$\alpha (HPO_4^{2-}) = \frac{[H^+] * K'_{a1,T} * K'_{a2,T}}{[H^+]^3 + [H^+]^2 * K'_{a1,T} + [H^+] * K'_{a1,T} * K'_{a2,T} + K'_{a1,T} * K'_{a2,T} * K'_{a3,T}} \quad (8.8)$$

$$= \frac{10^{-(pH+pKa1+pKa2)}}{10^{-3*pH} + 10^{-(2*pH+pKa1)} + 10^{-(pH+pKa1+pKa2)} + 10^{-(pKa1+pKa2+pKa3)}}$$

9 Oxygen

Oxygen is another important model component. The balance equation is:

$$\frac{dOxygen}{dt} = + Reaeration + PhotosynthesisO2 - DetritusRespiration - ZooplanktonCRespiration - PhytoplanktonCRespiration - NitrificationO2 - SedimentOxygenDemand \quad (9.1)$$

9.1 Reaeration

The oxygen exchange with the atmosphere is modelled as a temperature depended process:

$$Reaeration = K_2 * f_{rear, Temperature} * (CS_{air} - Oxygen) \quad (9.2)$$

Where

K_2	= Reaeration rate coefficient
$f_{rear, Temperature}$	= Temperature dependency
CS_{air}	= Oxygen saturation concentration

K_2 , reaeration rate coefficient

Depending on the application domain, the model can be parameterised to use a typical river reaeration coefficient or an open surface expression for estuaries/lakes. The river reaeration expression is a modified O'Conner/Dubbins expression, taking the effects of wind into account (see /2/):

$$K_{2, River} = \frac{3.93 * U^{0.5}}{H^{1.5}} + \frac{(0.728 * U_{Wind}^{0.5} - 0.371 * U_{Wind} + 0.0372 * U_{Wind}^2)}{H} \quad (9.3)$$

Where

U	= horizontal flow speed [m/s]
H	= mean Water (layer) depth [m]
U_{Wind}	= Wind speed 10 m above water surface [m/s]

The open surface expression based on /3/:

$$K_{2, Surface} = \frac{K_L}{H} \quad (9.4)$$

Where

K_L	= Liquid film transfer coefficient for oxygen [m/d]
-------	---

$$K_L = \begin{cases} \text{if } (U_{Wind} > 3.5) \text{ then } 0.057 * U_{Wind}^2 \\ \text{if } (U_{Wind} \leq 3.5) \text{ then } 0.2 * U_{Wind} \end{cases} \quad (9.5)$$

Temperature dependency

The temperature dependency is a simple Arrhenius temperature correction:

$$f_{rear, Temperature} = rho_{rear} * e^{Temperature - 20.0} \quad (9.6)$$

Where

rho_{rear} = Reaeration temperature coefficient
 Temperature = (ambient) Temperature in °C
 20.0 = Reference temperature (20.0 °C)

Oxygen saturation concentration

The oxygen saturation concentration is computed using the expression given by /4/. It is dependent on salinity and temperature.

9.2 Photosynthesis, phytoplankton carbon uptake

The oxygen production by photosynthesis is directly coupled to the carbon uptake due to growth.

$$PhotosynthesisO_2 = PhytoplanktonCUptake * PhytoDO \quad (9.7)$$

Where

$PhytoDO$ = Phytoplankton oxygen production/consumption relative to phytoplankton carbon (default 3.5 g O₂/g C)

9.3 Respiration terms

The oxygen balance takes the respiration by phytoplankton, zooplankton and detritus mineralisation into account. Generally, these processes are limited by the oxygen availability and temperature. The carbon contents are used as direct oxygen consumption equivalents.

9.3.1 Nitrification oxygen demand

The oxygen demand of the nitrification is directly given by the stoichiometry of the individual involved reactions (see above):

$$Nitrification O_2 = 0.5 * \left(\frac{3 * 2 * M_O}{2 * M_N} * Nitritation + \frac{2 * M_O}{2 * M_N} * Nitration \right) \quad (9.8)$$

9.3.2 Sediment oxygen demand

The sediment oxygen demand in the bed layer is given by

$$\frac{SedimentOxygenDemand}{dz} = \frac{SedimentNMineralisation * DetritusCtN}{dz} \quad (9.9)$$

Where

- SedimentNMineralisation* = Sediment nitrogen respiration [g N/m²/d]
dz = (Bed) layer height
DetritusCtN = It is assumed that the carbon content in the sediment corresponds to the carbon content of the detritus material, therefore the same conversion constant is used.

10 Total dissolved inorganic carbon (DIC)

Total dissolved inorganic carbon represents the dissolved components of the carbonate buffer system, i.e. the concentrations of dissolved carbon dioxide, hydrogen carbonate and bicarbonate.

$$[DIC] = \sum [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (10.1)$$

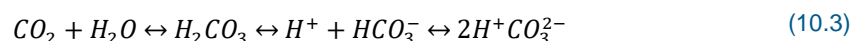
Various processes change the total dissolved carbon concentrations:

$$\begin{aligned} \frac{dDIC}{dt} = & + CO2Flux \\ & + DetritusRespiration \\ & + ZooplanktonRespiration \\ & + PhytoplanktonRespiration \\ & - PhytoplanktonCUptake \end{aligned} \quad (10.2)$$

Where

<i>CO2Flux</i>	=	CO ₂ air-sea flux with atmosphere
<i>DetritusRespiration</i>	=	Detritus respiration
<i>ZooplanktonRespiration</i>	=	Zooplankton respiration
<i>PhytoplanktonRespiration</i>	=	Phytoplankton respiration
<i>PhytoplanktonCUptake</i>	=	Phytoplankton Carbon uptake

The template provides dissolved carbon dioxide, hydrogen carbonate and bicarbonate as additional outputs. For simplicity, these concentrations are reported as “C” concentrations, i.e. just considering the carbon part. The exact distribution/relation of each component is derived from the pH value.



10.1 CO₂ sea-air flux with atmosphere

The gas exchange with the atmosphere follows in principle the same equations as described for the oxygen reaeration process, i.e.

$$F = k * (C_a - C_w) \quad (10.4)$$

Where

F	=	the flux
k	=	the gas transfer velocity
C _a and C _w	=	the concentrations in the in air (more exactly at the top of the boundary layer adjacent to the atmosphere) and in water.

Please note that the above equation describes the **sea-air flux**, i.e. the gas transfer **from** the water **into** the air (contrary to some literature that uses the air-sea flux, i.e. a difference in the sign). The transfer velocity is generally dependent on the gas type and environmental parameters like temperature and wind speed whereas the concentrations typically depend on temperature and other dissolved substances like salinity.

The model computes the transfer velocities and the CO₂ sea-air flux based on the equations given in /5/.

10.2 Respiration process

Any respiration process in the water column produces CO₂, i.e. enlarges the total DIC concentration by producing CO₂.

10.3 Phytoplankton carbon uptake

Phytoplankton growth consumes CO₂ and thus decreases the DIC concentration.

11 Total alkalinity (ALK)

Alkalinity, commonly also known as “buffering capacity”, is the water’s capacity to resist changes in pH that would make the water more acidic. It is equal to the sum of bases in the solution and thus typically expressed in molar equivalents (i.e. the number of H⁺ ions to balance a charge of a specie). The total alkalinity is defined as:

$$ALK_{total} = m_{HCO_3} + 2m_{CO_3^{2-}} + m_{B(OH)_4^-} + m_{H_3(SiOH)_4^-} + m_{HS^-} + m_{org.anion} + m_{OH^-} - m_{H^+} \tag{11.1}$$


Where

m_x = is the molar equivalent of specie X.

Usually most anions, except the ones from the carbonate system, have low concentrations; thus the most contributing part is the carbonate alkalinity

$$ALK_{Carbonate} = m_{HCO_3} + 2m_{CO_3^{2-}} \tag{11.2}$$

Many natural processes will increase or decrease alkalinity. Generally, processes that cause an addition of positive ions like NH₄⁺ will add positively to the alkalinity (as these cause a decline in free [H⁺] and an increase in [OH⁻] to maintain electro-neutrality). Consequently, a decrease in the number of positive ions will decrease the alkalinity (because more [H⁺] and a decrease in [OH⁻] is required to maintain electro-neutrality). If negatively charged ions are consumed, the alkalinity increases (as less [H⁺] and more in [OH⁻] are needed to maintain electro-neutrality) whereas adding negatively charged ions decreases the alkalinity (more [H⁺] and less [OH⁻] needed for electro-neutrality).

--	Alkalinity change	++
		
Consuming positive ions		Producing positive ions
Producing negative ions		Consuming negative ions

The change of the alkalinity in the model is expressed as

$$\frac{dALK}{dt} = + ftNH4 * (-2 * Nitritation + DetritusNMineralisation + SedimentNLeakVolum + PhytoplanktonNGrowth * + ZooplanktonNExcretion) + Denitrification + aPO4 * (+ PhytoplanktonPGrowth - DetritusPMineralisation) \tag{11.3}$$

Where

<i>ftNH4</i>	= Average charge of total ammonium
<i>Nitritation</i>	= Nitritation process, consumes NH_4^+ and produces NO_3^-
<i>DetritusNMineralisation</i>	= Detritus mineralisation, produces NH_4^+
<i>SedimentNLeakVolum</i>	= Sediment leakage, produces NH_4^+
<i>PhytoplanktonNGrowth*</i>	= Phytoplankton growth, will consume either NH_4^+ or NO_3^- depending on the nitrogen source
<i>ZooplanktonNExcretion</i>	= Excretion, produces NH_4^+
<i>Denitrification</i>	= Denitrification, consumes NO_3^-
<i>aPO4</i>	= Average charge of total phosphorus
<i>PhytoplanktonPGrowth</i>	= Phytoplankton growth, consumes HPO_4^-
<i>DetritusPMineralisation</i>	= Detritus mineralisation, produces HPO_4^-

12 Additional outputs

12.1 BOD estimate

The model provides an estimate of the BOD measurement. The BOD, the bio-geochemical oxygen demand, is usually determined as the oxygen consumption of a sample kept closed and in the dark at 20°C for about 5 days. In the model, the BOD is estimated by taking only the detritus and phytoplankton carbon contents into account using the relation given by /6/:

$$BOD_{estimate} = (DetritusC + PhytoplanktonC) * 1.57 \quad (12.1)$$

12.2 DIC, ALK molar concentrations

The model provides conversions of the total dissolved carbon and alkalinity concentrations from the standard model units to molal units:

$$DIC_M [mmol/m^3] = \frac{DIC[mg/l] * 10^3 [l/m^3]}{12.011 [g/mol]} \quad (12.2)$$

$$ALK_M [mmol/m^3] = ALK[mol/l] * 10^3 [l/m^3] \quad (12.3)$$

12.3 Concentrations of the carbonate buffer species

The model provides the pH dependent concentration of the single carbonate buffer species

12.4 CO₂ fugacity/partial pressure

The model provides the CO₂ fugacity/partial pressure.

13 Reference

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